Elementary Condensed Matter Physics

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Chapter 1

Atoms and Molecules

1.1 Interactions in Isolated Atoms

In order to understand the properties of solids one has to be able to describe their constituents and how they interact with each other. Solids are made out of arrays of atoms that are composed of electrons, protons and neutrons. Elementary quantum mechanics describes very well the behavior of isolated atoms such as Hydrogen. Most of the properties of solids depend on the behavior of electrons and protons. These are entities that have opposite charge, a large mass difference (the mass of the proton, m_p, is approximately 1000 times the electron mass, m_e). and different spatial position in the atom. The nucleus occupies the center of the atom and its much smaller than the surrounding electronic cloud which is extended over large distances ($10^{-8} m = 1 \mathring{A}$) if compared with the nucleus size ($10^{-15} m = 1 fm$). Since the characteristic distances in solids are of order of a few $\mathring{A}$ it is the electron who plays a major role on the properties of solids.

The basic physics of atoms can be understood starting from the Hydrogen atom. The Hamiltonian that describes the Hydrogen atom is given by

$$H = \frac{\mathbf{p}_P^2}{2m_p} + \frac{\mathbf{p}_e^2}{2m_e} - \frac{e^2}{|\mathbf{r}_P - \mathbf{r}_e|} \tag{1.1}$$

where $\mathbf{p}_P$ ($\mathbf{p}_e$) is the momentum, $\mathbf{r}_P$ ($\mathbf{r}_e$) the position of the proton (electron) and e is the electric charge. Remember that in quantum mechanics these quantities are operators that act on a Hilbert space of functions. Moreover, momentum and position are conjugated so that they obey commutation rules, namely,

$$[x_i, p_j] = i\hbar\delta_{i,j} \tag{1.2}$$

where we have introduced the components of the vector as $\mathbf{r} = (x_1, x_2, x_3)$ and $\mathbf{p} = (p_1, p_2, p_3)$ ($\delta_{i,j} = 1$ if $i = j$ and 0 otherwise is called the Kronecker delta). Moreover, the operators for the electron and proton commute among themselves since they are distinct from each other. The state of the system can be represented in terms of the positions of electron and proton by a bra $|\mathbf{r}_P, \mathbf{r}_e, \sigma_e, \sigma_P\rangle$ where σ is the spin degree of freedom of each one of the particles. From basic quantum mechanics one knows that protons and electrons have spin 1/2 and therefore are called fermions. In this case σ can only have two possible projections on a fixed axis, that is, up (↑) or down (↓). Observe that although $|\mathbf{r}_P, \mathbf{r}_e, \sigma_e, \sigma_P\rangle$ is a legitimate state of the problem and span the whole Hilbert space of solutions it does not represent an eigenstate of the Hamiltonian. The reason for that is that the momentum operator which appears in the kinetic term of (1.1) does not commute with the position operator and therefore it induces transitions between states with different positions (that is, the electron and proton move around!).

As usual in any problem in quantum mechanics one has to find the basis that properly describe the system of interest. The obvious thing to do, as in classical mechanics, it is to transform the Hamiltonian (1.1) to the center of mass and relative coordinate. In order to do it we define

$$\begin{aligned} \mathbf{R} &= \frac{1}{2}(\mathbf{r}_P + \mathbf{r}_e) \\ \mathbf{r} &= \mathbf{r}_P - \mathbf{r}_e\,, \end{aligned} \tag{1.3}$$

which are the center of mass and relative coordinate of the system. In terms of these new coordinates the Hamiltonian becomes,

$$H = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} - \frac{e^2}{r} \tag{1.4}$$

where $M = m_e + m_p$ is the total mass and $\mu = 1/m_e + 1/m_p$ is the reduced mass of the system. Observe that since $m_p \approx 1000 m_e$ we can rewrite $M \approx m_p$ and $\mu \approx m_e$ with good accuracy. Hamiltonian (1.4) already represents a major simplification in regards to (1.1). First of all we realize that the center of mass motion decouples from the relative motion since $\mathbf{R}$ does not appear in (1.4) (observe that almost all kinetic energy of the center of mass is carried by the proton which is much heavier). It implies that we can diagonalize the problem in the basis of total momentum operator $\mathbf{P}$:

$$\mathbf{P}|\mathbf{K}\rangle = \hbar\mathbf{K}|\mathbf{K}\rangle \tag{1.5}$$

which is just to say that the electron-proton system moves freely in space. The non-trivial part of the problem is the solution of the relative motion. Because the potential is central the problem has a symmetry of rotation in space.

Rotations in space are generated by the angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ which can be rewritten in a very convenient form: $L_i = \sum_{j,k} \epsilon_{i,j,k} x_j p_k$ where $\epsilon_{i,j,k}$ is the Levi-Civita tensor which is completely anti-symmetric (that is, $\epsilon_{i,j,k} = 0$ if $i = j$ or $i = k$ or $j = k$ and the other components are defined such that $\epsilon_{1,2,3} = +1$ as well as all other cyclic permutations, $\epsilon_{2,3,1} = \epsilon_{3,1,2} = +1$ and all the non-cyclic permutations are -1: $\epsilon_{1,3,2} = -1$). This definition of the angular momentum is good only in classical mechanics where x and p are not operators. In the case of operators we define the symmetrized form

$$L_i = \frac{1}{2} \sum_{j,k=1}^{3} \epsilon_{i,j,k} \left(x_j p_k + p_k x_j \right) \tag{1.6}$$

which obeys the so-called Lie algebra

$$[L_i, L_j] = i\hbar\epsilon_{i,j,k} L_k \tag{1.7}$$

which you can easily show from (1.6) and (1.2). The fact that the angular momentum operators do not commute among themselves implies that one cannot classify the states in terms of these operators independently. Instead we use one of them, say, L_3 (L_z) and its module $\mathbf{L}^2 = \sum_i L_i^2$. It is indeed trivial to show that the Hamiltonian (1.4) commutes with these operators, $[H, \mathbf{L}^2] = [H, L_3] = 0$ and therefore the states of the system can be classified according to the eigenvalues of these operators, namely,

$$\begin{aligned} \mathbf{L}^2|l,m\rangle &= \hbar^2 l(l+1)|l,m\rangle \\ L_3|l,m\rangle &= \hbar m|l,m\rangle \end{aligned} \tag{1.8}$$

where $m = -l, ..., l$ in unit steps. The Schrödinger equation for the problem determines the principal quantum number n. Thus, we can define an eigenstate of the Hamiltonian has the form $|\mathbf{K}, l, m, n, \sigma_e, \sigma_P\rangle$ so that,

$$H|\mathbf{K}, n, l, m, \sigma_e, \sigma_P\rangle = \left(\frac{\hbar^2 K^2}{2M} - \frac{13.6(eV)}{n^2}\right)|\mathbf{K}, n, l, m, \sigma_e, \sigma_P\rangle \tag{1.9}$$

is the full solution of the problem. Observe that the solution of this problem does not involve $l = 0, 1, 2..., n-1$ (these are usually called $s, p, d, f, ...$ states) , $m = -l, ..., +l$ or the spin degrees of freedom. Thus the states of the system are degenerate in this quantum numbers (there is more than one state of the system with the same energy). Moreover, it is obvious that the ground state corresponds to put the electron in $n = 1$ and set $K = 0$ corresponding to a static Hydrogen atom. The eigenstates of the problem can be represented in real space by projecting $|\mathbf{K}n, l, m, \sigma_e, \sigma_P\rangle$, that is,

$$\begin{aligned} \psi_{\mathbf{K},n,l,m}(\mathbf{R}, r, \theta, \phi) &= \langle \mathbf{R}, r, \theta, \phi|\mathbf{K}, l, m, n\rangle \\ &\propto e^{i\mathbf{K}\cdot\mathbf{R}} Y_{l,m}(\theta, \phi) R_{n,l}(r) \end{aligned} \tag{1.10}$$

where $Y_{l,m}(\theta, \phi)$ is a spherical harmonic and $R_{n,l}(r)$ is the so-called radial wavefunction that extends over a distance of order of the Bohr radius, $a_0 = \hbar^2/(\mu e^2)$. The shape of some of these functions is shown in Fig.1.1.

Things are relatively simple in the H atom because the proton only acts as an external potential. In atoms with more than one electrons the situation is not so simple because electrons interact among themselves via the Coulomb repulsion. Consider, for instance, the case of the He atom that has 2 electrons and 2 protons. The nucleus of the atom has mass $2m_p$ and the full Hamiltonian of the problem reads

$$H = \frac{\mathbf{p}_P^2}{4m_p} + \frac{\mathbf{p}_1^2}{2m_e} + \frac{\mathbf{p}_2^2}{2m_e} - \frac{2e^2}{|\mathbf{r}_P - \mathbf{r}_1|} - \frac{2e^2}{|\mathbf{r}_P - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1.11}$$

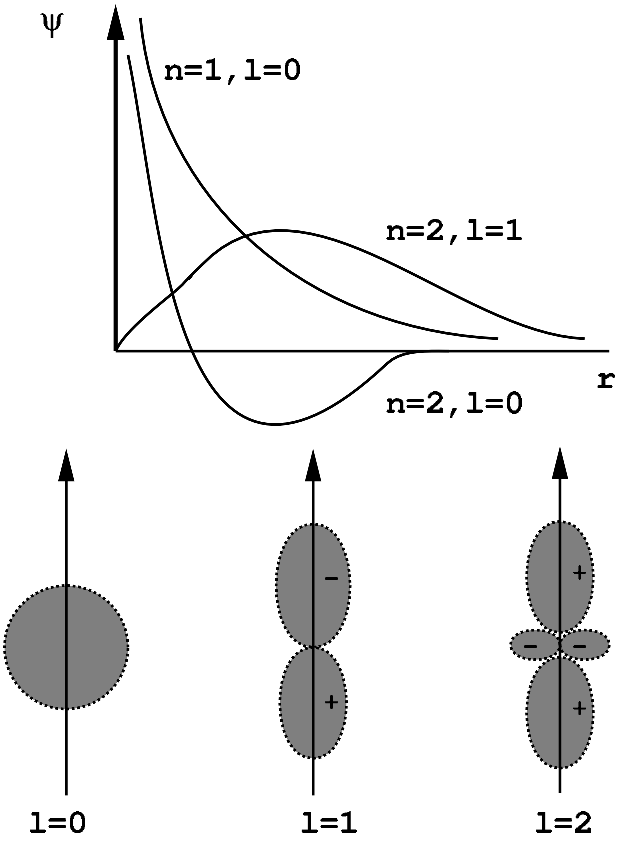

Figure 1.1: *Radial and angular dependence of some of the wavefunctions of the H atom.*

where $\mathbf{r}_{1,2}$ is the position of the two electrons. This is a quite complicated problem. The wavefunction of the system is a function of the coordinates, $\Psi(\mathbf{r}_P, \mathbf{r}_1, \mathbf{r}_2)$. What we need, however, is not the complete solution of the problem but an approximate solution that provides qualitative understanding. Since the mass of the proton is so much larger than the mass of the electron one expects the kinetic energy of the protons to be small compared to the other terms, that is, we expect the light electron to move distances much larger than the protons in the same time interval. During this time interval the protons "look" static for the fast electron. If the protons are static then we are back to our one-body quantum mechanics problem where the electron moves under a potential field created by the two protons. This potential is parameterized by the distance between the protons (it implies that we can solve the Schrödinger equation for each configuration of the protons). If this is the case the wavefuntion of the electrons can be written as $\psi_{\mathbf{r}_p}(\mathbf{r}_1, \mathbf{r}_2)$, and depends on the proton coordinates as a parameter. Therefore, it is intuitive to look for a variational solution of the quantum mechanical problem with the form:

$$\Psi(\mathbf{r}_p, \mathbf{r}_1, \mathbf{r}_2) = \psi_{\mathbf{r}_p}(\mathbf{r}_1, \mathbf{r}_2)\phi(\mathbf{r}_p) \tag{1.12}$$

where $\phi(\mathbf{r}_P)$ is the nucleus wavefunction. Eq.(1.12) is known as the *Born-Oppenheimer* approximation. In order for this wavefunction to make any sense one imposes that $\psi_{\mathbf{r}_p}(\mathbf{r}_1, \mathbf{r}_2)$ is an eigenstate of

$$H_S(\mathbf{r}_P) = \frac{\mathbf{p}_1^2}{2m_e} + \frac{\mathbf{p}_2^2}{2m_e} - \frac{2e^2}{|\mathbf{r}_P - \mathbf{r}_1|} - \frac{2e^2}{|\mathbf{r}_P - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1.13}$$

with energy $E_\alpha(\mathbf{r}_P)$ where α labels the possible quantum numbers of (1.13). Once the eigenenergies of (1.13) are known the nucleus wavefunction $\phi(\mathbf{r}_p)$ is an eigenstate of

$$H_N = \frac{\mathbf{p}_P^2}{4m_p} + E_\alpha(\mathbf{r}_P)\,. \tag{1.14}$$

This separation of energy scales between nucleus and electrons is very natural and it will de discussed in more detail later.

The quantum mechanical problem of three bodies described above is impossible to solve analytically (contrary to its classical counterpart).

We can understand the physics of these many electron atoms qualitatively based on what we know about the H atom and Pauli's exclusion principle which states that *there are no two electrons with the same quantum numbers*. As you probably know this is a consequence of the Fermi-Dirac statistics obeyed by electrons. Let us go back to He atom in the Born-Oppenheimer approximation (1.13) and set $\mathbf{r}_P = 0$ for simplicity, that is,

$$H_S = \frac{\mathbf{p}_1^2}{2m_e} + \frac{\mathbf{p}_2^2}{2m_e} - \frac{2e^2}{|\mathbf{r}_1|} - \frac{2e^2}{|\mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} . \tag{1.15}$$

which describes two electrons moving in the Coulomb potential of a charge $+2e$ and interacting with each other. Observe that because the electrons are practically in the same volume, the direct interaction between the electrons and the nucleus is approximately 2 times larger than the electron-electron interaction and has to be considered first.

At short distances the electron sees the full potential of the nucleus with charge $+2e$ while at larger distances it will see a smaller effective charge because of the other electron, that is, it sees a Coulomb potential with charge $2e - e = +e$. This effect only happens because the electrons are free to move and adapt to the changes in the Coulomb potential. In a static system (that is, a problem where $m_e \to \infty$) this is not so and the electron actually "feels" the full charge of the nucleus. This process in which the kinetic energy of the electrons leads to a smaller "effective" charge of the nucleus is called *screening*. What we are proposing is that beyond the Hamiltonian (1.11) there is a simpler Hamiltonian, or effective theory, that describes the problem. For the moment this effective theory is hidden due to our current ignorance and lack of sophistication. But the main thing is that because of the symmetry of the problem the form of the potential will not change substantially with distance since the charge distribution is spherically symmetric. Therefore the wavefunction of the problem looks like a H-like state with a slightly different energy than the H atom. Thus, the He atom is obtained by filling up the $1s$ state ($n = 1$ and $l = 0$) of the H atom with electrons of opposite spin (Pauli's principle). Observe, moreover, that because the first shell is filled, the He atom will not be very reactive since, as seen from far away, it will look like a neutral object to a foreign electron. Indeed, the ionization energy of the He atom is $24.6eV$ instead of the $13.6eV$ of the H atom.

Consider now a somewhat more complicated situation: the Li atom which has charge $+3e$ in the nucleus. Again using our effective theory we conclude that the wavefunctions are H-like and that in the ground state we can occupy the first allowed $1s$ state with two electrons with opposite spins. That is, we form first a He$^+$ atom. Where does the second electron go? Naturally it should go to a $n = 2$ state which can be s or p ($l = 0$ or $l = 1$, respectively). In the H atom these two states are degenerate but is this true for the Li atom? The reason for the non-degeneracy of the Li atom is related with the charge of the nucleus and the shape of the wavefunctions in the s and p states. In Fig.1.2 we show the result of the combination of the radial and angular part of the wavefunction as shown in Fig.1.1. Observe that in the s state the electron is closer to the nucleus that has charge $+3e$, while in the p orbital the electronic charge is distant from nucleus. Thus, the s state has lower electron-proton Coulomb energy than the p state and will be occupied first. Again, it is the preponderance of the Coulomb attraction (which in the case of Li is 3 times larger than the electron-electron interaction) which determines the ground state properties. Observe that since the first $1s$ shell if filled this state is very H-like and the ionization energy for this electron is $5.4eV$ showing that Li is chemically very reactive. Most of the atoms in the periodic table can be understood by simple arguments like these ones. The understanding of the atoms and how one describes the their ground state is fundamental for the understanding of solids. The formation of a solid depends very much on how the protons interact with the electrons and how the electrons interact among themselves.

1.2 Atomic Magnetism

While the order and classification of energy levels in atoms is determined by the gross value of the Coulomb interaction between the electrons and the nucleus (which is order of 1 eV $\approx 10,000K$) the magnetic behavior of isolated atoms depends on a delicate balance of energy scales. When we talk about magnetism what we really mean is the

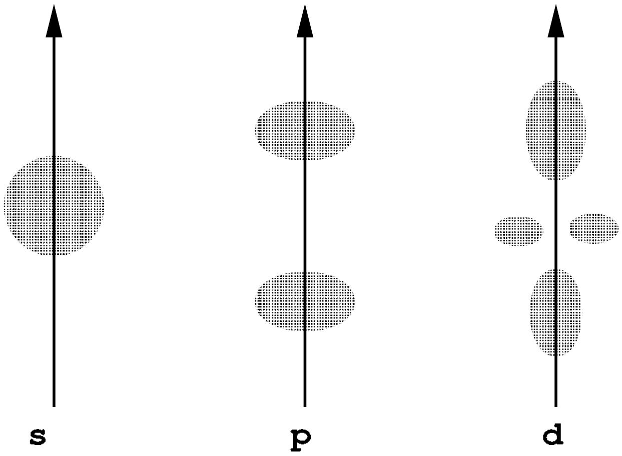

Figure 1.2: *The shaded areas are proportional to the probability of finding the electron in each orbital.*

magnetic response of the atoms to an applied magnetic field. In the presence of a magnetic field the Hamiltonian of the problem reads

$$\begin{aligned} H &= H_0 + H_I \\ H_0 &= \sum_{i=1}^{N} \frac{1}{2m}\left(\mathbf{p}_i + \frac{e}{c}\mathbf{A}(\mathbf{r}_i)\right)^2 + \mu_B g_0 \sum_{i=1}^{N} \mathbf{B}\cdot\mathbf{S}_i/\hbar \end{aligned} \tag{1.16}$$

where $\mathbf{r}_i$ and $\mathbf{p}_i$ are the coordinate and momentum of the i^{th} electron in the atom, $\mathbf{A}(\mathbf{r})$ is the vector potential ($\mathbf{B} = \nabla \times \mathbf{A}$) the last term is the Zeeman energy of the electron spin in a field $\mathbf{B}$ (S_i is the spin of the i^{th} electron, ($\mu_B = e\hbar/(2mc)$ is the Bohr magneton and $g_0 \approx 2$ is the g-factor) and

$$H_I = -\sum_{i=1}^{N} \frac{Ze^2}{|\mathbf{r}_i|} + \sum_{i,j=1,i\neq j}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1.17}$$

describes the Coulomb energies for the interaction between the electron and the nucleus (Z is the nuclear charge) and between the electron themselves. We assume that the magnetic field is applied in the z direction and choose an electromagnetic gauge such that

$$\mathbf{A} = \frac{B}{2}\left(x\mathbf{y} - y\mathbf{x}\right) \tag{1.18}$$

which is called the symmetric gauge (notice that $\mathbf{B} = B\mathbf{z}$). Substituting (1.18) into (1.16) we get

$$H_0 = \sum_i \frac{\mathbf{p}_i^2}{2m} + \mu_B B \sum_i (L_{z,i} + g_0 S_{z,i})/\hbar + \frac{e^2B^2}{8mc^2}\sum_i \left(x_i^2 + y_i^2\right) \tag{1.19}$$

We will show that for practical purposes the magnetic field terms are very small compared to the field independent terms and can be treated in perturbation theory. Thus, assuming the magnetic field to be small we find that, up to second order in perturbation theory, the ground state energy is given by:

$$\delta E_0 = \mu_B B \langle 0|\sum_i (L_{z,i} + g_0 S_{z,i})/\hbar|0\rangle$$

$$\begin{aligned} &+ \quad (\mu_B B)^2 \sum_{m\neq 0} \frac{|\langle m|\sum_i (L_{z,i}+g_0 S_{z,i})/\hbar|0\rangle|^2}{E_0 - E_m} \\ &+ \quad \frac{e^2B^2}{8mc^2}\langle 0|\sum_i (x_i^2+y_i^2)|0\rangle\,. \end{aligned} \tag{1.20}$$

We can immediately estimate the size of these terms. The first order correction is $\mu_B B\langle n|\sum_i (L_{z,i}+g_0 S_{z,i})/\hbar|n\rangle \approx \mu_B B \approx \hbar\omega_c$ where

$$\omega_c = \frac{eB}{mc} \tag{1.21}$$

is the cyclotron frequency. This term is of order of 10^{-4} eV (≈ 1 K) for a field of 1 Tesla. For the third term we have $e^2B^2/(8mc^2)\langle n|\sum_i r_i^2|n\rangle \approx (e^2B^2a_0^2)(8mc^2) \approx (\hbar\omega_c)^2/(e^2/a_0)$ which is of order of 10^{-9} eV ($\approx 10^{-5}$ K!) for a field of 1 Tesla. Indeed these terms are very small when compared to the characteristic atomic energies that are of order of electron Volts.

In order to calculate the perturbative shift in energy given in (1.20) one needs to know the nature of the ground state of the atom in the absence of the field. In the absence of interactions among the electrons this is given by the energy levels of the H atom. The system is degenerate because the problem has rotational symmetry and for each state l there are $2l+1$ degenerate states corresponding to the possible projections of l, that is, to the quantum numbers $m=-l,...,l$. In a system with N electrons we can distribute the electrons along these $2(2l+1)$ states (the factor of 2 comes from the two possible spin orientations) without changing the energy of the state. The total number of possible combinations of quantum numbers is $[2(2l+1)]!/(N![2(2l+1)-N]!)$.

Let us consider the problem of an atom with filled shell, that is, with $N=2l+1$. This is the case of noble gases such as He, Ar, etc. It is clear that in the ground state we have $L^z|0\rangle = S^z|0\rangle = 0$ and the only term that matters is the last one in (1.20). Using that fact that $\langle x_i^2\rangle = \langle y_i^2\rangle = \langle z_i^2\rangle = \langle r_i^2\rangle/3$ for the case of a spherically symmetric potential we have

$$\delta E = \frac{Ne^2B^2}{12mc^2}a^2 \tag{1.22}$$

where

$$a^2 = \frac{1}{N}\sum_i \langle r_i^2 \rangle\,. \tag{1.23}$$

The magnetization per unit of volume in the system for N_a atoms is given by

$$M = -\frac{N_a}{V}\frac{\partial \delta E}{\partial B} = -\frac{Ne^2a^2B\rho}{6mc^2} \tag{1.24}$$

which has a negative sign which implies that the response is *diamagnetic*, that is, in responding to an applied field the atoms want to reduce its value ($\rho = N_a/V$ is the atomic density). The magnetic susceptibility susceptibility is given by

$$\chi = \frac{\partial M}{\partial B} = -\frac{Ne^2a^2\rho}{6mc^2}\,. \tag{1.25}$$

Of course the situation described above is very simple because we are dealing with a system with a closed shell. Most atoms have only partially filled shells. In this case the matrix elements in (1.20) do not vanish. The interaction among the electrons becomes important and the degeneracy of the orbitals is lifted by the Coulomb interaction. We observe that because the Coulomb interaction is spherically symmetric the total angular momentum, **L**, and the total spin, **S**, are constants of motion and the states can still be classified in terms of the eigenstates of these two operators, that is, all states can be written as: $|L, S, L_z, S_z\rangle$. Moreover, the system is degenerate since for a fixed value of L and S we can have $(2L+1)(2S+1)$ states for different values of L_z and S_z corresponding to different projections of **L** and **S**. This is called a *multiplet*. Consider, for instance, an atom with a configuration like $4f^2$. The f orbital can comport 14 electrons. Since there are two electron they can be put into the orbitals in $14!/(2!12!) = 91$ different ways! In this case we have $S = 0, 1$ and $L = 0, 1, 2, 3, 4, 5$ and for each value of S and L there are $(2S+1)(2L+1)$ degenerate states.

The relevant question is: which state, $|S, L\rangle$ has the lowest energy? Of course to answer this question one needs a *quantitative* calculation which involves the coupling of all the electrons via the Coulomb term.

Observe however that exclusion principle does not allow two electrons with the same spin to be in the same place in space. Thus, electrons with the same spin effectively *repel* each other. Naturally this effect lowers the Coulomb energy. Thus, electrons in an atom tend to have all their spins aligned. This is called *Hund's first rule*: in an atom the electrons want to maximize the total spin S. This rule solves the problem of the spin but not of the orbital angular momentum. Again the name of the game here is: *minimize the Coulomb energy between electrons*! On the one hand, in states with small L (like an s-state) the electrons spend much of their time close to the nucleus and therefore pay an energetic price of the repulsion among themselves. On the other hand, in states with large L the electrons are apart from the nucleus and feel a weaker Coulomb repulsion. This gives rise to the *Hund's second rule*: For a maximum value of S the energy is minimized by the largest value of L. The first and second Hund's rules specify the values of L and S for which the energy is minimum but still for fixed L and S we have $(2L+1)(2S+1)$ degenerate states. Is this degeneracy real in an atom? The answer is: no! The reason being that the orbital motion is coupled to the spin of the electron by the so-called *spin-orbit* effect.

Consider one electron moving with velocity $\mathbf{v}$ around a nucleus. From the point of view of the electron (that is, looking at the problem at the frame co-moving with the electron) the nucleus moves around with velocity $-\mathbf{v}$. Since the nucleus is charged we can imagine the nucleus motion as a little current of charge circulating around the electron. This current generates a magnetic field at the position of the electron which is proportional to $\mathbf{r} \times \mathbf{v} \propto \mathbf{L}$. Thus, the Zeeman energy created by this field is also proportional to $\mathbf{L} \cdot \mathbf{S}$ which is the spin-orbit coupling. One usually writes the Hamiltonian associated with this coupling as

$$H_{SO} = \lambda \mathbf{L} \cdot \mathbf{S} \tag{1.26}$$

where λ depends on details of the atomic problem and can be obtained from the atomic spectra. Indeed, if one adds (1.26) to our original Hamiltonian (1.16) we see that $\mathbf{L}$ and $\mathbf{S}$ do not indeed commute with the Hamiltonian separately. However, the total angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{1.27}$$

commutes with the Hamiltonian. It means that we can still classify the eigenstates of the problem in terms of $\mathbf{J}$, that is, the states can be labeled as: $|J, J_z, L, S\rangle$. This implies that the degeneracy of the $(2L+1)(2S+1)$ states is lifted and the states split into $(2J+1)$ degenerate states corresponding to different values of J_z. Indeed we can rewrite (1.26) in terms of this operator as

$$H_{SO} = \frac{\lambda}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right) \tag{1.28}$$

since the Hamiltonian commutes with $\mathbf{J}$, $\mathbf{L}^2$ and $\mathbf{S}^2$. Observe that due to (1.27) the allowed values of J go from $|L-S|$ to $L+S$ in unit steps and the allowed valued of J_z go from $-J$ to J (which gives the degeneracy of $2J+1$). The energy associated with each one of these states is

$$E(J, J_z, S, L) = \frac{\lambda}{2}\left[J(J+1) - L(L+1) - S(S+1)\right] . \tag{1.29}$$

It is observed experimentally that $\lambda > 0$ for shells that are less than half filled ($n \leq 2l+1$) and $\lambda < 0$ for shells that are more than half filled ($n \geq 2l+1$). If $\lambda > 0$ it is clear from (1.29) that the energy will be minimized for a given S and L for a configuration with smallest J, that is, $J = |L-S|$. Otherwise, if $\lambda < 0$, the energy is minimized for the largest value of J, that is, $J = L+S$. This is the so-called *Hund's third rule.*

Hund's rules can guide us to understand the response of an atom to a magnetic field. Consider a system in which $J = 0$. In this case we can use the Wigner-Eckart theorem and show that the first term in the energy in (1.20) actually vanishes. We are left with the two other terms. The third term is just the *diamagnetic* response we studied for the case of atoms with filled shell. The second term is negative (remember that second order perturbation theory *always* lowers the energy of the ground state) and therefore it will give rise to a susceptibility with positive sign. This is the so-called *Van Vleck paramagnetic* response.

If $J \neq 0$ then the first term in (1.20) does not vanish and it is the largest contribution for the energy shift. We can rewrite this term in a more appropriate form

$$H_Z = \mu_B \mathbf{B} \cdot (\mathbf{L} + g_0 \mathbf{S}) = \mu_B \mathbf{B} \cdot (\mathbf{J} + (g_0 - 1)\mathbf{S}) \tag{1.30}$$

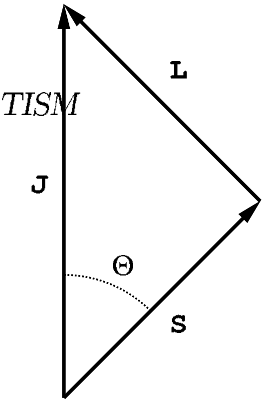

Figure 1.3: *Angular momentum geometry.*

which allows us to interpret $\mathbf{J} + (g_0 - 1)\mathbf{S}$ as the effective magnetic moment of the atom,

$$\mathbf{M} = -\mu_B(\mathbf{J} + (g_0 - 1)\mathbf{S}) \tag{1.31}$$

which is not a constant of motion since $\mathbf{S}$ is not conserved. It turns out, however, that $\mathbf{J}$ is a constant of motion and we can think of $\mathbf{J}$ as being fixed and that $\mathbf{L}$ and $\mathbf{S}$ rotate around $\mathbf{J}$ as in Fig.1.3. Thus the magnetic moment is given by the component of $\mathbf{L} + g_0\mathbf{S}$ parallel to $\mathbf{J}$. This is the only component of the magnetic moment that contributes in first order perturbation theory since the components of $\mathbf{S}$ in the direction transverse to $\mathbf{J}$ will introduce transition between different values of J_z and give zero average when we calculate with an unperturbed state $|J, J_z, L, S\rangle$. The parallel component of $\mathbf{S}$ can be calculated from the angle between $\mathbf{J}$ and $\mathbf{S}$,

$$\begin{aligned}\mathbf{S}_J &= \frac{(\mathbf{J}\cdot\mathbf{S})}{\mathbf{J}^2}\mathbf{J} \\ &= \frac{(\mathbf{J}^2 - \mathbf{L}^2 + \mathbf{S}^2)}{2\mathbf{J}^2}\mathbf{J} \end{aligned} \tag{1.32}$$

which, in a state $|J, J_z, S, L\rangle$ has a value

$$\langle \mathbf{S}_J \rangle = \frac{[J(J+1) - L(L+1) + S(S+1)]}{2J(J+1)}\,\mathbf{J} \tag{1.33}$$

and therefore the effective magnetic moment in the direction of $\mathbf{J}$ is given in (1.31)

$$\mathbf{M} = -g\mu_B\mathbf{J} \tag{1.34}$$

where

$$g(J,L,S) = \frac{(g_0+1)}{2} + \frac{(g_0-1)}{2}\,\frac{S(S+1)-L(L+1)}{J(J+1)} \tag{1.35}$$

is the *Landé g-factor*. The energy associated with (1.30) is

$$\delta E(J,J_z,S,L) = gJ_z\mu_B B \tag{1.36}$$

where $J_z = -J, ..., J$. This final expression gives the splitting between the energy levels of a multi-electron atom.

Thermal effects

One interesting application of (1.36) is the calculation of the magnetic response of a set of isolated identical atoms in a magnetic field. Observe that the partition function for the problem defined in (1.36) is given by ($\beta = 1/(k_BT)$)

$$\begin{aligned} Z &= \sum_{J_z=-J}^{J} e^{-\beta E(J,J_z,S,L)} = \sum_{J_z=-J}^{J} e^{-\beta g(J,L,S)J_z\mu_B B} \\ &= \frac{\sinh\left[\beta g\mu_B B(J+1/2)\right]}{\sinh\left[\beta g\mu_B B/2\right]} \end{aligned} \tag{1.37}$$

where in the last line we used the sum of a geometric series. The magnetization is obtained like in (1.24) and it is given by

$$M(B) = \rho g\mu_B J B_J(\beta g J\mu_B B) \tag{1.38}$$

where

$$B_J(x) = \frac{(2J+1)}{2J} coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} coth\left(\frac{x}{2J}\right) \tag{1.39}$$

is the so-called *Brillouin function*. Notice that for $\beta g\mu_B B >> 1$ (that is, low temperatures) the magnetization *saturates* at $M \to \rho g\mu_B J$ as expected since all the moments are aligned. At high temperatures, that is, $\beta g\mu_B B << 1$ we find

$$M \approx \rho\frac{J(J+1)(g\mu_B)^2 B}{3k_BT} \tag{1.40}$$

and gives a magnetic susceptibility

$$\chi(T) = \rho\frac{J(J+1)(g\mu_B)^2}{3k_BT} \tag{1.41}$$

which is known as the *Curie susceptibility*.

1.3 Molecules

1.3.1 The H_2^+ molecule

We have seen that the physics of many-electron atoms can be quite complicated if one is interested in the detailed behavior of the electrons. Things become even more complicated if we now allow the atoms to interact among themselves. Let us consider here the problem of the formation a molecule (which is the first step toward a solid). To get a qualitative understanding of the problem let us consider first the problem of two protons and one electron, that is, the H_2^+ molecule. The Hamiltonian of this problem can be written as

$$H = \frac{\mathbf{p}_e^2}{2m_e} + \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2m_p} + -e^2 \left(\frac{1}{|\mathbf{r}_e - \mathbf{R}_1|} + \frac{1}{|\mathbf{r}_e - \mathbf{R}_2|} - \frac{1}{|\mathbf{R}_1 - \mathbf{R}_2|} \right) \tag{1.42}$$

where $\mathbf{r}$ is the position of the electron and R_1 and $\mathbf{R}_2$ are the positions of the two protons. The first three terms are the kinetic energies of each one of these particles and the last three their interaction energy. This is a quite complicated problem. The wavefunction of the system is a function of all the coordinates, $\Psi(\mathbf{r}_e, \mathbf{R}_1, \mathbf{R}_2)$. We make use of the Born-Oppenheimer approximation and assume that the protons are static during the time of motion of the electron.

Suppose that initially the protons are infinitely apart. For simplicity assume $\mathbf{R}_1 = 0$ and $\mathbf{R}_2 = \mathbf{R}$. In this case the problem has two solutions which are degenerate with each other, that is, the electron is bound to proton 1 with energy E_0 and the proton 2 is empty or vice-versa. The wavefunction of the electron, ψ_0, is well localized in each proton (it is a H-like wavefunction). Let us consider a simplification of the problem which forgets about all the other states of the problem except for the states in which the electron is localized in one of the protons as in Fig.1.4. Let $\langle 1|$ ($\langle 2|$) be the state of the electron bound to proton 1(2). If $R \to \infty$ one has

$$\begin{aligned} H_0|1\rangle &= E_0|1\rangle \\ H_0|2\rangle &= E_0|2\rangle \end{aligned} \tag{1.43}$$

where $\langle 1|2\rangle = 0$ and $\langle 1|1\rangle = \langle 2|2\rangle = 1$.

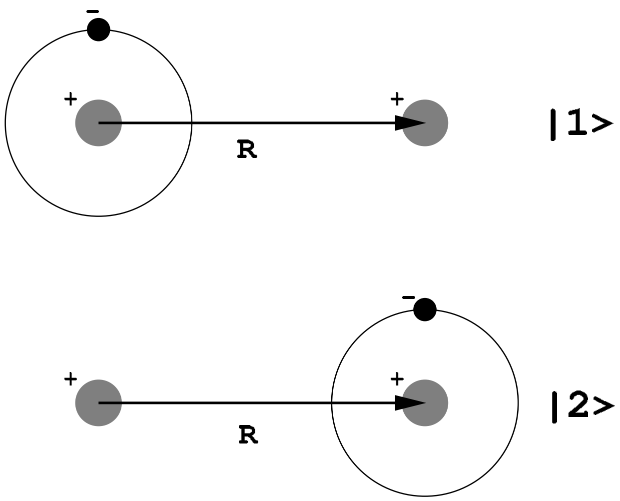

Figure 1.4: *Two states retained in the two-level system approximation of* H_2^+.

Equation (1.43) can be rewritten as

$$H_0 = E_0 \left(|1\rangle\langle 1| + |2\rangle\langle 2| \right) . \tag{1.44}$$

As the protons get closer to each other there is a finite probability that the electron can jump from proton 1 to proton 2 and vice-versa. This is the so-called *quantum tunneling* and is depicted on Fig.1.5. The tunneling depends on the amount of overlap between the wavefunction of the electron in the two different protons. There is an energy scale associated with the tunneling which we are going to call t. t is a function of R and vanishes when $R \to \infty$ and becomes large when $R \to 0$. Thus, in order to incorporate tunneling into the problem one has to add a perturbation that mixes the two states. This perturbation we call H_T and it has to be such that

$$H_T \psi_1 \propto \psi_2 \tag{1.45}$$

and of course $H_T^2 \propto I$ since if we hop the electron twice it has to return to the same atom. It is obvious that the tunneling Hamiltonian must have the form:

$$H_T = -t \left(|1\rangle\langle 2| + |2\rangle\langle 1| \right) . \tag{1.46}$$

Any eigenstate of $H = H_0 + H_T$ has to be a linear combination of states $\langle 1|$ and $\langle 2|$. This problem can be studied by rewriting the Hamiltonian in matrix form. The matrix elements are:

$$\begin{aligned} \langle 1|H|1\rangle &= \langle 2|H|2\rangle = E_0 \\ \langle 1|H|2\rangle &= \langle 2|H|1\rangle = -t \end{aligned} \tag{1.47}$$

which can be rewritten in matrix form:

$$[H] = \begin{bmatrix} E_0 & -t \\ -t & E_0 \end{bmatrix} . \tag{1.48}$$

Observe that in terms of the matrix formulation the states are represented by vectors

$$[\Psi_1] = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{1.49}$$

$$[\Psi_2] = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{1.50}$$

Of course our goal is to solve the Schrödinger equation

$$H|\psi\rangle = E|\psi\rangle\,. \tag{1.51}$$

From basic quantum mechanics the most general solution of this problem has to be a linear combination of base states, that is, $|\psi\rangle = a|1\rangle + b|2\rangle$. Normalization of the wavefunction (or probability) insures that $\langle\psi|\psi\rangle = 1 = |a|^2 + |b|^2$. In the language of (1.48) we have

$$[\Psi] = \begin{pmatrix} a \\ b \end{pmatrix} \tag{1.52}$$

and the Schrödinger equation becomes a simple eingenvalue problem

$$\begin{aligned} [H][\Psi] &= E[\Psi] \\ ([H] - E[I])[\Psi] &= 0 \end{aligned} \tag{1.53}$$

where

$$[I] = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{1.54}$$

is the identity matrix. It is a simple exercise to show that eigenstates of the problem are:

$$\begin{aligned} H|A\rangle &= (E_0 + t)|A\rangle \\ H|B\rangle &= (E_0 - t)|B\rangle\,. \end{aligned} \tag{1.55}$$

where

$$\begin{aligned} |A\rangle &= \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \\ |B\rangle &= \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}\,. \end{aligned} \tag{1.56}$$

These states are called anti-bonding and bonding, respectively. Observe that the bonding state is the ground state of the problem. In the representation of position these two states can be easily written as

$$\begin{aligned} \langle \mathbf{R}, \mathbf{r}|B\rangle &= \psi_{B,\mathbf{R}}(\mathbf{r}) = \psi_0(\mathbf{r}) + \psi_0(\mathbf{r}-\mathbf{R}) \\ \langle \mathbf{R}, \mathbf{r}|A\rangle &= \psi_{A,\mathbf{R}}(\mathbf{r}) = \psi_0(\mathbf{r}) - \psi_0(\mathbf{r}-\mathbf{R}) \end{aligned} \tag{1.57}$$

where ψ_0 is the ground state wavefunction of the H atom ($\psi_{n=0,l=0,m=0}(r)$). Observe that the anti-bonding state has a node in the middle position between the protons ($\psi_{A,\mathbf{R}}(\mathbf{r} = \mathbf{R}/2) = 0$) while the bonding state is always finite. Thus in the bonding state the amount of "charge" between the protons is larger (the probability of finding the electron) than in the bonding state. That is the reason its energy is lower and it keeps the two protons together. In the anti-bonding case the electronic charge is mostly around the two protons which are therefore "shielded" from each other. Thus, the anti-bonding state is unstable. A plot of square of the wavefunction for each one of these states is shown on Fig. 1.6.

Another way to understand the problem is to realize that at finite R we can expand the potential term in (1.42) in powers of r/R and it is clear that the first term is of order r/R^2. Since this term is very small we can do perturbation theory. The first order term cancels due to symmetry $\langle\psi_0|\mathbf{r}|\psi_0\rangle = 0$. The second order term has the form $\delta E = \sum_{n\neq 0} |\langle\psi|V|\psi_n\rangle|^2/(E_0 - E_n)$. This term is always negative if E_0 is the ground state. From the previous argument it is clear that $|t| = -\delta E > 0$. Thus, in this way, we relate our original problem with the two-level system calculation. On the one hand, the energy of the ground state (in this case a bonding state) has to decrease as we decrease the distance between atoms. On the other hand the first excited state (the anti-bonding state) increases in energy as we decrease the distance between the protons (since $t \to 0$ as $R \to \infty$). When the distance between atoms goes to zero the energy has to go to infinity since the Coulomb energy term $1/R$ diverges. Thus we conclude that there must be a minimum of the ground state energy at some distance R_0 (see Fig.1.7). In first approximation the energy close to the minimum is parabolic and therefore the energy is quantized in units of $\hbar\omega_0 \approx E_0$. Moreover, since this corresponds to the potential where the electron is

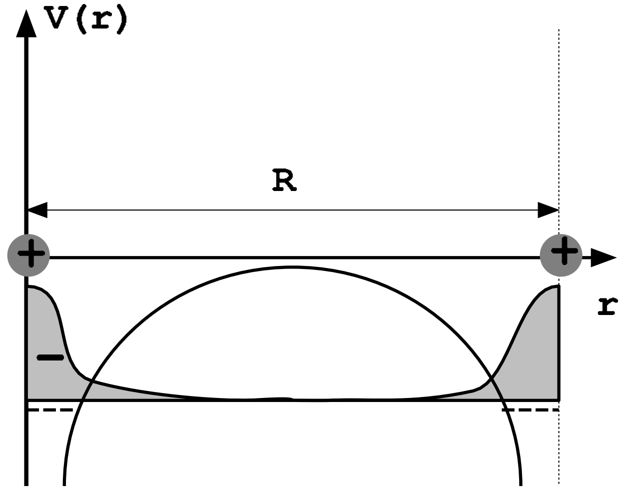

Figure 1.5: *Potential energy for* H_2^+ *molecule showing the overlap of the electron wavefunction in the two different protons.*

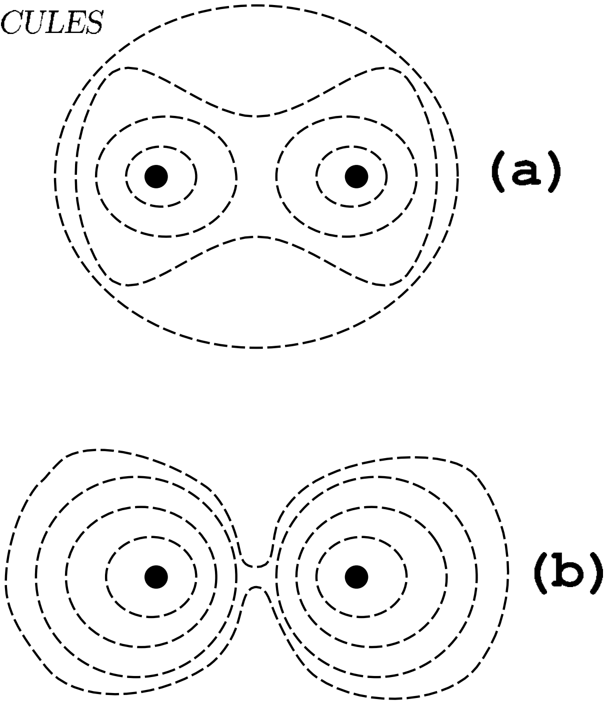

Figure 1.6: *Contour plot for the square of the wavefunction for: (a) Bonding state; (b) Anti-bonding state.*

trapped we can write

$$E_e(R) \approx E^0 + \frac{k m_e E_0^2}{2\hbar^2}(\mathbf{R} - \mathbf{R}_0)^2 \tag{1.58}$$

where k is a constant of order unit. Thus, by direct substitution in (1.14) we see that the protons undergo harmonic motion around the equilibrium position with a frequency $\approx \sqrt{m_e/m_p}E_0/\hbar$.

Let us check now the validity of our approximation. By direct substitution of (1.42) and (1.14) into the Schrödinger equation we find that the have neglected terms of the form $-\hbar^2\nabla_1\psi \cdot \nabla_1\phi/m_p$. Since variations in R_1 will produce variations in r we can write this term as approximately $|\mathbf{p}_e||\mathbf{p}_p|/(m_p)$. Thus in order for our approximation to be valid we have to require $\mathbf{p}_p^2/m_p >> |\mathbf{p}_e||\mathbf{p}_p|/m_p$ or $|\mathbf{p}_p| >> |\mathbf{p}_e|$. The momentum of the electron in a bound state of the H-atom is approximately $p_e \approx \sqrt{m_e E_0}$ while for the protons undergoing harmonic motion we have $p_p \approx \sqrt{m_p\sqrt{m_e/m_p}E_0}$. Thus the Born-Oppenheimer

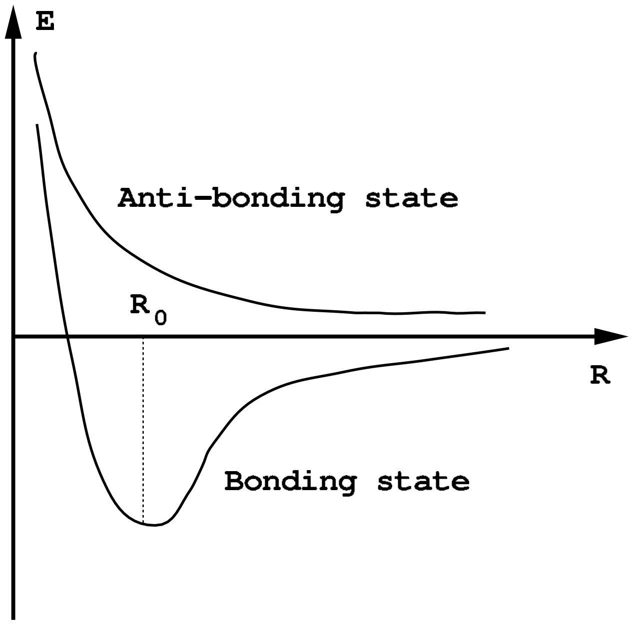

Figure 1.7: *Energy of the* H_2^+ *system as a function of the distance between the protons R.*

approximation works when

$$m_e^{1/4} << m_p^{1/4} \tag{1.59}$$

which is a good approximation in most cases ($(m_e/m_p)^{1/4} \approx 0.16$). Thus we have shown that within these approximations the protons undergo harmonic motion and within a period of oscillation of the protons the electron can be found in a bonding state. This is an example of a *covalent bond* where the electron is shared by the protons.

1.3.2 The H_2 molecule

The argument given above does not apply to neutral atoms since we have to introduce the Coulomb repulsion between the electrons in different atoms. Consider the H_2 molecule. The two electrons are tightly bound to each proton. We can still do perturbation theory by assuming that the atoms are very far apart from each other and start from the *atomic* limit. In this case, since the atoms are neutral, the electric monopole terms of H_2 vanish and one has to consider the next term in the multipole expansion of the Coulomb potential. The next contribution comes from a dipole term that behaves like $1/R^3$. Thus, if we do perturbation theory again on this term the first order is null (as before) and the second order perturbation theory for the ground state is negative. Thus the second order perturbation theory produces an effective interaction that behaves like

$$H_{VdW} = -\frac{\alpha_1 \alpha_2}{R^6} \tag{1.60}$$

where $\alpha_{1,2}$ are the polarizability of the atoms. This is a very short range interaction compared with the bare Coulomb interaction and moreover it is attractive. This is known as the *Van der Walls* interaction.

Our reasoning here is very similar to the one in the problem of the H_2^+ system. Within the Born-Oppenheimer approximation consider the wavefunction of the problem with two electrons and two protons separated by a fixed distance R. We have various possibilities among the various arrangements of the electrons around the protons. We can have one electron around each proton or we can have the two electrons around one proton. It turns out, however, that in this last situation the Coulomb repulsion between the electrons is large and therefore the ground state has to have one electron per proton. This is the so-called *Heitler-London* approach. Thus we have two states which are degenerated when the protons are infinitely apart, that is, with the electrons in their original position or with the electrons exchanged between the protons. These two states are depicted on Fig.1.8.

The situation here is completely equivalent to the H_2^+ system and as the protons approach each other they can exchange their electrons. Let $\mathbf{r}_{1,2}$ be the position of each electron. The most general wavefunction for this problem has the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \alpha\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) + \beta\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) \tag{1.61}$$

where α, β are coefficients and $\psi_i(\mathbf{r}_j)$ means the state of electron j on atom i. If the distance between the atoms is infinity, any linear combination of the type (1.61) is a solution. As we approach the H atoms the electrons from each atom can tunnel from one proton to another

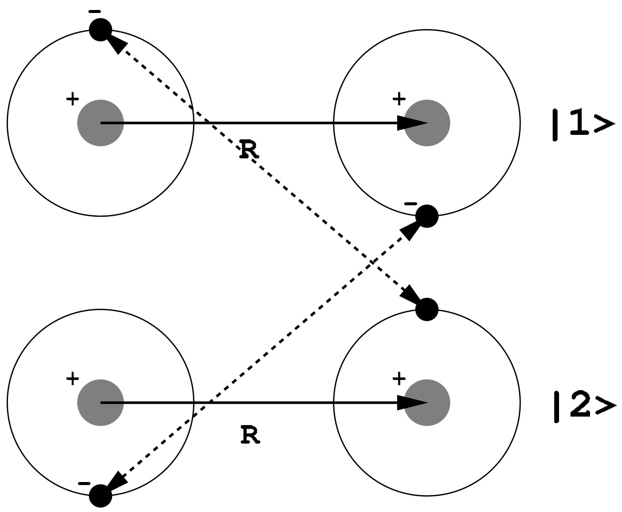

Figure 1.8: *Two states retained in the two-level system approximation of* H_2.

(but always there is one electron per proton!). Using the two-level system approach we find that the states that matter are the bonding and anti-bonding states which can be written as,

$$\begin{aligned}\Psi_A(\mathbf{r}_1,\mathbf{r}_2) &= N_A\left(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)\right)\\ \Psi_B(\mathbf{r}_1,\mathbf{r}_2) &= N_B\left(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) + \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)\right) \qquad (1.62)\end{aligned}$$

where $N_{A,B}$ are normalization constants. There is a possible problem here, however. The Pauli principle requires that when we exchange the electrons, the wavefunction has to change sign (indeed, one must have, $\Psi(\mathbf{r}_1,\mathbf{r}_2) = -\Psi(\mathbf{r}_2,\mathbf{r}_1)$ and therefore, $\Psi(\mathbf{r}_1,\mathbf{r}_1) = 0$). Thus, state Ψ_B (which we concluded to be the ground state) *cannot exist!* What is wrong with this picture? What is wrong is that we forgot the electron spin. We can still have a wavefunction that is symmetric with respect to the coordinates if we have a spin part which is anti-symmetric and vice-versa. Thus, from the four states available for the two electron problem the only spin states that matter are:

$$\begin{aligned}\chi_s(s_1,s_2) &= |s_1=\uparrow, s_2=\downarrow\rangle - |s_1=\downarrow, s_2=\uparrow\rangle\\ \chi_t(s_1,s_2) &= |s_1=\uparrow, s_2=\downarrow\rangle + |s_1=\downarrow, s_2=\uparrow\rangle \qquad (1.63)\end{aligned}$$

which are singlet and triplet combinations of the spins, respectively. Thus, accordingly to the Pauli principle the states allowed are

$$\begin{aligned}\Psi_s(\mathbf{r}_1,s_1;\mathbf{r}_2,s_2) &= \Psi_B(\mathbf{r}_1,\mathbf{r}_2)\chi_s(s_1,s_2)\\ \Psi_t(\mathbf{r}_1,s_1;\mathbf{r}_2,s_2) &= \Psi_A(\mathbf{r}_1,\mathbf{r}_2)\chi_t(s_1,s_2)\,. \qquad (1.64)\end{aligned}$$

The Pauli principle has strong consequences here. The tunneling of electrons between atoms favors the bonding state but if the electrons have the same spin projection this is not possible. Thus atoms with the same spin projection repel each other. In some way, as we bring two H atoms together we are trying to form a He atom. If the spins were the same the electronic configuration should be $1s^1 2s^1$ by the Pauli principle. If we had the atoms with electrons with opposite spin then we would get $1s^2$ which is lower in energy. For the anti-bonding state we can have the electrons with the same spin but in this case the atom will not be stable (as shown in Fig.1.7). Thus, the ground state of the H_2 atom has to be a singlet state. This discussion implies that the Pauli principle acts as a force between the electrons, that is, there is a quantum mechanical repulsion between the atoms with the same spin. There is no classical analogue to this effect. Moreover, at shorter distances the Coulomb repulsion between the electronic clouds becomes large and this effect also increases the repulsion. In principle it is very hard to calculate the combined effect of all interactions and one usually uses the a phenomenological approach and introduce a repulsive term of the form $1/R^{12}$ which is very short ranged and is called *Lennard-Jones* potential so that the atom has a minimum at some R_0 as before. Thus the energy of the molecule again looks very much like in Fig.1.7.

1.3.3 Ionic interactions

Another important interaction between atoms is the so-called ionic bond. This interaction happens when the atoms have strong tendency to form a filled electronic shell (that is, it gains more energy by binding strongly one electron to the nucleus instead of sharing it with the other atom). Standard examples are the combinations of the elements of the column 1A and 7A of the periodic table such as, NaCl. In order to understand that observe that the charge distribution of Na is $1s^2 2s^2 2p^6 3s^1$ while Cl is $1s^2 2s^2 2p^6 3s^2 3p^5$. Thus if Na donates one electron entirely to Cl it has the electronic configuration of Ne while Cl has the configuration of Ar which are noble gases. Thus, in the most stable configuration the molecule of NaCl has ions Na^+Cl^-. In this case there is almost no screening of the electronic clouds and the atoms actually feel the bare Coulomb interaction between them. At short distances, as we saw before, there is a strong repulsion between the atoms which can be accounted by the Lennard-Jones potential. Thus, for a molecule of NaCl the energy of the system will look again like in Fig.1.7 with some minimum at R_0. If we bring another molecule of NaCl close to the first one Coulomb attraction (repulsion) between the atoms will bind the molecules together.

1.4 Problems

1. Verify the following identities related with the Levi-Civita tensor:

(1) $\epsilon_{i,j,k}\epsilon_{l,m,n} = \delta_{i,l}\delta_{j,m}\delta_{k,n} + \delta_{i,m}\delta_{j,n}\delta_{k,l} + \delta_{i,n}\delta_{j,l}\delta_{k,m} - \delta_{i,n}\delta_{j,m}\delta_{k,l} - \delta_{i,m}\delta_{j,l}\delta_{k,n} - \delta_{i,l}\delta_{j,n}\delta_{k,m}$;

(2) $\sum_k \epsilon_{i,j,k}\epsilon_{k,l,m} = \delta_{i,l}\delta_{j,m} - \delta_{i,m}\delta_{j,l}$;

Use (1.6) and (1.2) and the properties of the Levi-Civita tensor to prove (1.7).

2. The ionization energy of the oxygen is 13.6 eV and it is lower than the energy of its neighbors on the periodic table (the ionization energy of N is 14.5 eV and of F is 17.4 eV). Explain qualitatively why this is so in terms of the interaction between the electrons. (*Hint: start the problem by thinking what is going on with B and go up in the atomic number.*

3. Argon (A) is a noble gas and has filled shell with a configuration 3 p^6. The next atom in the periodic table is potassium (K) which has the configuration of lowest energy with 4 s^1 instead of 3 d^1! Provide an argument that explains this observation.

4. Show that equation (1.19) is correct.

5. Show that the total angular momentum defined in (1.27) commutes with the Hamiltonian in the presence of spin-orbit coupling.

6. Use Hund's rules to find the configuration of lowest energy for an atom in which the last incomplete shell has a configuration: 1) d^8; 2) f^9. What is the value of the **total** magnetic moment in each one of these configurations.

7. What is the condition for which $J = 0$ in terms of n and l?

8. Use the Wigner-Eckert theorem to show that for $J = 0$ the first term in (1.20) vanishes.

9. Use the algebra of angular momentum (Clebsh-Gordon coefficients) and prove (1.34) and (1.35).

10. Prove equation (1.36).

11. Prove equation (1.37).

12. Prove equation (1.38).

13. Two localized spins 1/2 interact via an *exchange* mechanism which is described by a Hamiltonian

$$H = J\mathbf{S}_1 \cdot \mathbf{S}_2 \,. \tag{1.65}$$

i) What are all the possible configurations of the two spins in the basis of S_1, S_{1Z}, S_2, S_{2Z}?
ii) What are the energies and their respective eigenstates of the system when $J > 0$?
iii) What are the energies and their respective eigenstates of the system when $J < 0$?
iv) Suppose a magnetic field, B, is applied to the system so that we have to add the Zeeman energy to the Hamiltonian in (1.65):

$$H_B = -\mu_B B \left(S_{1Z} + S_{2Z}\right) \tag{1.66}$$

where $\mu_B > 0$ is the effective Bohr magneton. Make a plot of the energy of the states you found on item 2) as a function of magnetic field. What is the state with lowest energy when $B \to \infty$? What is its physical meaning?

14. Consider the Schrödinger equation (1.51). Assume that $|\Psi\rangle = a|1\rangle + b|2\rangle$ and calculate a and b by direct substitution.

15. Solve the eigenvalue problem of equation (1.53) in matrix form and show that the solution can be written in terms of (1.55) and (1.56).

16. Consider a one dimensional molecule described by the Hamiltonian

$$H = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{m\omega^2}{2}\left(|r| - \frac{R}{2}\right)^2 \tag{1.67}$$

where $R > 0$ is the relative coordinate of the nuclei with mass M, m is the mass of the electron and r is the coordinate of the electron relative to the center of mass. Using the Born-Oppenheimer approximation, that is, assuming

$$\Psi(r, R) = \psi_R(r)\phi(R) \tag{1.68}$$

find, by direct substitution of (1.68) into (1.67) which terms are neglected. Assuming that the energy has a minimum close to R_0 show that the nuclei oscillate with a frequency $\omega\sqrt{m/M}$. From this result show that we can use the Born-Oppenheimer approximation when $(m/M)^{1/4} << 1$.

17. Show that the dominant interaction between two H atoms has a dipole form at large values of the separation between them (call it R).

18. Now consider a molecule made out of three atoms as shown of Fig.1.9.

    In this case the states of the electrons localized in each one of the atoms can be written as:

$$\begin{aligned}\psi_1 &= \begin{pmatrix}1\\0\\0\end{pmatrix}\\ \psi_2 &= \begin{pmatrix}0\\1\\0\end{pmatrix}\\ \psi_3 &= \begin{pmatrix}0\\0\\1\end{pmatrix}.\end{aligned}$$

    (i) If tunneling between the atoms is allowed show that the Hamiltonian is written as

$$H = -t\begin{bmatrix}0 & 1 & 1\\1 & 0 & 1\\1 & 1 & 0\end{bmatrix}.$$

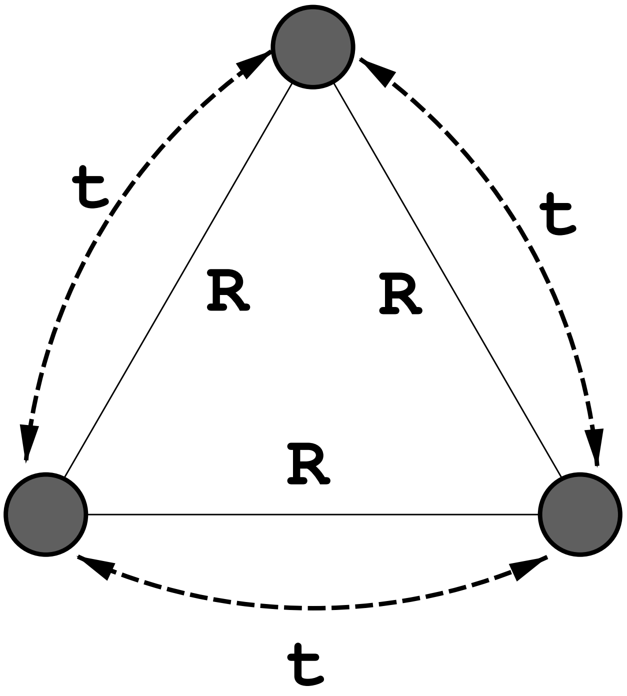

Figure 1.9: *Three atom molecule as a triangle of side R and hopping energy t.*

(*ii*) Diagonalize the Hamiltonian and show that the eigenvalue problem gives the following energies $-2t$ and t with eigenvectors,

$$\begin{aligned} \psi_G &= \frac{1}{\sqrt{3}}\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \\ \psi_{E1} &= \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix} \\ \psi_{E2} &= \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 1 \\ 0 \end{pmatrix} \end{aligned} \tag{1.69}$$

respectively. Observe that ψ_{E1} and ψ_{E2} are not orthogonal to each other and one has to orthogonalize them. Use the *Gram-Schmidt* method and find an orthogonal basis.

Note: Observe that the degeneracy of the problem was lifted by the tunneling. However, two of the states are still degenerate. This is because the problem has an extra symmetry which is due to rotation of $\pi/3$. *A similar thing happens in the benzene molecule which has 6 C atoms.*

Chapter 2

Crystals

2.1 Introduction

We have seen that by sharing or exchanging electrons stable molecules of atoms can be formed. Depending on external conditions such as temperature or pressure as atoms or molecules get closer to each other a solid can be formed. Solids are highly symmetric structures that can be formed in very different shapes. The shapes depend very on the type of orbitals that participate in the binding between different atoms.

As an illustration let us consider the famous high temperature superconductors (HTC) which are formed by planes of CuO_2 atoms. The atoms in these planes are arranged in squares as in Fig.2.1. An isolated O atom has an electronic structure $1s^22s^22p^4$ while Cu has $1s^22s^22p^63s^23p^63d^{10}4s^1$. Thus by getting two electrons the O atom can close its p-shell and acquire the same configuration of Ne. We say that O has valence -2. Thus, in the CuO_2 planes we have Cu^{+2} and O^{-2}. The O atom has a close p shell and the Cu is in a $3d^9$ configuration. It means that there is a place for a single electron in the d shell of Cu (there is one unpaired electron). Therefore, it is very reasonable to imagine that the bond between O and Cu is done by a *hybridization* (or mixing) of the p orbital of the O with the d orbital of Cu. Since these orbitals have an anisotropic structure and are oriented 90 degrees in respect to each other we expect a square lattice such the one in Fig.2.1(a). The orbitals overlap like in Fig.2.1(b). It is interesting to note that this simple orbital structure is probably responsible for the remarkable properties of these materials. We can predict a lot about the structure of a solid by looking at the periodic table but, of course.

A remarkable property of crystalline solid is its symmetry. Imagine yourself walking over a lattice of atoms which show a periodic structure such as the one in Fig.2.1(a). You immediately note that as you move from atom to atom you see exactly the same structure. Moreover, as you look at the system from some specific angles it looks the same. Thus, one expects based on this observation that in *perfect* crystals the physical properties are the same at each point of the lattice, that is, the physical properties of the system are invariant under symmetry operations. These symmetry operations can be mathematically defined and help us to predict many different properties of crystals. In terms of quantum mechanics this can be expressed by the fact that there are quantum mechanical operators $\mathcal{O}$ that generate these symmetries. For instance, the operator that generate translations by an amount $\mathbf{R}$ is

$$\mathcal{O}_T = e^{i\mathbf{P}\cdot\mathbf{R}/\hbar} \tag{2.1}$$

where $\mathbf{P}$ is the momentum operator. It is very simple to show that this is true. Suppose we apply this operator to a wavefunction $\Psi(\mathbf{r})$ and suppose the $\mathbf{R} = \delta\mathbf{r}$ is an infinitesimal quantity. Then,

$$\mathcal{O}_T\Psi(\mathbf{r}) \approx \Psi(\mathbf{r}) + \delta\mathbf{r}\cdot\nabla\Psi(\mathbf{r}) \approx \Psi(\mathbf{r}+\delta\mathbf{r}) \tag{2.2}$$

where we have expanded the exponential and used that $\mathbf{P} = -i\hbar\nabla$. For systems described by a Hamiltonian H which is translational invariant the operator $\mathcal{O}_T$ must be a constant, that is, it must commute with the Hamiltonian, $[H, \mathcal{O}_T] = 0$. In this way, we know from the fundamentals of quantum mechanics that the wavefunctions of the Hamiltonian can be *classified* accordingly to the eigenstates of the operator $\mathcal{O}_T$. This operator can be diagonalized straightforwardly since its eigenstates are the momentum eigenstates,

$$\mathcal{O}_T|\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{R}/\hbar}\,|\mathbf{k}\rangle \tag{2.3}$$

Thus, even when we do not know how to calculate exactly the eigenstates of the Hamiltonian (and we don't in most cases) we know that

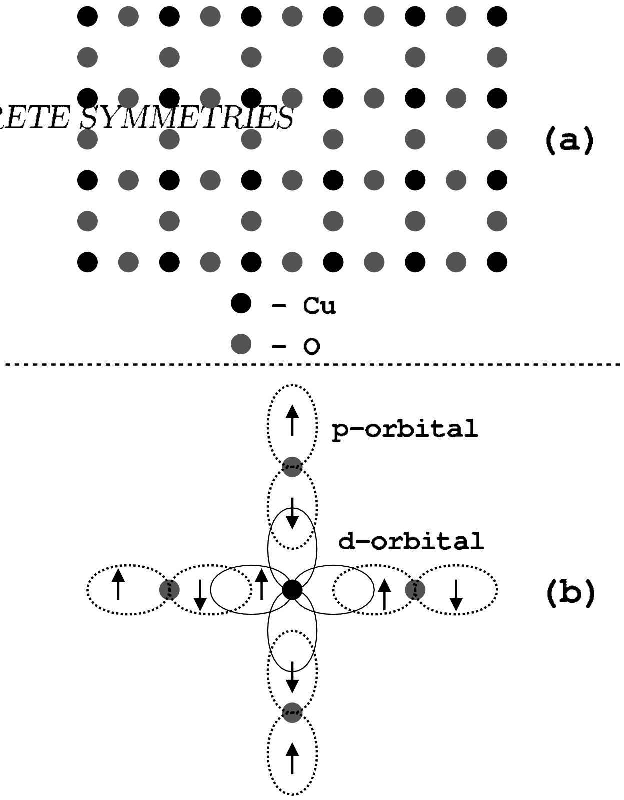

Figure 2.1: *(a) Spatial structure of a CuO_2 plane; (b) Atomic orbitals involved in the binding.*

the momentum is a good quantum number and therefore the wavefunctions can be labeled by the momentum. This is a major advantage since we can make predictions based on simple calculations as we are going to see. Translation is a simple example of a symmetry. There are many other symmetries that can be expressed in terms of operators as well.

2.2 Discrete Symmetries

The two most important symmetry operations are:

1) **Translations** by one lattice spacing;

2) **Point operations**: rotations and reflections.

In order to define a translation we have to define first two mathematical concepts: lattice and basis. *Lattice* is a periodic array of points which can be described by a translation vector

$$\mathbf{T} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \tag{2.4}$$

where $\mathbf{a}_{1,2,3}$ are three independent vectors and $n_{1,2,3}$ three arbitrary integers (in two dimensions we have, of course, only two of them). A periodic array of points is called a lattice if given $\mathbf{R}$ on the array then $\mathbf{R}' = \mathbf{R} + \mathbf{T}$ is also on the array. Thus by choosing different sets of integers we can generate the whole lattice. For each lattice point we can assign different atoms. In this case we have a *basis.* Let $\mathbf{R}_\alpha$ be the coordinate of these atoms with respect to a lattice point. Here, $\alpha = 1, 2, ..., N_b$, where N_b is the number of atoms in a basis. A crystal structure is combination of a lattice plus a basis, that is, any distance between two atoms on a lattice can be written as $\mathbf{T} + \mathbf{R}_\alpha$.

Observe that there is no unique way to define a lattice but it is common to define the *primitive* quantities as the most economic way to describe the crystal. We call the primitive translation vectors as the smallest $\mathbf{a}_{1,2,3}$ that still allow the definition of a lattice. An example of a two-dimensional lattice is shown on Fig.2.2.

We also define what is called as the *unit cell* as a certain volume that fill out the space when translated by all possible $\mathbf{T}$. It is clear that this definition is not unique. We can define a primitive unit cell which is the one with the smallest volume or the Wigner-Seitz unit cell which is obtained by linking the nearest neighboring atoms together and then cutting these lines in the middle by planes (see Fig.2.3). Observe that if $\mathbf{a}_i$ are the primitive vectors then the volume of the primitive unit cell is simply

$$V_0 = \left|\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)\right|. \tag{2.5}$$

Together with the translation symmetry the point symmetries define what is known as the *Bravais* lattices. To each symmetry we have an operator which changes the coordinates of the system around a point on the lattice with an axis through it. The principal axis is the axis with the highest symmetry (that is, the one with the largest number of symmetry operations). The symmetry operations are: (*i*) Identity ($\mathbf{R} \to \mathbf{R}$); (*ii*) Inversion ($\mathbf{R} \to -\mathbf{R}$); (*iii*) Rotations, C_n, by an angle of $2\pi/n$ where n is an integer; (*iv*) Reflection by a plane; (*v*) Improper

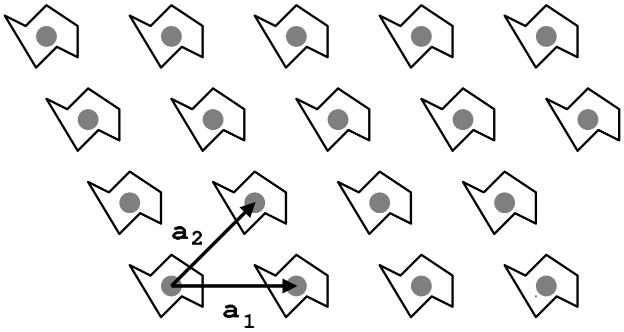

Figure 2.2: *Example of a two-dimensional lattice with a basis.*

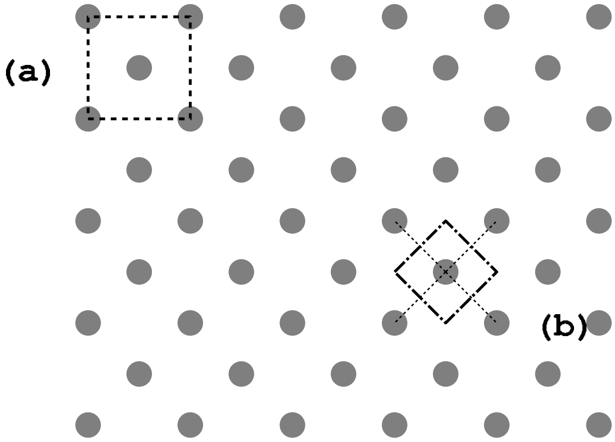

Figure 2.3: *(a) Conventional unit cell; (b) Wigner-Seitz cell.*

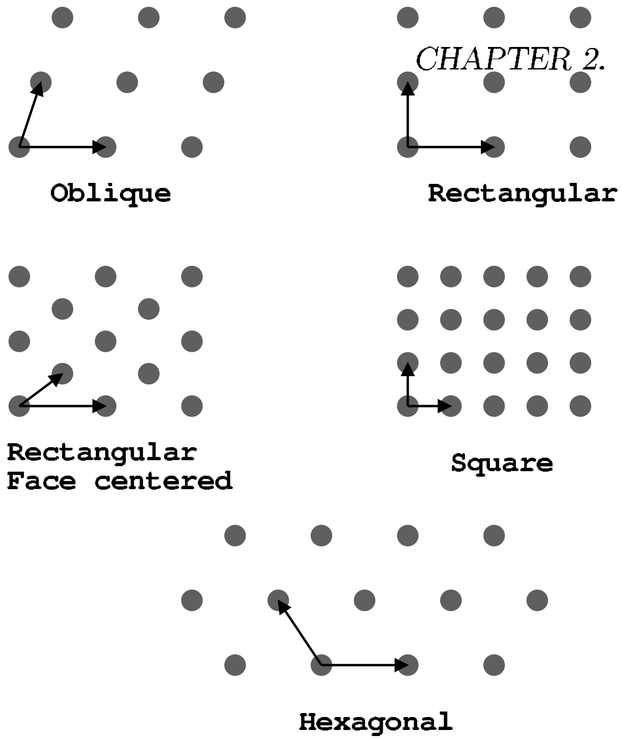

Figure 2.4: *Possible Bravais lattices in two-dimensions.*

rotations which are combinations of a rotation and a reflection through a plane perpendicular to a principal axis. These operations can be easily identified by inspection.

In two dimensions there are only five types of Bravais lattices that can be obtained from the operations above. They are shown in Fig.2.4. It is easy to show that in two dimensions it is not possible to have a Bravais lattice with 5 fold symmetry (that is, it is not possible to fill out the plane with pentagons) and there are not Bravais lattice with rotations higher than six-fold symmetry. Thus we are only left with the Bravais lattices of Fig.2.4: (1) Oblique (which is symmetric only under C_2); (2) Rectangular (which is symmetric under C_2 and has two reflection planes); (3) Rectangular face centered; (4) Square (which is symmetric under C_4 and three reflection planes); (5) Hexagonal (which is symmetric under C_6, C_3, and six reflection planes).

Observe that the hexagonal lattice is the most symmetric of all Bravais lattice in two dimensions (that is, is invariant under the largest number of symmetry operations). Moreover, the hexagonal lattice is

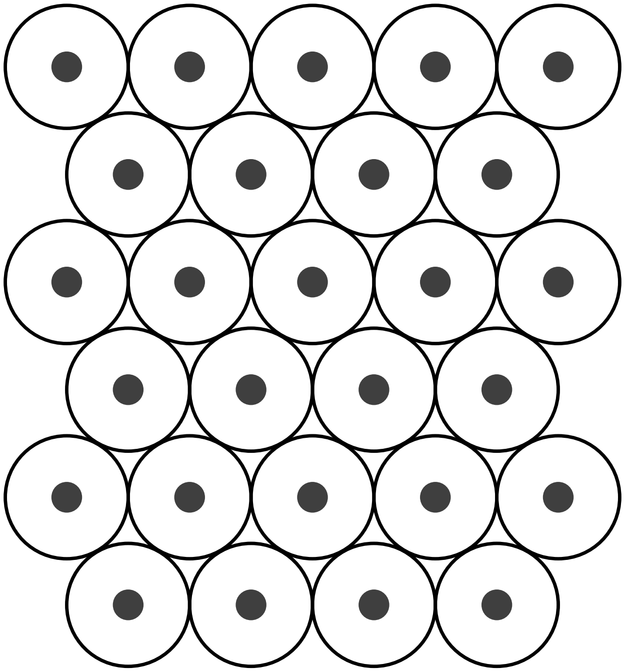

Figure 2.5: *Close packing structure for the hexagonal lattice.*

special because it is *close packed*, that is, it is a lattice that has the densest packing of hard spheres. Indeed, in the hexagonal lattice we can densely fill the lattice by placing spheres of radius $a/2$ (where a is the lattice spacing) in the center of a triangular lattice as in Fig.2.5.

In three dimensions there are fourteen Bravais lattices in seven different types of structures. One of the most important is the cubic structure that has three Bravais lattices: Simple Cubic (SC); Body Centered Cubic (BCC); Face Centered Cubic (FCC). These Bravais lattices can be again classified by the symmetry operations described before and are shown in Fig.2.6.

2.2.1 The reciprocal lattice

As we said before the symmetries are very useful in helping to describe the various physical properties of materials. In a perfect crystal the properties of the system should not vary as me move through a lattice. One of the most important properties is the density, $n(\mathbf{r})$. Given a set

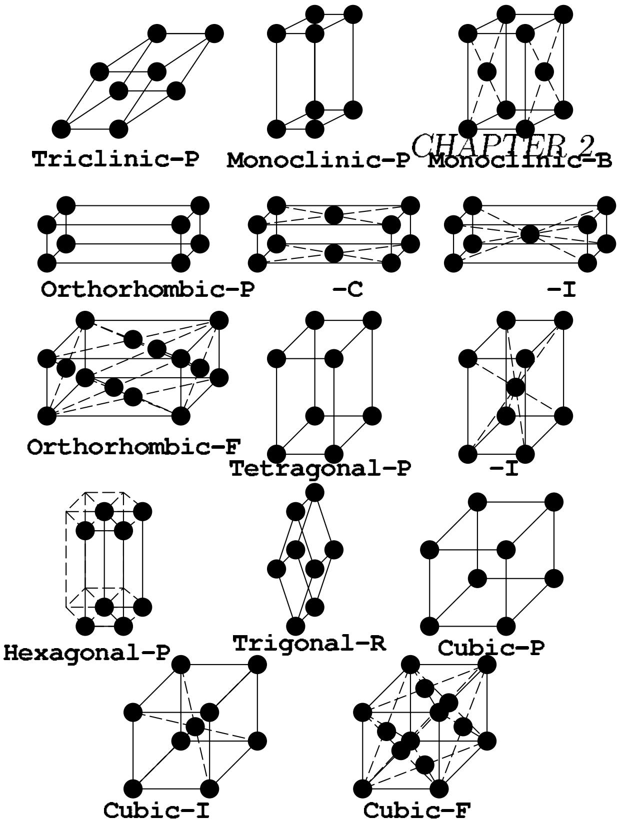

Figure 2.6: *Bravais lattices in three dimensions.*

of N atoms at positions $\mathbf{R}_i$ with $i = 1, ..., N$ the density is simply

$$n(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{R}_i) \tag{2.6}$$

(observe that if we integrate the above expression in all space we obtain N which is the total number of particles). Observe that from our previous discussion we can rewrite for a crystal

$$\mathbf{R}_i = \mathbf{T} + \mathbf{R}_\alpha\,. \tag{2.7}$$

Therefore, for a crystal, one can rewrite the density as

$$n(\mathbf{r}) = \sum_{\mathbf{T}} \sum_{\alpha} \delta(\mathbf{r} - \mathbf{T} - \mathbf{R}_\alpha)\,. \tag{2.8}$$

Observe therefore that if we have N_s unit cells with N_b atoms in a basis we must have $N = N_s N_b$.

The translation symmetry of the crystal requires that

$$n(\mathbf{r}) = n(\mathbf{r} + \mathbf{T}) \tag{2.9}$$

for *all* **T**. This can automatically concluded if we use (2.8) and notice that the sum of two lattice vectors is another lattice vector. Observe that this property has strong consequences if we write the Fourier series of the density:

$$n(\mathbf{r}) = \sum_{\mathbf{q}} n(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \tag{2.10}$$

then from (2.9) we must have $\mathbf{q} = \mathbf{G}$ where

$$\mathbf{G} \cdot \mathbf{T} = 2\pi n \tag{2.11}$$

where n is an integer. It is clear from the definition of **T** in (2.4) that we can always define **G** by

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 \tag{2.12}$$

where $m_{1,2,3}$ are three arbitrary integer and $\mathbf{b}_{1,2,3}$ three independent vectors such that

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} \tag{2.13}$$

$\delta_{ii} = 1$ and $\delta_{ij} = 0$ if $i \neq j$ is a Kronecker delta. It is simple to show that

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \tag{2.14}$$

and the other vectors are just cyclic permutations of the above equation. By the same token one has

$$\mathbf{a}_1 = 2\pi \frac{\mathbf{b}_2 \times \mathbf{b}_3}{\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)} \,. \tag{2.15}$$

Observe that these new vectors span a new lattice. This lattice is called *reciprocal lattice*. Everything we said before in regards to Bravais lattices is also valid for reciprocal lattices. In particular, the Wigner-Seitz cell of the reciprocal lattice is called *Brillouin zone*. Moreover, observe that (2.11) defines planes in the real space such that each plane is perpendicular to $\mathbf{G}$ (see Fig.2.7). In order to see that this is true remember that the density is now written as

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \tag{2.16}$$

thus, for each $\mathbf{G}$ the density is given by a plane wave of the form $\cos(\mathbf{G}\cdot\mathbf{r})$ in the direction of $\mathbf{G}$. Each maximum of the wave corresponds to a plane of atoms (since the density is maximum at these planes) where the empty space between the planes corresponds to a minimum in the wave. Since the wavelength of this wave is $2\pi/|\mathbf{G}|$ and the distance between planes perpendicular to $\mathbf{G}$ is d we must have

$$d = \frac{2\pi}{|\mathbf{G}|} \,. \tag{2.17}$$

Another way to see this relation if through (2.11). Consider two points in neighboring planes, say $\mathbf{R}_n$ and $\mathbf{R}_{n-1}$, such that $|\mathbf{R}_n - \mathbf{R}_{n-1}| = d$ is the distance between planes. Then from (2.11) one has

$$|\mathbf{G}| = \frac{2\pi}{d} \,. \tag{2.18}$$

Thus $\mathbf{G}$ labels an infinite number of parallel planes in real space. The classification of these planes in particularly useful in crystallography. Since we saw that $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ we can label planes by the set of number $[hkl]$ which are called Miller indices. For instance, for a set of planes in the $\mathbf{x}$ direction we have (100) and for a set of planes in the $\mathbf{x}+\mathbf{y}$ direction we would have (110), etc. Observe that the planes (200) and $(-100) = (\bar{1}00)$, for instance, are parallel to the planes (100). In this way it is very simple to think at the planes in real space as labeled by reciprocal lattice vectors.

We have seen that the density can be written in terms of a Fourier series of reciprocal lattice vectors $\mathbf{G}$, as in (2.16), which guarantees the periodic properties required by symmetry. The Fourier components $n_{\mathbf{G}}$ can be calculated by the inverse transform. This is done by multiplying (2.16) by $e^{-i\mathbf{K}\cdot\mathbf{r}}$ where $\mathbf{K}$ is a reciprocal lattice vector and integrating in the volume of the unit cell, V_0. Observe therefore that we are left with the integral

$$\int_{V_0} d^d r e^{i(\mathbf{G}-\mathbf{K})\cdot\mathbf{r}} = V_0 \delta_{\mathbf{G},\mathbf{K}} \,. \tag{2.19}$$

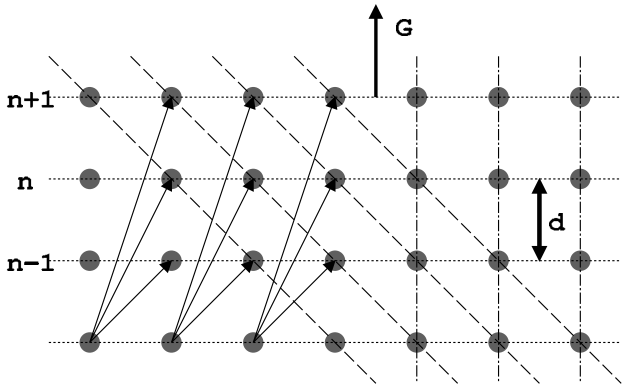

Figure 2.7: *Series of planes and its associated reciprocal lattice vector.*

In order to prove that this is indeed true we first remember that the sum of two reciprocal lattice vectors is another reciprocal lattice vector which can be written in the form (2.12). The result is trivial if $\mathbf{G} = \mathbf{K}$. Moreover, observe that the integrand has the periodicity of the lattice and its integral over a unit cell cannot depend on the choice of cell. In particular, it cannot change if we translate the unit cell by an arbitrary vector $\mathbf{R}$. Therefore, from this result we have

$$n_{\mathbf{G}} = \frac{1}{V_0} \int_{V_0} d^d r e^{-i\mathbf{G}\cdot\mathbf{r}} n(\mathbf{r}) \ . \tag{2.20}$$

2.2.2 One dimensional chain

Consider a circular chain of N atoms as depicted on Fig.2.8. The atomic density along the chain (which we parameterize by x) is simply

$$n(x) = \sum_{j=0}^{N} \delta(x - ja) \tag{2.21}$$

where a is the lattice spacing. (2.21) has a simple Fourier series

$$n(x) = \sum_k e^{ikx} n_k \tag{2.22}$$

and because the system has discrete translational symmetry by a, that is, $n(x+a) = n(x)$ (in (2.21) the shift by a is just equivalent to a renumbering of the lattice sites!), we must have

$$\begin{aligned} e^{ika} &= 1 \\ k_j &= \frac{2\pi j}{a} \end{aligned} \tag{2.23}$$

Thus, the values allowed by symmetry form a lattice with lattice spacing $2\pi/a$ which is the reciprocal lattice. The reciprocal lattice vectors are simply $G = \frac{2\pi n}{a}$. Also it is very simple to show that (2.19) and (2.20) are correct. Let us rewrite (2.22) in terms of the allowed values of k

$$n(x) = \sum_j e^{2\pi i j \frac{x}{a}} n_j \tag{2.24}$$

where the sum runs over all integers (positive and negative). Multiply both sides of the above equation by $e^{-2\pi i m \frac{x}{a}}$ and integrate from 0 to a

$$\int_0^a dx e^{-2\pi i m \frac{x}{a}} n(x) = \sum_j n_j \int_0^a dx e^{2\pi i (j-m) \frac{x}{a}} . \tag{2.25}$$

Now observe that for $j \neq m$ one has

$$\int_0^a dx e^{2\pi i (j-m) \frac{x}{a}} = a \frac{e^{2\pi i (j-m)} - 1}{2\pi i (j-m)} = 0 \tag{2.26}$$

because $e^{2\pi i (j-m)} = 1$. If $j = m$ the integral obviously gives a. Thus, we conclude that,

$$\int_0^a dx e^{2\pi i (j-m) \frac{x}{a}} = a \delta_{m,j} \tag{2.27}$$

which is the one dimensional version of (2.19). Going back to (2.25) one finds

$$n_j = \frac{1}{a} \int_0^a dx e^{-2\pi i j \frac{x}{a}} n(x) \tag{2.28}$$

which is the one-dimensional version of (2.20).

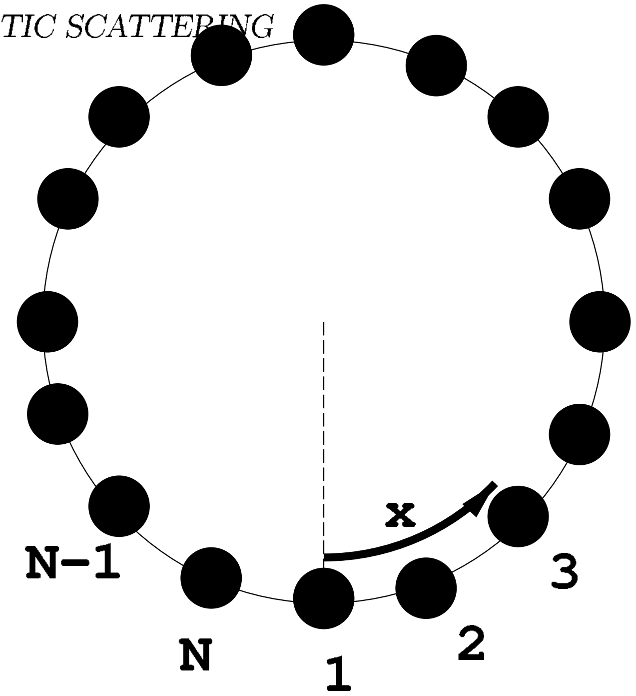

Figure 2.8: *Model for a one-dimensional crystal.*

2.3 Elastic scattering

In order to illustrate the importance of the reciprocal lattice let us consider the problem of scattering of the crystal lattice by light with wavelength λ. Imagine we send light into a crystal from very far away with a wave-vector $\mathbf{k}$ such that $k = 2\pi/\lambda$. The atoms in the crystal absorb the light and re-emit it in spherical waves as in Fig.2.9. These waves interfere with each other and an observer located at $\mathbf{R}$ observes a scattered wave with wave-vector $\mathbf{k}'$. Here we consider only the *elastic* scattering by the crystal so that no energy is lost in the collision of light with the crystal, that is,

$$k' = k = 2\pi/\lambda\,. \tag{2.29}$$

Consider an atom located at a position $\mathbf{r}$ in the crystal. The amplitude of the electric field of incident light at that position is

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}} \tag{2.30}$$

where $\mathbf{E}_0$ is a constant vector. The atom at $\mathbf{r}$ re-emits the light so that the contribution of this atom to the observed light at $\mathbf{R}$ is

$$\mathbf{E}(\mathbf{R}) \propto \mathbf{E}(\mathbf{r}) e^{i\mathbf{k}'\cdot\mathbf{r}'} \tag{2.31}$$

where $\mathbf{r}' = \mathbf{R} - \mathbf{r}$ (see Fig.2.9). Thus,

$$\mathbf{E}(\mathbf{R}) \propto \mathbf{E}_0 e^{i\mathbf{r}\cdot(\mathbf{k}-\mathbf{k}')} e^{i\mathbf{k}'\cdot\mathbf{R}} . \tag{2.32}$$

The contribution from the whole crystal is obtained by integrating (2.32) over the entire crystal

$$\mathbf{E}(\mathbf{R}) \propto \mathbf{E}_0 e^{i\mathbf{k}'\cdot\mathbf{R}} \int_{crystal} dV n(\mathbf{r})\, e^{i\mathbf{r}\cdot\delta\mathbf{k}} \tag{2.33}$$

where $\delta\mathbf{k} = \mathbf{k} - \mathbf{k}'$ and $n(\mathbf{r})$ is the density of atoms. Observe that the first factor in (2.33) is just a phase factor which is not important since it does not include the superposition of all the fields created by all atoms. Now the fact that the crystal has a periodic structure enters into place. Since the crystal is composed by N unit cells we do not have to integrate over all crystal, we just have to integrate over one cell and sum over all the other cells. This means that we can rewrite $\mathbf{r} = \mathbf{T} + \mathbf{r}'$ where $\mathbf{r}'$ describes the position of each atom in the unit cell. Thus, we can rewrite (**whole**) as

$$\begin{aligned}
\mathbf{E}(\mathbf{R}) &\propto \mathbf{E}_0 \sum_{\mathbf{T}} \int_{Cell} dV' n(\mathbf{T} + \mathbf{r}') e^{i(\mathbf{T}+\mathbf{r}')\cdot\delta\mathbf{k}} \\
&\propto \mathbf{E}_0 \sum_{\mathbf{T}} e^{i\mathbf{T}\cdot\delta\mathbf{k}} \int_{Cell} dV' n(\mathbf{r}') e^{i\mathbf{r}'\cdot\delta\mathbf{k}}
\end{aligned} \tag{2.34}$$

where we have used the translational symmetry of the problem, that is, $n(\mathbf{T} + \mathbf{r}') = n(\mathbf{r}')$.

Let us now focus on the first term of (2.34). For an arbitrary $\delta\mathbf{k}$ the sums of the exponential is only different from zero if

$$\mathbf{T} \cdot \delta\mathbf{k} = 2\pi n \tag{2.35}$$

where n is an integer. This condition means that in order to have a constructive interference we have to require that

$$\delta\mathbf{k} = \mathbf{G} \tag{2.36}$$

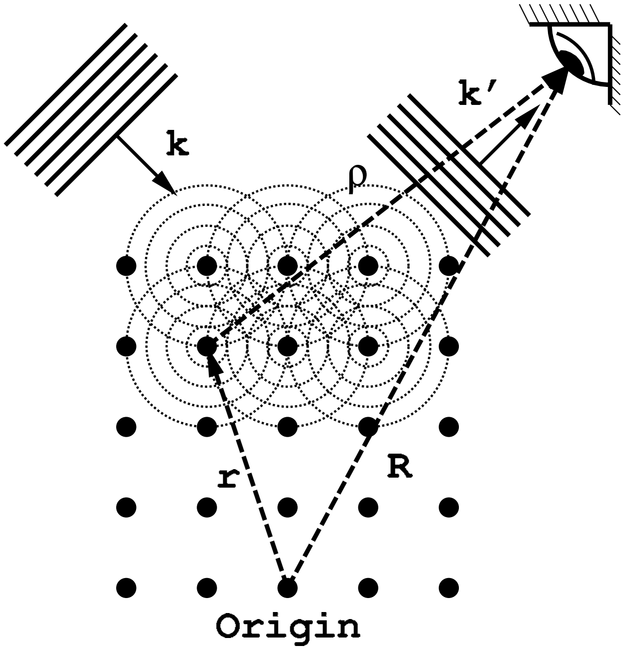

Figure 2.9: *Geometry for scattering of light by a crystal.*

is a reciprocal lattice vector. Thus, (2.36) tells us is that there is only scattering if $\mathbf{k}' = \mathbf{k} - \mathbf{G}$, that this, the incoming and the out-going plane waves can only differ by a reciprocal lattice vector. This has profound consequences. In the elastic scattering the energy of the incident and scattered beam is the same and therefore $|\mathbf{k}'| = |\mathbf{k}|$. Thus, as a consequence we have,

$$\begin{aligned} (\mathbf{k}')^2 &= (\mathbf{k})^2 + (\mathbf{G})^2 - 2\mathbf{k}\cdot\mathbf{G} \\ 2|\mathbf{k}|\cos\phi &= |\mathbf{G}| \end{aligned} \tag{2.37}$$

where ϕ is the angle between $\mathbf{k}$ and $\mathbf{G}$. But we know from (2.18) that associated with each vector $\mathbf{G}$ we have a set of planes such that $|\mathbf{G}| = 2\pi/d$ and given a plane wave we also have $|\mathbf{k}| = 2\pi/\lambda$ where λ is the wavelength of the beam. If instead of ϕ we use the angle between the incident beam and the plane (see Fig.2.10) the above equation can be written as

$$2\,d\sin\theta = \lambda \tag{2.38}$$

which is the famous *Bragg law* for elastic scattering.

We use basic quantum mechanics to calculate the differential cross-section for scattering of a plane wave with wave-vector $\mathbf{k}$ into another wave-vector $\mathbf{k}'$. This is given in the *Born approximation* by

$$\frac{d^2\sigma}{d\Omega} \approx \frac{2\pi}{\hbar}|\langle\mathbf{k}|V|\mathbf{k}'\rangle|^2 \tag{2.39}$$

where V is the scattering potential. In a condensed systems (gas, liquid or solid) this potential is the atomic potential of each atom. Thus we can write

$$V(\mathbf{r}) = \sum_{i=1}^{N} V_i(\mathbf{r} - \mathbf{R}_i) \tag{2.40}$$

where $\mathbf{R}_i$ is the position of each atom. Using the fact that this potential is periodic we can write

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \tag{2.41}$$

where the Fourier components can be obtained as in (2.20). Thus the matrix element can be written as

$$\begin{aligned}\langle\mathbf{k}|V|\mathbf{k}'\rangle &= \frac{1}{V}\int d^d r e^{-i\mathbf{q}\cdot\mathbf{r}} V(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{G}} V_{\mathbf{G}} \int d^d r e^{-i(\mathbf{q}-\mathbf{G})\cdot\mathbf{r}} \\ &= \frac{(2\pi)^d}{V}\sum_{\mathbf{G}} V_{\mathbf{G}}\delta(\mathbf{q}-\mathbf{G}) \end{aligned} \tag{2.42}$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}'$. What this last equation tells us is that there is only scattering if $\mathbf{k}' = \mathbf{k} - \mathbf{G}$, that this, the incoming and the out-going plane waves can only differ by a reciprocal lattice vector in complete agreement with our previous discussion.

We can now rewrite the differential cross-section as

$$\frac{d^2\sigma}{d\Omega} \propto |\langle\mathbf{k}|V|\mathbf{k}'\rangle|^2 = \frac{1}{(2\pi)^d}\sum_{\mathbf{G}} |V_{\mathbf{G}}|^2 \delta_{\mathbf{q},\mathbf{G}}\,, \tag{2.43}$$

where we used the results of Appendix (2.5.1) for the substitution of the Dirac delta function for the Kronecker delta. This equation is

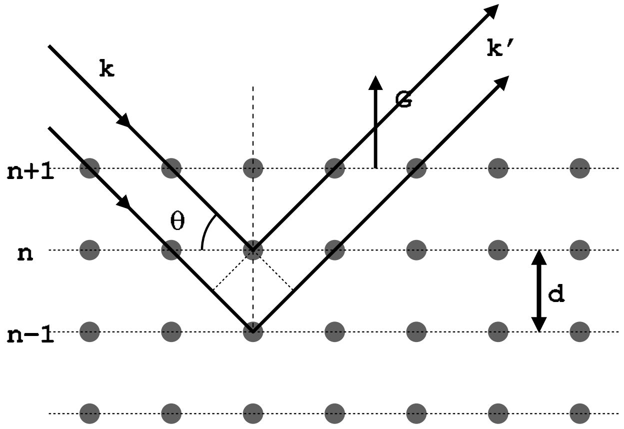

Figure 2.10: *Bragg reflection through a set of planes.*

quite interesting because it tells us that the intensity of the reflection at $\mathbf{q} = \mathbf{G}$ is proportional to $|V_{\mathbf{G}}|^2$. Thus, the Bragg condition is not sufficient in order to see elastic scattering at some vector $\mathbf{G}$ but also it is required that the potential has a finite Fourier component at this wavevector.

We can get even more insight into (2.43) if we rewrite the Fourier components of the potential in terms of the potential created by isolated atoms. In this case, within the unit cell, we write

$$V(\mathbf{r}) = \sum_{\alpha} U_{\alpha} \delta(\mathbf{r} - \mathbf{R}_{\alpha}) \tag{2.44}$$

where U_α is the strength of the potential for a particular atom α. Using (2.20) we find

$$V_{\mathbf{G}} = \frac{1}{V_0} \sum_{\alpha} U_{\alpha} e^{-i\mathbf{G}\cdot\mathbf{R}_{\alpha}} \tag{2.45}$$

which depends only on the atoms on a unit cell. In this case (2.43) becomes

$$\begin{aligned}\frac{d^2\sigma}{d\Omega} &\propto \frac{1}{V_0^2}\sum_{\mathbf{G}}\sum_{\alpha,\gamma} U^*_\alpha U_\gamma e^{i\mathbf{G}\cdot(\mathbf{R}_\alpha-\mathbf{R}_\gamma)} \\ &= \frac{1}{V_0}\sum_{\alpha,\gamma} U^*_\alpha U_\gamma F(\mathbf{R}_\alpha-\mathbf{R}_\gamma)\end{aligned} \tag{2.46}$$

where

$$F(\mathbf{R}_\alpha) = \frac{1}{V_0}\sum_{\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{R}_\alpha}\,. \tag{2.47}$$

This result implies that the scattering depends strongly on the local structure of the atoms on the unit cell.

These equations simply considerably if we assume that the atoms are the same. In this case one can write

$$V(\mathbf{r}) = U_0\sum_{\alpha}\delta(\mathbf{r}-\mathbf{R}_\alpha) \tag{2.48}$$

and therefore

$$V_{\mathbf{G}} = U_0\rho_{\mathbf{G}} \tag{2.49}$$

where

$$\rho_{\mathbf{G}} = \frac{1}{V_0}\sum_{\alpha} e^{-i\mathbf{G}\cdot\mathbf{R}_\alpha} \tag{2.50}$$

is the Fourier transform of the density. It is straightforward to conclude from the above equations that

$$\frac{d^2\sigma}{d\Omega} \propto |U_0|^2 S(\mathbf{q}) \tag{2.51}$$

where

$$S(\mathbf{q}) = (2\pi)^d\sum_{\mathbf{G}} |\rho_{\mathbf{G}}|^2\delta_{\mathbf{q},\mathbf{G}} \tag{2.52}$$

is called the *static structure factor*. Observe that a scattering at some vector $\mathbf{q} = \mathbf{G}$ is only possible if $\rho_{\mathbf{G}} \neq 0$. This factor is the same that appears in equation (2.34). Thus, even if the scattering is allowed the positions of the atoms on the unit cell determines if there is any intensity for that particular scattering.

The scattering in a disordered system such as a glass (or liquid very viscous fluid) can also be immediately obtained from these equations. Since the system is disordered the unit cell is the volume of the system itself. Moreover, the sum in (2.50) is a sum of random phases that leads to destructive interference if the phases vary wildly. Thus, from (2.50),

$$\rho_{\mathbf{G}} = \frac{1}{V}\sum_{\alpha} e^{-i\mathbf{G}\cdot\mathbf{R}_\alpha} = \bar{n}\delta_{G,0} \tag{2.53}$$

where $\bar{n} = N/V$ is the average density of the system. By direct substitution of this expression in (2.52) we find

$$S(\mathbf{q}) = (2\pi)^d \bar{n}^2 \delta_{\mathbf{q},0} \tag{2.54}$$

shows that in this case the system only has *forward scattering*.

2.3.1 Experimental constraints

So far we have discussed scattering but we did not specify what type of scattering we are talking about, that is, what kind of probes we are looking for. Observe that the only condition for scattering is given by the Bragg law, (2.38), that requires that the wavelength of the probe must be such that, $\lambda < 2d$. Since d is of order of $1\mathring{A}$ we need probes with very short wavelengths. The first probe that comes to mind is *light*. Light interact with the charged particles in the system via what is called *minimal coupling*, that is, we replace the momentum $\mathbf{p}$ of the charged particle by $\mathbf{p} - e\mathbf{A}/c$ where $\mathbf{A}$ is the vector potential. The energy of light can be written as

$$E = \hbar\omega = \hbar c|\mathbf{k}| = \frac{hc}{\lambda}. \tag{2.55}$$

For $\lambda \approx 1\mathring{A}$ one needs $E \approx 10^4$ eV which is the X-ray part of the spectrum. Another possibility is scattering by *electron* waves. In this case the scattering process is due to the electron-electron interaction in the system. The energy of an electron is given by

$$E = \frac{\hbar^2 \mathbf{k}^2}{2m_e} = \frac{h^2}{2m_e \lambda^2} \, . \tag{2.56}$$

For $\lambda \approx 1\mathring{A}$ one needs $E \approx 100$ eV. Another possibility is *neutron* scattering. Neutron has no electric charge and therefore is insensitive to charge degrees of freedom in the solid. It interacts with the magnetic moments in the solid (nuclear and/or electronic). The energy has the same form as above for the electron but since its mass is a thousand times larger the relevant energies are a thousand times smaller, that is, $E \approx 0.1$ eV. Although we have different probes it is easy to see that each one of them measures the system at different scales of energy. Thus, the choice of probe depends strongly on what kind of energy scale one wants to probe. In condensed matter physics one is usually interested in energies of the order of a few meV which is the energy scale of the neutrons. Neutron scattering is also particularly important because it probes directly the magnetic excitations. Electron scattering is a complicated probe because the scattered electron tends to interact strongly with the other electrons in the system (this is called multiple scattering) and our simple Born approximation formula is not valid any longer. We really need a probe that interacts weakly with the system of interest. X-rays have an energy that is usually orders of magnitude larger than the energy scales of interest and it is very hard to get good accuracy with X-ray measurements. It turns out, however, that they are excellent in order to measure static properties such as, $S(\mathbf{q})$, via elastic scattering.

2.4 Defects in solids

So far we have discussed only perfect crystalline structures where the atoms occupy sites of a periodic lattice. It turns out, however, that real crystals are not perfect and contain a series of different defects. The most common types of defects are vacancies and interstitials that are called point defects since they involve the subtraction of isolated atoms. There are also line defects which involve the entire displacement

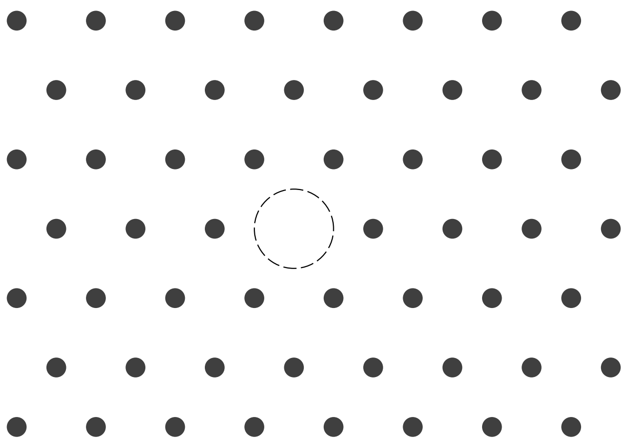

Figure 2.11: *Vacancy in a crystal.*

of planes or lines of atoms and for this reason are called dislocations. These defects are common in most materials and are responsible for many effects observed in crystals.

At finite temperatures all crystals contain a certain number of vacancies or interstitials. This is due to purely entropic effects. The simplest type of defect is depicted on Fig.2.11 and it is called a Schottky defect. In this kind of defect is essentially due to an atom which is missing from its original position. The missing atom in this case creates a "hole" in the crystal and therefore a local defect.

In order to understand the entropic nature of such a defect consider a perfect lattice made out of N atoms and M vacancies which are randomly organized (we are considering that there is no clustering of these vacancies and that the energy of the vacancies do not depend if there are other vacancies in its immediate neighborhood). In this case it is clear that the system has many equivalent configurations. The number of these configurations is simply $(N+M)!/(N!M!)$. Thus, the total entropy at zero temperature is:

$$S = k_B \ln\left(\frac{(N+M)!}{N!M!}\right) . \tag{2.57}$$

Here we are going to consider the case where $N, M >>> 1$ but M/N is finite. Thus we can use the Stirling approximation

$$\ln(N!) \approx N\ln(N) - N . \tag{2.58}$$

Now consider the free energy of the system which is given by

$$F(M) = U(M) - TS(M) \tag{2.59}$$

where U is the internal energy of the system with M vacancies. In the case under consideration the energy of create M vacancies is just M times the energy to create a single vacancy since we are disregarding vacancy-vacancy interactions. In this case we have

$$U(M) = \epsilon_0 M \tag{2.60}$$

where ϵ_0 is the energy required to create a single vacancy. For a fixed value of N the equilibrium is attained when the free energy is a minimum with respect to variations of M. Thus, we have to minimize

$$F(M) \approx \epsilon_0 M - k_B T \ln\left[\frac{(N+M)^{N+M}}{N^N M^M}\right] \tag{2.61}$$

with respect to M keeping $N + M = N_s$ the number of sites constant. We write

$$F(M) \approx \epsilon_0 M - k_B T \ln\left[\frac{N_s^{N_s}}{(N_s - M)^{N_s - M} M^M}\right] \tag{2.62}$$

and the derivative becomes

$$\frac{\partial F}{\partial M} = \epsilon_0 - k_B T \ln\left(\frac{N_s - M}{M}\right) \tag{2.63}$$

and thus

$$\epsilon_0 \approx k_B T \ln\left(\frac{N_s - M}{M}\right) \tag{2.64}$$

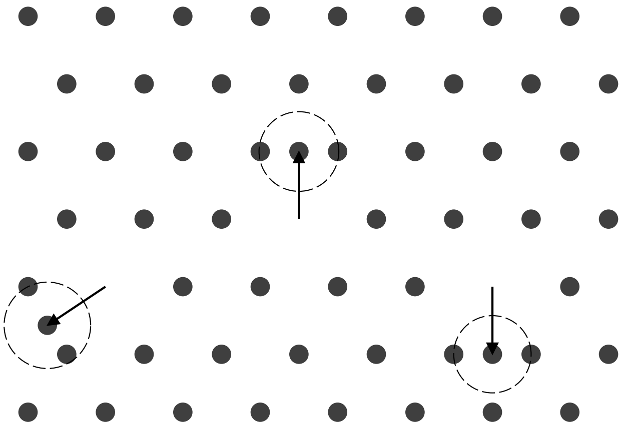

Figure 2.12: *Interstitials in a crystal.*

or

$$M(T) = \frac{N_s}{e^{\frac{\epsilon_0}{k_B T}} + 1} \tag{2.65}$$

which shows that there is always a finite number of vacancies in the crystal. Observe that when $k_B T >> \epsilon_0$ we have $M(T) \approx N_s/2$. However, in normal materials ϵ_0 is of order of 1 eV $(10,000K)$ and therefore one usually has the opposite limit, that is, $k_B T << \epsilon_0$, where

$$M(T)/N_s \approx e^{-\frac{\epsilon_0}{k_B T}} \tag{2.66}$$

that is, there is an exponentially small number of vacancies in a crystal.

Another type of defect is the interstitial which is similar to a vacancy but the atom, instead of leaving the bulk of the crystal, moves to an intermediary position between other atoms. This is shown on Fig.2.12 and it is called a Frenkel defect. This type of defects are more common in ionic crystal where a positively charged ion can move in between negatively charged ions in a crystalline matrix. In this case

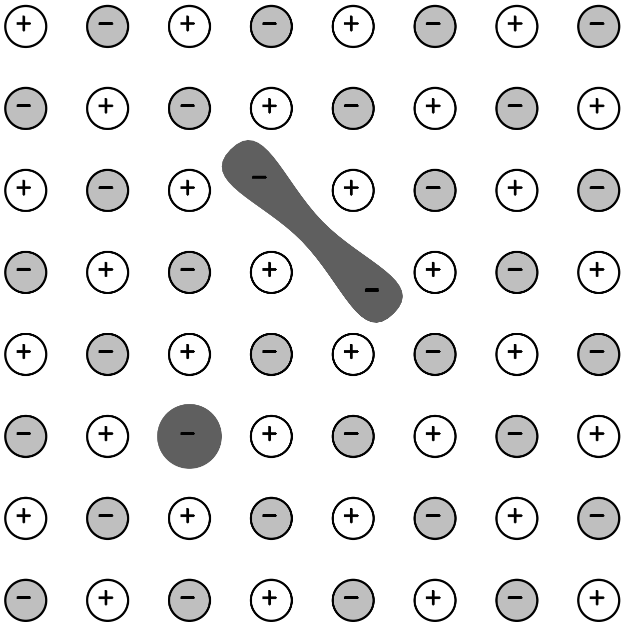

Figure 2.13: *Two types of color centers in an ionic crystal.*

charge neutrality requires that an equal number of negative and positive defects are generated.

It is also possible to replace a negative ion by an electron localized at the defect. In this case the electron is localized in a quantum well. Naturally the absorption of light in the crystal changes since the electrons in a quantum well absorbs light at different frequencies than in a perfect crystal. It implies that the crystal changes its color. For this reason this kind of defects are called color centers. An example is depicted on Fig.2.13.

2.5 Problems

1. Prove that for $n = 5$ it is not possible to define a smallest vector $\mathbf{a}_1$ that generates the lattice. The proof of the non-existence of Bravais lattices for $n \geq 7$ is analogous.

2. Prove that the Wigner-Seitz unit cell of a planar hexagonal lattice of lattice spacing $2R$ has an area of $2\sqrt{3}R^2$. Show that the fractional area occupied by the spheres relative to this unit cell area is 0.907.

3. Prove that the vectors $\mathbf{b}_i$ can be written as in (2.14).

4. Prove that (2.15) is indeed correct.

5. Prove that the volume of the Brillouin zone, $V_B = (2\pi)^3/V_0$ where V_0 is the unit cell volume.

6. Show that by translating the unit cell to another cell V_0' in (2.19) the integral is zero if $\mathbf{G} \neq \mathbf{K}$.

7. We have seen that a reciprocal lattice vector labels a series of planes (hkl). Show that a equivalent way to label the planes in real space consists of two steps: 1) find the intercept of the plane with the axes in terms of the vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$; 2)take the reciprocal of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. The result, that is, (hkl) is the index of the plane.

8. The primitive vectors for a bcc lattice are

$$\begin{aligned}
\mathbf{a}_1 &= \frac{a}{2}(-\mathbf{x}+\mathbf{y}+\mathbf{z}) \\
\mathbf{a}_2 &= \frac{a}{2}(\mathbf{x}-\mathbf{y}+\mathbf{z}) \\
\mathbf{a}_3 &= \frac{a}{2}(\mathbf{x}+\mathbf{y}-\mathbf{z}) \,. \qquad (2.67)
\end{aligned}$$

Find the reciprocal lattice vectors. What lattice does it form? Make a drawing of the two lattices.

9. The primitive vectors for a fcc lattice are

$$\begin{aligned} \mathbf{a}_1 &= \frac{a}{2}(\mathbf{y}+\mathbf{z}) \\ \mathbf{a}_2 &= \frac{a}{2}(\mathbf{x}+\mathbf{z}) \\ \mathbf{a}_3 &= \frac{a}{2}(\mathbf{x}+\mathbf{y})\,. \end{aligned} \tag{2.68}$$

   Find the reciprocal lattice vectors. What lattice does it form? Make a drawing of the two lattices.

10. In this problem we are going to study the effect of the second factor in (2.34), the static form factor. We write it as:

$$S_{\mathbf{G}} = \int_{Cell} dV n(\mathbf{r}) e^{i\mathbf{r}\cdot\mathbf{G}} \tag{2.69}$$

   since $\delta\mathbf{k} = \mathbf{G}$ is the Bragg condition. When there are N_b atoms in the unit cell we can write

$$n(\mathbf{r}) = \sum_{j=1}^{N_b} n_j(\mathbf{r}-\mathbf{r}_j) \tag{2.70}$$

   where n_j now depends on the particular atom. Show that

$$S_{\mathbf{G}} = \sum_{j=1}^{N_b} f_j e^{i\mathbf{r}_j\cdot\mathbf{G}} \tag{2.71}$$

   where

$$f_j = \int_{Cell} dV n_j(\mathbf{r}) e^{i\mathbf{r}\cdot\mathbf{G}} \tag{2.72}$$

   is called *atomic form factor* which depends only on the kind of atom is participating on the lattice formation. Consider now that $\mathbf{r}_j$ can be written in terms of the primitive vectors as

$$\mathbf{r}_j = x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3 \tag{2.73}$$

   where x_j, y_j, z_j are **any** real number. Using that $\mathbf{G} = \sum_{i=1}^{3} m_i\mathbf{b}_i$ show that

$$S_{\mathbf{G}} = \sum_{j=1}^{N_b} f_j e^{2\pi i(m_1x_j+m_2y_j+m_3z_j)}\,. \tag{2.74}$$

11. Calculate $S_{\mathbf{G}}$ in previous problem for a fcc lattice with one atom per unit cell assuming that the fcc lattice can be thought of a simple cubic lattice with a basis given by the vectors $(0,0,0)$, $(0,1/2,1/2)$, $(1/2,0,1/2)$, $(1/2,1/2,0)$. (*ii*) Assume that $f_j = f$ and show that if m_1, m_2, m_3 are all even or all odd we have $S_{\mathbf{G}} = 4f$. (*iii*) Show that if one of the m_j is even and the other two are odd then $S_{\mathbf{G}} = 0$. (*iv*) Show that if one of the m_j is odd and the other two are even then $S_{\mathbf{G}} = 0$. (*v*) Compare the scattered reflections that you would get from a fcc lattice without a basis and the ones you got from assuming that the fcc lattice can be seen as a simple cubic lattice with a basis. Do you get identical results?

12. Consider a two dimensional crystal in a square lattice with two different types of atoms with different cross-sections (a two dimensional version of NaCl). What would be a result of a neutron scattering experiment in such a system? What are the allowed values of momentum for scattering?

13. Consider an ionic crystal with positive and negative charges. Assuming that the energy required to create an interstitial with positive (negative) charge requires an energy ϵ_p (ϵ_n) and that the system has charge neutrality show that the number of positive and negative interstitials is

$$n_p = n_n = \sqrt{N_p N_n} e^{-\beta \frac{\epsilon_p + \epsilon_n}{2}}$$

where $N_p(N_n)$ is the number os sites with positive (negative) charge.

2.5.1 Appendix: Dirac and Kronecker delta functions

There is a little caveat about equation (2.42). Observe that $\mathbf{q}$ is defined in the continuum (that is, it can vary continuously from 0 to ∞) while the reciprocal lattice vector $\mathbf{G}$ is defined over a discrete set. Thus, in order for the summation in (2.42) to make sense we should have a Kronecker delta instead of a Dirac delta function. The solution for this little problem is given by the quantization of the scattering states in a box. If we require the plane waves outside the material to have periodic boundary conditions in a box of size L, then we must have

$$k_i = \frac{2\pi n_i}{L} \tag{2.75}$$

where $i = x, y, z$. Thus a Dirac delta can be written as

$$\begin{aligned} \delta(\mathbf{k}) &= \delta(k_x)\delta(k_y)\delta(k_z) = \delta(2\pi n_x/L)\delta(2\pi n_y/L)\delta(2\pi n_z/L) \\ &= \frac{V}{(2\pi)^d}\delta_{\mathbf{k},0} \end{aligned} \tag{2.76}$$

where $\delta_{\mathbf{k},0}$ is a Kronecker delta and $V = L^3$ is the volume of the quantization box. In this way one can replace sums by integrals,

$$\sum_{\mathbf{q}} \to \frac{V}{(2\pi)^d} \int d^d q \; . \tag{2.77}$$

Another way to rewrite this expression is due to the result of Problem 5: if N is the number of primitive cells and V_B is their volume we have immediately,

$$\sum_{\mathbf{q}} \to \frac{N}{V_B} \int d^d q \; . \tag{2.78}$$

Chapter 3

Elasticity Theory

3.1 Introduction

Point like defects are not the only type of defects that occur in crystals. There are extended defects that are responsible for very important mechanical properties of crystalline systems. Line or plane defects in crystals are possible under application of pressure or stress. When deformations due to stress are reversible we call them elastic deformations, otherwise, when they are not reversible, we call them plastic deformations. In order to understand the difference between plastic and elastic deformations consider the simple toy model proposed by Frenkel for a shear strength of a perfect crystal as shown in Fig.3.1. Suppose a stress, σ, is applied to a plane of atoms which is displaced by another plane of atoms by an amount x. Under Hook's law the stress, σ, is linearly related to the displacement by the shear modulus G

$$\sigma(x) \approx G\frac{x}{d} \tag{3.1}$$

where d is the distance between planes. Of course this equation is valid for small displacements. Suppose we apply a strong shear stress so that all the atoms move one lattice spacing a. In this case we are back to the original situation with the atoms in their equilibrium position in zero stress. This implies that the stress must be a periodic function of

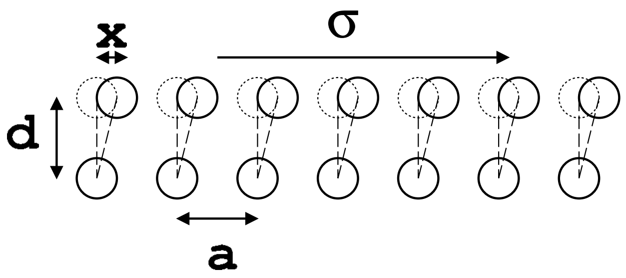

Figure 3.1: *Simple model for shear stress in a perfect crystal.*

the lattice spacing. For simplicity let us consider a harmonic function

$$\sigma(x) = G\frac{a}{2\pi d}\sin\left(\frac{2\pi x}{a}\right) \tag{3.2}$$

which becomes (3.1) in the limit of $x << a/(2\pi)$. Observe that (3.2) has a maximum for $x = a/4$ for which

$$\sigma_c = \sigma(a/4) = G\frac{a}{2\pi d}. \tag{3.3}$$

If the stress applied is larger than σ_c the upper plane in Fig.3.1 has to move freely and never return to the original unstressed situation. This would imply plastic flow of the crystal. Since $a \approx d \approx 1\mathring{A}$ the critical stress is approximately $G/6$. It turns out that this prediction is completely at odds with the experiments. For instance for a single crystal of Al we find that experimentally $\sigma_c \approx G/60,000$! Thus, the conclusion is that plastic deformations occur at a much smaller stress than the theory predict and they must be generated not by elastic

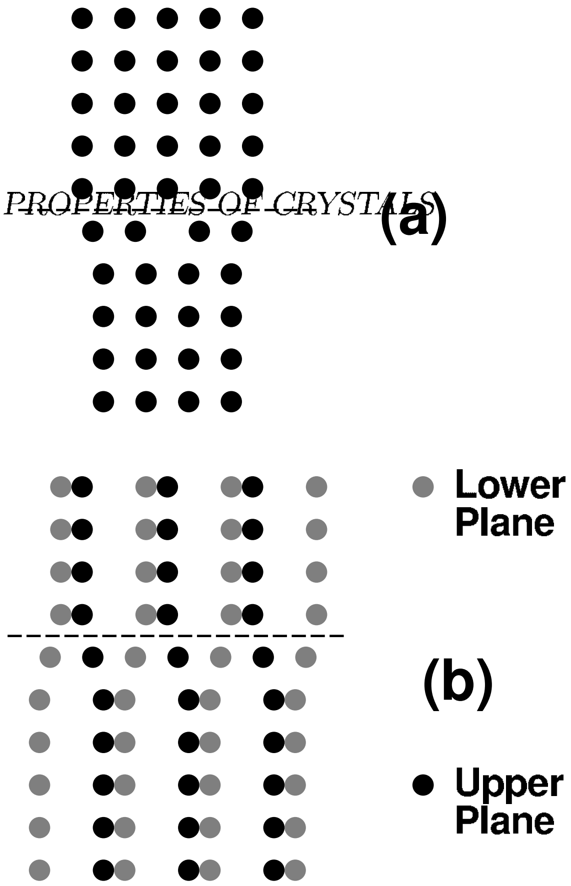

Figure 3.2: *(a) Edge dislocation; (b) Screw dislocation.*

deformations of the crystal but by defects. These defects are called dislocations.

Plastic deformations in crystals occur when planes of atoms slide over each other due the presence of dislocations. The simplest types of dislocations are edge dislocations and screw dislocations. In a edge dislocation there is a mismatch of planes as if an extra planes of atoms have been inserted in the crystal while in a screw dislocation there is a mismatch between planes of atoms as shown in Fig.3.2.

3.2 Elastic properties of crystals

As we have discussed in the last section the position of the i-th atom in a crystals is given by $\mathbf{R}_i = \mathbf{T} + \mathbf{R}_\alpha$ where $\mathbf{T}$ is a vector in the direct lattice and $\mathbf{R}_\alpha$ is a vector in the unit cell. Moreover, in Chapter 1 we have seen that the equilibrium position of atoms is given by the various electronic interactions. Usually one finds that the competition between a long range attractive force and a short range repulsive force lead to a mean distance between atoms that we call lattice spacing. In this section we are going to consider the elastic energy required to deform the atoms from their original equilibrium positions. Since the perfect crystal is the lowest energy state for the system, local deformations will cost energy. This energy is called elastic energy. Let us assume that some part of the crystal is displaced by a quantity $\mathbf{u}(\mathbf{r})$ which means a displacement of $|\mathbf{u}|$ in the direction of $\mathbf{u}$ at position $\mathbf{r}$. Obviously the free energy of the system due to this displacement is a function of $\mathbf{u}(\mathbf{r})$. Here we would like to know the functional form of the free energy which can be obtained from symmetry considerations.

The first obvious symmetry is the translations of all atoms of the crystal by a fix value $\mathbf{u}(\mathbf{r}) = \mathbf{u}_0$. It is clear that the free energy of the system cannot depend on the value of $\mathbf{u}_0$ and therefore it can only depend on derivatives of $\mathbf{u}(\mathbf{r})$ which we denote by

$$\partial_i u_j = \frac{\partial u_j}{\partial x_i} \tag{3.4}$$

where $i, j = 1, 2, 3, ..., d$ corresponding to $x, y, z....$ Observe that $\partial_i u_j$ can be seen as a matrix, or more formally, a tensor with $d \times d$ components. From this argument we conclude that the free energy has to be written as $F = F[\partial_i u_j]$. Another symmetry of the problem is inversion symmetry, that is the free energy has to be invariant under $\mathbf{u} \to -\mathbf{u}$. It implies that linear terms are not allowed and therefore $F = F[(\partial_i u_j)^2]$. Now let us consider another important symmetry which is the symmetry of rigid rotation of the lattice by an angle $\delta\theta$. Consider, for instance, a plane of atoms labeled by a reciprocal lattice vector $\mathbf{G}$ which is rotated by this angle. Along this plane all the atoms are displaced by $u(\mathbf{r}) = |\mathbf{r}|\delta\theta$ as shown in Fig.3.3. Another way to write this displacement is to consider the vector $\delta\vec{\theta}$ oriented anti-clockwise in the rotation direction. It is clear that

$$\mathbf{u}(\mathbf{r}) = \delta\vec{\theta} \times \mathbf{r}\,. \tag{3.5}$$

This relation can be easily inverted with the help of differential calculus to

$$\delta\vec{\theta} = \frac{1}{4}\nabla \times \mathbf{u}(\mathbf{r}) \tag{3.6}$$

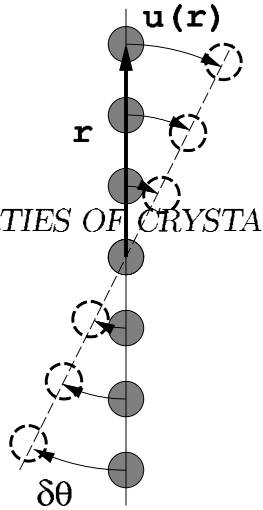

Figure 3.3: *Rigid rotation of an atomic plane*

which expresses the angle of rotation in terms of the displacement. Since the whole crystal is rigidly rotated the free energy cannot depend of $\delta\vec{\theta}$, that is, the system is invariant under rigid rotations. Observe that in (3.6) the displacements appear in combinations of the form $\partial_i u_j - \partial_j u_i$ which is the anti-symmetric part of the tensor $\partial_i u_j$. Thus, due to the rotation symmetry the free energy can only depend on the symmetric part of the tensor $\partial_i u_j$, that is,

$$u_{ij} = \frac{1}{2}\left(\partial_i u_j + \partial_j u_i\right) \tag{3.7}$$

which is called the *strain tensor.* In summary, due to rigid translations, inversions and rotations the free energy due to elastic deformations of a crystal can only be a function of $u_{ij}u_{kl}$.

It is very simple to understand the physical meaning of each component of the strain tensor. Consider for instance a compression or dilation of the system along the direction $\mathbf{x}$. If L_x is the size of the crystal in this direction then

$$\delta_x = \frac{\delta L_x}{L_x} \tag{3.8}$$

gives the relative compression in that direction (obviously for compression $\delta_x < 0$ and for dilation $\delta_x > 0$). In this case the volume of the whole crystal is changed by δV. By the same token the volume of the unit cell, $V_0 = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$ is changed by δV_0 because $\mathbf{a}_i$ changes under compression. It turns out, however, that since $V = NV_0$ where N is the total number of atoms we must have

$$\frac{\delta V}{V} = \frac{\delta V_0}{V_0}\,. \tag{3.9}$$

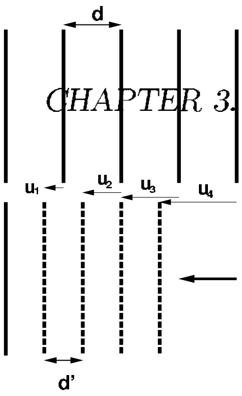

Figure 3.4: *Compression of a series of planes.*

This relation is valid because we are considering the crystal in the absence of vacancies and interstitials. In the presence of defects (3.9) has to be modified. Moreover, since the reciprocal lattice vectors are tied to the direct lattice vectors by $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ it is clear that a compression in real space will lead to a dilation in reciprocal space and vice-versa. Consider the set of N planes separated by a distance d in the $\mathbf{x}$ direction before the application of pressure. In this case we have $L_x = Nd$. After pressure is applied the distance between planes becomes d' so that $L'_x = Nd'$. Therefore

$$\frac{L'_x - L_x}{L_x} = \frac{d' - d}{d} = \delta_x \,. \tag{3.10}$$

We will label the displacement of the nth plane of the crystal by u_n. Let us assume that the first plane is fixed before and after pressure is applied so that $u_0 = 0$. It is simple to in Fig. 3.4 that second plane is displaced by $u_1 = d' - d = \delta_x d$, the second plane is displaced by $u_2 = 2d' - 2d = 2\delta_x d$ and so on. In general

$$u_n = n\delta_x d \,. \tag{3.11}$$

If we label the position of each plane by $x = nd$ we see that this last expression can be rewritten as

$$\begin{aligned} u(x) &= \delta_x x \\ \partial_x u(x) &= \delta_x \,. \end{aligned} \tag{3.12}$$

In a more general way we can consider a set of planes labeled by the reciprocal lattice vector $\mathbf{G}$. We know that $|\mathbf{G}| = 2\pi/d$ where d is the distance between planes. After compression or dilation we must have $d' = (1+\delta_x)d$ and therefore the reciprocal lattice vector changes for an infinitesimal value of δ_x by

$$\begin{aligned} \mathbf{G}' &= (1-\delta_x)\mathbf{G} \\ \mathbf{G}'-\mathbf{G} &= -\delta_x\mathbf{G}\,. \end{aligned} \tag{3.13}$$

Moreover, in this case, the displacement of the atoms due to the compression or dilation can be written as

$$\begin{aligned} \mathbf{G}\cdot\mathbf{u}(\mathbf{r}) &= (\mathbf{G}-\mathbf{G}')\cdot\mathbf{r} \\ &= \delta_x\mathbf{G}\cdot\mathbf{x} \end{aligned} \tag{3.14}$$

and therefore

$$\mathbf{u} = \delta_x\mathbf{x} \tag{3.15}$$

and therefore

$$u_{xx} = \delta_x \tag{3.16}$$

and all other derivatives vanish. Thus, it is clear that u_{ii} measures the lattice compression or dilation in the direction of the vector $\mathbf{x}_i$. The total volume of the system is $V = L_xL_yL_z$ and therefore we must have $\delta V = \delta L_xL_yL_z + L_x\delta L_yL_z + L_xL_y\delta L_z$. Thus, it is simple to show that

$$\frac{\delta V}{V} = \sum_i u_{ii} \tag{3.17}$$

that is, the relative change in the volume of the solid is given by the trace of the strain tensor. Equation (3.17) has to be interpreted with a little care, however. Observe that $u_{ii}(\mathbf{r})$ is a local function of the position and of course δV is a global change in the system. Thus (3.17) is really only valid in a perfect crystal without defects like vacancies where changes in volume can be non-uniform. In general the diagonal elements of the strain tensor are related to the local changes in the unit cell volume such that,

$$\frac{\delta V_0(\mathbf{r})}{V_0(\mathbf{r})} = \sum_i u_{ii}(\mathbf{r}) \tag{3.18}$$

which is a local relation. Of course, for ordered systems equation (3.9) is valid and (3.17) is identical to (3.18).

We can always decompose the distortion of a solid in terms of volume changes and shear (which never changes the volume). We have seen that volume changes have to do with the diagonal elements of the strain tensor. The other off-diagonal components of the strain tensor represent the shear distortion of the system as you can easily show. Since shear does not change the volume of the crystal it is represented by a traceless tensor

$$s_{ij} = u_{ij} - \delta_{ij}\frac{\sum_k u_{kk}}{d} \, . \tag{3.19}$$

Notice that indeed $\sum_i s_{ii} = 0$ since $\sum_i \delta_{ii} = d$.

From now on we are going to consider only small distortions of the crystal and from the symmetry arguments the free energy has to be written as

$$F = \frac{1}{2}\int d\mathbf{r} \sum_{i,j,k,l} C_{ijkl} u_{ij} u_{kl} \tag{3.20}$$

where C_{ijkl} are the so-called elastic constants of the crystal which in principle can have d^4 components. Now observe that $u_{ij} = u_{ji}$ and therefore we must have the following symmetries:

$$C_{ijkl} = C_{jikl} = C_{ijlk} = C_{jilk} = C_{klij} \, . \tag{3.21}$$

In addition the free energy has extra symmetries which depend on the point symmetries of the crystal itself. Highly symmetric crystal will have less independent elastic constants than less symmetric crystals. For instance, a three dimensional cubic crystal has 3 independent elastic constants while a triclinic crystal has 21 independent elastic constants. Moreover, it is very simple to estimate the order of magnitude of the elastic constants if we remember that u_{ij} is a dimensionless quantity and therefore C_{ijkl} has dimensions of energy divided by length^d, that is, energy density. The energy here is just the biding energy per atom of the solid which is of order of a few electron volts while the length is of order of the lattice spacing, that is, a few angstroms.

Things simplify considerably in isotropic solids where compression and shear stress are independent of the direction they are applied. It must be clear that in this case there are only two elastic constants: one associated with compressions and dilations (the so-called bulk modulus, B) and another associated with shear distortions (the so-called shear modulus, G). Since we have seen that compressions have to do with u_{ii} and shear are related to s_{ij} the free energy has to be written as

$$F = \frac{1}{2} \int d\mathbf{r} \left[B \left(\sum_i u_{ii} \right)^2 + 2G \sum_{ij} s_{ij}^2 \right] . \tag{3.22}$$

In order to see that this expression has indeed the form of (3.20) we use (3.19) and rewrite (3.22) as

$$F = \frac{1}{2} \int d\mathbf{r} \left[\left(B - \frac{2G}{d} \right) \left(\sum_i u_{ii} \right)^2 + 2G \sum_{i,j} u_{ij}^2 \right] \tag{3.23}$$

which has the form of (3.20) with

$$C_{ijkl} = \left(B - \frac{2G}{d} \right) \delta_{ij}\delta_{kl} + G \left(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl} \right) \tag{3.24}$$

which has the symmetry properties as required.

Of course the expression for the free energy as given by (3.20) is useful if we can relate the internal distortions (the strain) with the external agents such as pressure or strain. In order to do that one has to calculate the work done on the system by an external force. Consider an external force $\mathbf{F}$ applied to an element of volume δV. If the interaction between the atoms is short range this force will be transmitted by the neighboring volumes through the surface δS that surrounds the volume δV. The total force in the volume in the ith direction is

$$F_i = \int_{\delta V} d\mathbf{r} f_i \tag{3.25}$$

where $\mathbf{f}$ is the force per unit of volume of the undistorted solid. Since the force applied is a local function of the position it can be expressed as a gradient with respect to the undistorted crystal and we write

$$f_i = \sum_j \partial_j \sigma_{ij} \tag{3.26}$$

where σ_{ij} is the *stress tensor*. Substitution of (3.26) into (3.25) leads to

$$F_i = \int_{\delta S} \sum_j dS_j \sigma_{ij} \tag{3.27}$$

where we used Gauss theorem. Observe that the stress tensor σ_{ij} gives the force per unit of area in the direction i exerted by the surrounding medium on a volume element across its surface oriented on the direction j. Consider a solid surrounded by an isotropic fluid at pressure P. This solid will experience an stress given by the hydrostatic pressure which is $-P$. In this case the stress tensor is simply

$$\sigma_{ij} = -P\delta_{ij} \, . \tag{3.28}$$

Suppose uniaxial pressure T is applied along the x axis of a crystal. In this case it is obvious that

$$\sigma_{xx} = T \tag{3.29}$$

and all other components are zero. In the more generic case consider the work done by a force density $\mathbf{f}$ which displaces the volume elements of a crystal by $\mathbf{u}(\mathbf{r})$. This work is simply

$$\begin{aligned} \delta W &= -PV = \int d\mathbf{r} \mathbf{f} \cdot \mathbf{u}(\mathbf{r}) \\ &= \int d\mathbf{r} \sum_{i,j} \partial_j \sigma_{ij} u_i(\mathbf{r}) \\ &= -\int d\mathbf{r} \sum_{i,j} \sigma_{ij} u_{ij} \end{aligned} \tag{3.30}$$

where we have integrated by parts and neglected the surface terms. The change in the free energy due to the changes in the strain field is the negative of the work done by the internal forces, thus,

$$\delta F = -\delta W = \int d\mathbf{r} \sum_{i,j} \sigma_{ij} u_{ij} \tag{3.31}$$

Observe that this leads to the important relation:

$$\sigma_{ij} = \frac{\partial F}{\partial u_{ij}} \tag{3.32}$$

which relates the strain tensor with the stress tensor.

For the case of the isotropic crystal, accordingly to (3.22), we have:

$$\sigma_{ij} = B \sum_l u_{ll} \delta_{ij} + 2G s_{ij} \tag{3.33}$$

which we can invert to write the strain in terms of the stress. Firstly we observe that for $i \neq j$ we have

$$\sigma_{ij} = 2G s_{ij} = 2G u_{ij} \tag{3.34}$$

where we have used (3.19). Secondly, for $i = j$ we have

$$\sigma_{ii} = 2G u_{ii} + \left(B - \frac{2G}{d}\right) \sum_l u_{ll} \tag{3.35}$$

and therefore $\sum_i \sigma_{ii} = dB \sum_i u_{ii}$. Thus, we conclude that

$$u_{ij} = \delta_{ij} \frac{\sum_l \sigma_{ll}}{d^2 B} + \frac{1}{2G} \left(\sigma_{ij} - \delta_{ij} \frac{\sum_l \sigma_{ll}}{d}\right). \tag{3.36}$$

This last equation is very useful. Consider a solid subject to a hydrostatic pressure P. Then, from (3.36) one has

$$\sum_i u_{ii} = \frac{1}{dB} \sum_i \sigma_{ii} = -\frac{P}{B}. \tag{3.37}$$

From (3.17) one finds immediately

$$\begin{aligned} \frac{\delta V}{V} &= -\frac{P}{B} \\ \frac{1}{B} &= -\frac{1}{V}\frac{\delta V}{P} \end{aligned} \tag{3.38}$$

which is the usual thermodynamic definition of the bulk modulus as expected. Suppose that uniaxial stress T is applied in the z direction. Again we have

$$\begin{aligned} u_{zz} &= \frac{T}{d}\left(\frac{1}{dB} + \frac{d-1}{2G}\right) \\ u_{xx} &= u_{yy} = -\frac{T}{d}\left(\frac{1}{2G} - \frac{1}{dB}\right). \end{aligned} \tag{3.39}$$

Observe that the change in the size of the system along z always follows the applied force while in the transverse directions it will depend on the ration $dB/(2G)$. The Young's modulus, Y, of the system is defined as

$$\begin{aligned} Y &= \frac{T}{u_{zz}} \\ Y &= \frac{2d^2GB}{2G + d(d-1)B} \end{aligned} \tag{3.40}$$

and the Poisson's ration ν is defined as

$$\begin{aligned} \nu &= -\frac{u_{xx}}{u_{zz}} \\ &= \frac{dB - 2G}{d(d-1)B + 2G}\,. \end{aligned} \tag{3.41}$$

3.3 Problems

1. Write down the elastic free energy for a three dimensional crystal with cubic symmetry. Show that the elastic tensor C_{ijkl} has only 3 independent components, namely, C_{1111}, C_{1122} and C_{1212} $(1, 2, 3$ refers to x, y, z, respectively$)$. Calculate: 1)the bulk modulus;

   2)the Poisson ratio for stresses along one of the symmetry axes in terms of the elastic constants.

Chapter 4

Atoms in motion

4.1 Introduction

In the previous section we studied the problem of static deformation of a crystal. As we have seen previously a crystalline structure each time we take an atom from its position we have to pay an energetic price which for elastic deformations. For small deformations the energy is a simple quadratic function of the displacement. It is known from basic quantum mechanics that even at zero temperature motion does not to cease to exist entirely due to quantum fluctuations. The basic example of this effect is the harmonic oscillator problem which is described by a potential $V(x) = m\omega^2 x^2/2$ where m is the oscillator mass and ω its oscillation frequency. In quantum mechanics the ground state of this problem has finite energy $\hbar\omega/2$ and therefore even in the ground state the oscillator is not static but fluctuates with amplitude $A \approx \hbar/(m\omega)$ (since $V(A) \approx \hbar\omega/2$). In classical mechanics the lowest energy state have zero energy and therefore $A = 0$ (indeed, when $\hbar \to 0$ we recover the classical case). Therefore, in order to understand the behavior of solids at very low temperatures one has to take into consideration the kinetic energy of the oscillations in the solid.

4.1.1 Motion in $d = 1$

As an example let us consider the simplest case of atoms with mass M attached to each other by springs with strength κ as shown in Fig.4.1.

Classically the lowest state of the problem has all atoms at rest at some characteristic distance a between them. This characteristic distance can be traced back to the equilibrium position of atoms in a molecule as we discussed in Chapter 1. Let us now displace the n^{th} atom by a small value u_n. Because the atoms are tied to each other by electrostatic forces the displacement of one of them will cause the displacement of the others. This energy, as discussed in the last chapter, can be written as

$$U = \sum_n \frac{\kappa}{2}(u_n - u_{n+1})^2 \tag{4.1}$$

since we are assuming that only the nearest neighbor atoms are coupled. If U was everything we would have it is clear that the configuration of lowest energy has $u_n = 0$ for all n. But in quantum mechanics we have to include the kinetic energy of the atoms which is given by

$$K = \sum_n \frac{p_n^2}{2m} \tag{4.2}$$

where p_n is the momentum of the n^{th} atom. The quantization condition for this problem is that the displacement and the momentum are canonically conjugated and therefore have well defined commutation relations:

$$[u_n, p_m] = i\hbar\delta_{n,m} \,. \tag{4.3}$$

As we all know from basic quantum mechanics the fact that two operators do not commute imply the Heisenberg uncertainty principle, that is, $\delta p_n \delta u_n > \hbar$, which implies that even we are certain that the oscillator is at certain position u_n from equilibrium we lose completely the information about its momentum. This is exactly what causes the harmonic oscillator to have a ground state with finite amplitude.

There are many ways to study the Hamiltonian $H = K + U$. Here we are going to study the problem via the equations of motion by using the Heisenberg representation for the problem. In this representation the operators evolve in time accordingly to:

$$\begin{aligned} i\hbar\frac{\partial u_n}{\partial t} &= [u_n, H] \\ i\hbar\frac{\partial p_n}{\partial t} &= [p_n, H] \end{aligned} \tag{4.4}$$

which can be easily calculated by using (4.3) and the Hamiltonian':

$$\begin{aligned}\frac{\partial u_n}{\partial t} &= \frac{p_n}{M} \\ \frac{\partial p_n}{\partial t} &= -\kappa\left(u_{n+1} - 2u_n + u_{n-1}\right)\end{aligned} \tag{4.5}$$

which can be rewritten by substituting the first equation into the second one:

$$\frac{\partial^2 u_n}{\partial t^2} = -\frac{\kappa}{M}\left(u_{n+1} - 2u_n + u_{n-1}\right) \tag{4.6}$$

which is the equation for the time evolution of the operator u_n. This equation is simply a simple second order linear differential equation and can be solved by assuming $u_n(t)$ has a simple harmonic form, that is, $u_n(t) = u_n e^{i\omega t}$ which leads to

$$\left(\omega^2 + 2\kappa/M\right) u_n - \kappa/M \ \left(u_{n+1} + u_{n-1}\right) = 0\,. \tag{4.7}$$

Notice that the above equation relates the displacement at n^{th} atom with the displacement at $n+1$ and $n-1$ atoms. The solution to this problem is given again by a simple harmonic solution:

$$u_n = u e^{ikna} \tag{4.8}$$

where u is a constant. Direct substitution of (4.8) into (4.7) requires that

$$\omega(k) = 2\sqrt{\frac{\kappa}{M}}\left|\sin(ka/2)\right|\,. \tag{4.9}$$

Which shows that there is a one to one correspondence between the frequency of oscillation and k the wave-number of the oscillation. Observe that the periodicity of the chain requires that $u_{N+1} = u_1$ which, by (4.8) requires that

$$\begin{aligned} e^{ikNa} &= 1 \\ k(m) &= \frac{2\pi m}{Na}\end{aligned} \tag{4.10}$$

where m is an integer. Observe, therefore that the wave-numbers are quantized in units of $2\pi/(Na)$ and these give the allowed quantum states of the problem. Observe, however, that the total number of states in the problem has to be conserved. In the absence of interactions between the atoms there are N allowed states in the problem corresponding to the rotation of the chain by $N \times 2\pi/N$. We have to end up with the same number of states in momentum space, as well. If N is even the allowed values of m are $m = 0, \pm 1, \pm 2, ..., \pm(N/2-1), N/2$ and for N odd, $m = 0, \pm 1, \pm 2, ..., \pm(N-1)/2$. . Thus, we see that k defined above varies between $-(\pi/(2a)(1-1/N) \leq k \leq \pi/(2a)$. In the limit of a macroscopic number of atoms, $N \to \infty$, the distance between the allowed states shrinks to zero and the wave-numbers form a continuum in the interval $-\pi/(2a) < k \leq \pi/(2a)$. Observe that this is exactly the Brillouin zone for a one dimensional system, as expected from the periodicity of the problem.

Finally, we should point out that in the limit of very long wavelengths, that is, when $k << 1/a$ we can expand (4.9) as

$$\omega(k) \approx a\sqrt{\frac{\kappa}{M}}|k| \tag{4.11}$$

and we see that the frequency of oscillation is linear with the wavenumber. This relationship is identical to the dispersion of photons: $\omega(k) = c|k|$ where c is the light velocity. Like photons the oscillations we are discussing propagate through the solid which a characteristic velocity $c_s = a\sqrt{\frac{\kappa}{M}}$ which is called the sound velocity. Indeed, from basic quantum mechanics we know that the group velocity of a wave $v(k)$ is given by $\hbar v(k) = dE_k/dk$. Remember that in quantum mechanics there is no distinction between waves (or oscillations) and particles. Indeed we could say that we have discovered a new particle which has been named *acoustic phonon* which propagates with the sound velocity. At longer wave-lengths $k \approx \pi/(2a)$ the phonon does not propagate since $\omega(k) \approx 2\sqrt{\frac{\kappa}{M}}$ does not depend on k and therefore its group velocity vanishes. Observe that phonons are an effect of the interaction between atoms (when $\kappa \to 0$ we find $\omega(k) = 0$) and they do not exist outside of the many-body system. This is the major difference between condensed matter physics and high energy physics where particles exist in the vacuum.

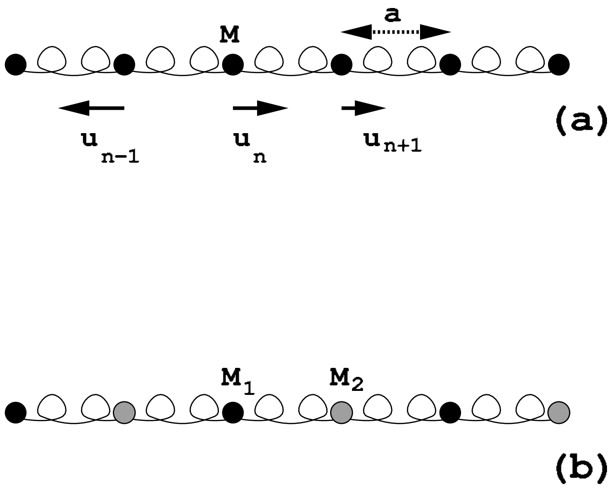

Figure 4.1: *One-dimensional lattice: (a) one atom per basis; (b) two atoms per basis.*

4.2 Phonons in higher dimensions

We can now generalize the discussion of the one dimensional problem to higher dimensions quite easily. We label each atom in a Bravais lattice by a vector $\mathbf{R}+\mathbf{R}_\alpha$. If we allow the atoms to move by an amount $\mathbf{u}_\alpha(\mathbf{R})$ then the instantaneous position of the atom is

$$\mathbf{r}_\alpha(\mathbf{R}) = \mathbf{R} + \mathbf{R}_\alpha + \mathbf{u}_\alpha(\mathbf{R})\,. \tag{4.12}$$

Since the atoms undergo harmonic oscillation the potential energy associated with the displacement has the generic form

$$U = \frac{1}{2}\sum_{\mathbf{R},\mathbf{R}'}\sum_{\alpha,\beta}\sum_{\mu,\nu} u_{\alpha,\mu}(\mathbf{R})\mathcal{K}^{\mu,\nu}_{\alpha,\beta}(\mathbf{R}-\mathbf{R}')u_{\beta,\nu}(\mathbf{R}') \tag{4.13}$$

where $\mathcal{K}^{\mu,\nu}_{\alpha,\beta}$ with $\mu,\nu = x,y,z$ and $\alpha,\beta = 1,...,N_b$ is a matrix $dN_b \times dN_b$ which tells us how the energy of the system change when displace an atom α in some unit cell at position $\mathbf{R}$ in the direction μ, relative to another atom β in the unit cell located at $\mathbf{R}'$ in the direction ν. Observe that this matrix can only depend on the relative position of the atoms. This is an important property as we are going to see. In the one dimensional problem discussed previously where we have just one atom in the unit cell and just one direction to move them this matrix has a very simple form which you can directly check, namely,

$$\mathcal{K}(n-m) = \kappa(2\delta_{n-m,0} - \delta_{n-m,1} - \delta_{n-m,-1}\,. \tag{4.14}$$

The kinetic energy of the atoms is simply

$$K = \sum_{\mathbf{R},\alpha}\frac{\mathbf{P}^2_\alpha(\mathbf{R})}{2M_\alpha} \tag{4.15}$$

where M_α is the mass of each atom in the basis and $\mathbf{P}_\alpha$ the momentum of each atom. Observe that the momentum and the displacement are canonically conjugated, that is,

$$\left[u^\mu_\alpha(\mathbf{R}), P^\nu_\beta(\mathbf{R}')\right] = i\hbar\delta_{\mu,\nu}\delta_{\alpha,\beta}\delta_{\mathbf{R},\mathbf{R}'}\,. \tag{4.16}$$

The commutation relation leads to a quantum problem we want to solve.

Notice that the Hamiltonian of the system $H = K + U$ is rather complex and will change depending on the type of lattice we are working on. In order to simplify the problem one has to look for generic properties which are common to *all* Bravais lattices. There are two of these properties: (1) the harmonic interaction between atoms only depends on the relative distance between the atoms; (2) all Bravais lattices have inversion symmetry.

Because $\mathcal{K}$ only depends on the relative distance between the atoms it is convenient to Fourier transform the displacement operators:

$$\mathbf{u}_\alpha(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} \mathbf{u}_\alpha(\mathbf{k}) \tag{4.17}$$

where $\mathbf{k}$ is the wave-vector of the problem. If, like in the one dimensional case we studied previously, we impose periodic boundary conditions in all directions, that is $\mathbf{u}_\alpha(x+N_x a_x, y, z) = \mathbf{u}_\alpha(x, y+N_y a_y, z) = \mathbf{u}_\alpha(x, y, z+N_z a_z) = \mathbf{u}_\alpha(x, y, z)$, where N_μ is the number of atoms in each direction (observe that the total number of atoms is $N = N_x N_y N_z$) and a_μ is the lattice spacing in each direction, we will have quantized values for the components of $\mathbf{k}$:

$$k_\mu = \frac{2\pi n_\mu}{N_\mu a_\mu}. \tag{4.18}$$

where $-N_\mu/2 < n_\mu \leq N_\mu/2$ when $N_\mu \to \infty$.

In this case the potential term in (4.13) becomes

$$U = \frac{1}{2} \sum_{\alpha,\beta,\mu,\nu} \sum_{\mathbf{k}} u^\mu_\alpha(\mathbf{k}) \mathcal{K}^{\mu,\nu}_{\alpha,\beta}(\mathbf{k}) u^\nu_\beta(-\mathbf{k}) \tag{4.19}$$

where

$$\mathcal{K}^{\mu,\nu}_{\alpha,\beta}(\mathbf{k}) = \sum_{\mathbf{R}} \mathcal{K}^{\mu,\nu}_{\alpha,\beta}(\mathbf{R}) e^{-i\mathbf{k}\cdot\mathbf{R}}. \tag{4.20}$$

The kinetic term transforms accordingly

$$K = \sum_{\mathbf{k},\alpha} \frac{\mathbf{P}_\alpha(\mathbf{k}) \cdot \mathbf{P}_\alpha(-\mathbf{k})}{2M_\alpha}. \tag{4.21}$$

Notice that (4.19) is *diagonal* in momentum space. Thus part of our problem is solved and we just have to diagonalize the problem in the discrete indices $\mu = x, y, z$ and $\alpha = 1, ..., N_b$. In order to do that observe that we would like to find a transformation of coordinates such that (4.19) is diagonal. Therefore there must be a *unitary* transformation $\mathcal{U}$ ($\mathcal{U}^{-1} = \mathcal{U}^T$) between u^μ_α and a new set of coordinates q^μ_α, that is,

$$u^\mu_\alpha(\mathbf{k}) = \sum_{\nu,\beta} \mathcal{U}^{\mu,\nu}_{\alpha,\beta}\, q^\nu_\beta(\mathbf{k}) \tag{4.22}$$

such that

$$\sum_{\mu',\nu',\alpha',\beta'} \left[\mathcal{U}^{-1}\right]^{\mu,\mu'}_{\alpha,\alpha'} \mathcal{K}^{\mu',\nu'}_{\alpha',\beta'} \mathcal{U}^{\nu',\nu}_{\beta',\beta} = M_\alpha \omega^2_{\alpha,\mu} \delta_{\alpha,\beta} \delta_{\mu,\nu} \,. \tag{4.23}$$

Observe that this problem involves $dN_b \times dN_b$ matrices and therefore we will find dN_b values of $\omega_{\alpha,\mu}$. Instead of working with two indices, α and μ it is common to use a short notation and introduce a single index $s = 1, ..., dN_b$ for the eigenvalues ω_s. To each eigenvalue one has a corresponding eigenvector.Each eigenmode is related to a different *polarization* vector $\mathbf{e}_s(\mathbf{k})$. From (4.22) we see that each polarization vector corresponds to a row (or column) of the matrix $\mathcal{U}$. Thus (4.22) can be rewritten as

$$\mathbf{u}_\alpha(\mathbf{k}) = \sum_s \mathbf{e}_{s,\alpha}(\mathbf{k}) q_s(\mathbf{k}) \tag{4.24}$$

where the polarization vectors are orthogonal. The orthogonality condition is simply given by the condition that $\mathcal{U}\mathcal{U}^T = I$, which can be written as

$$\sum_{s=1}^{dN_b} e^\mu_{s,\alpha}(\mathbf{k}) e^\nu_{s,\beta}(-\mathbf{k}) = \delta_{\alpha,\beta} \delta_{\mu,\nu} \tag{4.25}$$

or conversely,

$$\sum_{\alpha=1}^{N_b} \mathbf{e}_{s,\alpha}(\mathbf{k}) \cdot \mathbf{e}_{s',\alpha}(-\mathbf{k}) = \delta_{s,s'} \,. \tag{4.26}$$

It is clear that after the diagonalization that the Hamiltonian of the system is written

$$H = \sum_s \sum_{\mathbf{k}} \left(\frac{p_s(\mathbf{k}) p_s(-\mathbf{k})}{2M} + \frac{1}{2} M \omega_s^2(\mathbf{k}) q_s(\mathbf{k}) q_s(-\mathbf{k}) \right) \tag{4.27}$$

where p_s is the momentum canonically conjugated to q_s. Thus we have reduced the problem to decoupled harmonic oscillators as one would expect from the beginning since we used the fact that the forces among the atoms are harmonic. Therefore, the excitation spectrum of the system is given by

$$E_s(\mathbf{k}) = \hbar\omega_s(\mathbf{k}) \left(n_s(\mathbf{k}) + \frac{1}{2} \right) \tag{4.28}$$

to each mode of this spectrum we associate a *elementary excitation* that we call *phonon*. In condensed matter physics we are interested in obtaining these elementary excitations. The problem of vibrating atoms is particularly simple since it involves only harmonic forces.

Let us now go back to the problem of obtaining the frequencies through eq. (4.23). Multiplying this equation by the left by $\mathcal{U}$ one obtains

$$\left[\mathcal{K} - M\omega^2 I \right] \mathcal{U} = 0 \tag{4.29}$$

which only has a non-trivial solution ($\mathcal{U} \neq 0$) if

$$\det \left[\mathcal{K}(\mathbf{k}) - M\omega_s^2(\mathbf{k}) I \right] = 0 \tag{4.30}$$

which is the equation that defines the eigenmodes. Observe that it involves the diagonalization of a $dN_b \times dN_b$ matrix and therefore, for each value of s, the eigenvectors have dimension dN_b. Each one of these eigenvectors represent the polarization of the phonon waves in the solid. In order to proceed we need more information about $\mathcal{K}(\mathbf{k})$. Since we are not dealing with a specific lattice we have to use the most general properties of these systems, that is, we have to use their symmetries.

The first important symmetry which is true for any crystal is the inversion symmetry, that is,

$$\mathcal{K}(\mathbf{R}) = \mathcal{K}(-\mathbf{R}) \,. \tag{4.31}$$

This property implies, from definition (4.20), that

$$\mathcal{K}(\mathbf{k}) = \sum_{R} \mathcal{K}(\mathbf{R}) \cos(\mathbf{k} \cdot \mathbf{R}) \tag{4.32}$$

which is an even function of the momentum, that is, $\mathcal{K}(\mathbf{k}) = \mathcal{K}(-\mathbf{k})$. Another important property of the system is that if we translate *all* the atoms by the same fixed but arbitrary amount, say $\mathbf{u}_\alpha(\mathbf{R}) = \mathbf{R}_0$, then the energy of the system has to be the same. This is called *Galilean invariance.* Thus, from (4.13), one finds

$$\sum_{\mathbf{R},\mathbf{R}',\alpha,\beta} \mathbf{R}_0 \cdot \mathcal{K}_{\alpha,\beta}(\mathbf{R} - \mathbf{R}') \cdot \mathbf{R}_0 = 0 \tag{4.33}$$

which, for arbitrary $\mathbf{R}_0$ implies

$$\sum_{\mathbf{R},\alpha,\beta} \mathcal{K}_{\alpha,\beta}(\mathbf{R}) = 0 \tag{4.34}$$

which in terms of the Fourier transform (4.20) implies

$$\sum_{\alpha,\beta} \mathcal{K}_{\alpha,\beta}(\mathbf{k} = 0) = 0\,. \tag{4.35}$$

This condition imposes even stronger constraints on the form of $\mathcal{K}$.

Let us consider, as an illustration, the case of a basis with just one type of atom ($N_b = 1$). It implies that we will have d modes in the system only. In this case (4.35) becomes $\mathcal{K}(\mathbf{k} = 0) = 0$. Thus, using (4.32) one can write

$$\begin{aligned} \mathcal{K}(\mathbf{k}) &= \sum_{R} \mathcal{K}(\mathbf{R}) \left[\cos(\mathbf{k} \cdot \mathbf{R}) - 1\right] \\ &= -2 \sum_{R} \mathcal{K}(\mathbf{R}) \sin^2(\mathbf{k} \cdot \mathbf{R}/2)\,. \end{aligned} \tag{4.36}$$

Observe therefore that for $|\mathbf{k}| << 1/d$ we can rewrite

$$\mathcal{K}(\mathbf{k}) \approx -\frac{k^2}{2} \sum_{\mathbf{R}} (\mathbf{n}_\mathbf{k} \cdot \mathbf{R})^2 \mathcal{K}(\mathbf{R}) \tag{4.37}$$

where $\mathbf{n}_\mathbf{k}$ is the unit vector on the direction of $\mathbf{k}$. The matrix

$$\mathcal{C}(\mathbf{n}_\mathbf{k}) = -\frac{1}{2M} \sum_{\mathbf{R}} (\mathbf{n}_\mathbf{k} \cdot \mathbf{R})^2 \mathcal{K}(\mathbf{R}) \tag{4.38}$$

has no information on the amplitude of $\mathbf{k}$ but only its direction. Then, by direct substitution in (4.30), we obtain

$$\omega_s(\mathbf{k}) = c_s(\mathbf{n_k})k \tag{4.39}$$

where

$$\det\left[\mathcal{C}(\mathbf{n_k}) - c_s^2(\mathbf{n_k})I\right] = 0 \tag{4.40}$$

determine the phonon velocity $c_s(\mathbf{n_k})$ in the direction of $\mathbf{k}$. Phonons which have a linear dispersion with momentum, such the ones described by (4.39) are called *acoustical phonons*. Observe that our approximation in (4.37) requires that the sum in (4.38) to converge. We can estimate this sum by replacing it by an integral over R and we see that $\mathcal{C} \propto \int dR R^{d-1} R^2 \mathcal{K}(R)$ only converges if $\mathcal{K}$ behaves at least like $1/R^{d+2}$ at large distances which is usually the case in solids.

For atoms with more than one atom in the basis the matrix $\mathcal{K}$ does not necessarily vanish at $k = 0$ although the sum of the components of the matrix must vanish as explicit in (4.35). However, the form (4.32) is still valid. It implies that when $k = 0$ we are going to have solutions such that the frequency $\omega_s(k = 0) \neq 0$. These modes can be obtained directly from (4.30) by setting $k = 0$,

$$\det\left[\mathcal{K}(\mathbf{k} = 0) - M\omega_{O,s}^2 I\right] = 0\,. \tag{4.41}$$

These modes which are dispersionless at very small k are called *optical phonons*. Observe that we have concluded that in a lattice with a basis we must have d branches of acoustical phonons and $d(N_b - 1)$ branches of optical phonons. The typical dispersion for the phonon modes is shown on Fig.4.2. Observe that we have to plot the dispersion only in the unit cell of the reciprocal lattice, that is, on the Brillouin zone, because of the periodicity of the system. Moreover, from the fact that the crystal has inversion symmetry (4.32) we know that $\mathcal{K}(\mathbf{k}) = \mathcal{K}(-\mathbf{k})$ and therefore we only need to know half of the Brillouin zone.

We have shown that for atoms interacting through harmonic forces the problem reduces to a set of decoupled harmonic operators as given in the Hamiltonian (4.27). We can therefore use all the technology we have for decoupled harmonic oscillators for this problem. In particular

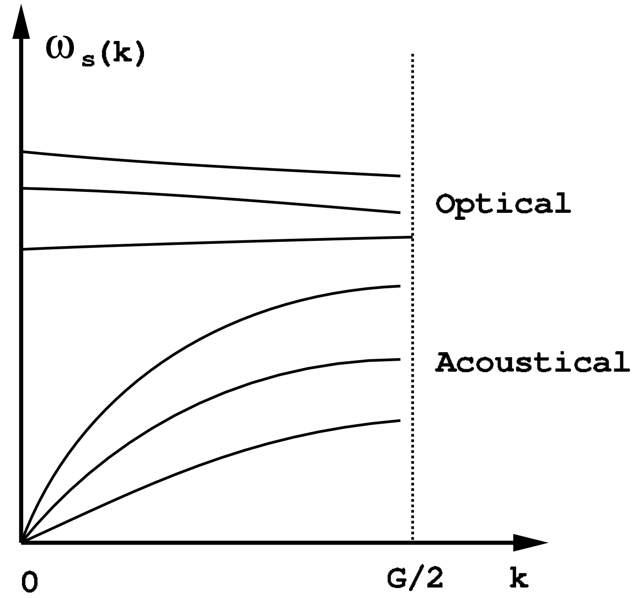

Figure 4.2: *Typical dispersions for a three-dimensional with two atoms in the basis.*

we are interested in the operators that create or destroy phonons in the system. The annihilation and creation operators for harmonic modes are defined as,

$$\begin{aligned} a_s(\mathbf{k}) &= \sqrt{\frac{M\omega_s(\mathbf{k})}{2\hbar}}\left(q_s(\mathbf{k}) + \frac{i}{M\omega_s(\mathbf{k})}p_s(-\mathbf{k})\right) \\ a_s^\dagger(\mathbf{k}) &= \sqrt{\frac{M\omega_s(\mathbf{k})}{2\hbar}}\left(q_s(-\mathbf{k}) - \frac{i}{M\omega_s(\mathbf{k})}p_s(\mathbf{k})\right) \end{aligned} \tag{4.42}$$

respectively. Notice that the displacements can now be written with help of (4.17), (4.24) and (4.42) as

$$\mathbf{u}_\alpha(\mathbf{R}) = \sum_s \sum_{\mathbf{k}} \mathbf{e}_{s,\alpha}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}} \sqrt{\frac{\hbar}{2MN\omega_s(\mathbf{k})}} \left(a_s(\mathbf{k}) + a_s^\dagger(-\mathbf{k})\right) . \tag{4.43}$$

Notice that $\mathbf{e}^*_{s,\alpha}(-\mathbf{k}) = \mathbf{e}_{s,\alpha}(\mathbf{k})$.

In terms of these operators the Hamiltonian (4.27) can be rewritten as

$$H = \sum_{s,\mathbf{k}} \hbar\omega_s(\mathbf{k}) \left(a_s^\dagger(\mathbf{k}) a_s(\mathbf{k}) + \frac{1}{2}\right) . \tag{4.44}$$

where

$$\left[a_s(\mathbf{k}), a_{s'}^\dagger(\mathbf{k}')\right] = \delta_{s,s'}\,\delta_{\mathbf{k},\mathbf{k}'} . \tag{4.45}$$

Thus the states of the system can be labeled by the occupation in each phonon state, $|n_s(\mathbf{k})\rangle$ and the energy is given by (4.28). The creation and annihilation operators act in these states according to

$$\begin{aligned} a_s(\mathbf{k})|n_s(\mathbf{k})\rangle &= \sqrt{n_s(\mathbf{k})}|n_s(\mathbf{k}) - 1\rangle \\ a_s^\dagger(\mathbf{k})|n_s(\mathbf{k})\rangle &= \sqrt{n_s(\mathbf{k}) + 1}|n_s(\mathbf{k}) + 1\rangle . \end{aligned} \tag{4.46}$$

The ground state of the system is therefore the empty state, $|0\rangle$ which is defined by

$$a_s(\mathbf{k})|0\rangle = 0 \tag{4.47}$$

since there are no phonons to be destroyed. The excitations of the problem are therefore obtained by applying creation operators $a^\dagger$ to $|0\rangle$.

4.3 Phonons at finite temperature

We have discussed only the properties of crystals at zero temperatures. At finite temperatures we have to consider the excitation of the phonons out of the ground state. In order to do that we study the partition function of the problem which is defined as

$$Z(\beta) = tr\left[e^{-\beta H}\right] = \sum_n \langle n|e^{-\beta H}|n\rangle = \sum_n e^{-\beta E_n} \tag{4.48}$$

where *tr* is the trace of the operator and the sum is extended over *all* eigenstates E_n and $\beta = 1/(k_B T)$. The free energy, F, of a given statistical mechanical problem is related to the partition function via

$$\begin{aligned} Z &= e^{-\beta F} \\ F = &= -\frac{1}{\beta}\ln(Z)\,. \end{aligned} \tag{4.49}$$

Observe that the mean energy density of the problem is giving by

$$\begin{aligned} \bar{E} &= \frac{1}{V}\frac{tr\left[He^{-\beta H}\right]}{tr\left[e^{-\beta H}\right]} \\ &= \frac{1}{V}\frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = -\frac{1}{V}\frac{1}{Z}\frac{\partial Z}{\partial \beta}\,. \end{aligned} \tag{4.50}$$

When a given system is made out of independent parts the free energy is an additive quantity, that is, $F = \sum_i F_i$, and thus from (4.49) the partition function is a product of the partition function of the parts, $Z = \prod_i Z_i$.

From the phonon problem we have shown that the system decouples into a set of harmonic oscillators which are labeled by s and $\mathbf{k}$. Thus, the partition function reads,

$$Z = \prod_{s,\mathbf{k}} \sum_{n_s(\mathbf{k})=0}^{\infty} e^{-\beta\hbar\omega_s(\mathbf{k})(n_s(\mathbf{k})+1/2)} \tag{4.51}$$

where we have to sum over all possible occupations. The sum over the occupations is just a geometric series and one gets

$$Z = \prod_{s,\mathbf{k}} \frac{e^{\beta\hbar\omega_s(\mathbf{k})/2}}{e^{\beta\hbar\omega_s(\mathbf{k})} - 1} = \prod_{s,\mathbf{k}} \frac{1}{2\sinh(\beta\hbar\omega_s(\mathbf{k})/2)} \tag{4.52}$$

and, from (4.50), one finds

$$\bar{E} = \sum_{s,\mathbf{k}} \hbar\omega_s(\mathbf{k}) \left(\bar{n}_s(\mathbf{k}) + \frac{1}{2}\right) \tag{4.53}$$

where

$$\bar{n}_s(\mathbf{k}) = \frac{1}{e^{\beta\hbar\omega_s(\mathbf{k})} - 1} \tag{4.54}$$

is the mean number of phonons on a given eigenstate at some temperature T. This is called the *Bose-Einstein* distribution function. Observe that the term $E_0 = \sum_{s,\mathbf{k}} \hbar\omega_s(\mathbf{k})/2$ is the ground state of the problem (take the limit of $T \to 0$ in (4.53). This energy is not a observable quantity. We can however observe how a system exchange energy with a heat bath at some temperature T. The quantity that characterizes this exchange of energy is the *specific heat* at constant volume, C_V. The specific heat measures how the energy changes as we vary the temperature of the system. Since temperature is related to the number of excited states, the specific heat is essentially a counting of the number of available states in the system. This quantity is given by

$$C_V = \frac{1}{V}\frac{\partial \bar{E}}{\partial T} = \frac{\partial}{\partial T}\frac{1}{V}\sum_{s,\mathbf{k}} \frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(\mathbf{k})} - 1}\,. \tag{4.55}$$

In order to calculate the thermodynamic quantities we define the concept of *density of states*. The density of states is the number of states with a given energy E. Mathematically it is given by,

$$N(E) = \frac{1}{V}\sum_n \delta(E - E_n)\,. \tag{4.56}$$

For phonons the density of states is just

$$N(E) = \frac{1}{V}\sum_{s,\mathbf{k}} \delta(E - \hbar\omega_s(\mathbf{k}))\,. \tag{4.57}$$

In terms of this quantity the specific heat can be written

$$C_V = \frac{\partial}{\partial T}\int_0^\infty dE\, \frac{N(E)E}{e^{\beta E} - 1} \tag{4.58}$$

which can be proved by direct substitution. Thus, all the thermodynamic function can be obtained directly from the knowledge of the density of states.

In general, the density of states is a very complicated function of the energy due to the shape of the phonon dispersion relation. We have seen, however, that we have d acoustic modes and $d(N_b - 1)$ optical modes. Moreover, these modes are characterized by the fact that the acoustical modes have a dispersion proportional to k while the optical modes are dispersionless at small k. What is the effect of temperature on the phonons? At low temperatures only acoustical modes are excited since to excite an optical mode one has to pay an energy $\hbar\omega_0$. Therefore for $k_B T << \hbar\omega_0$ we do not expect to excite any optical mode. The acoustical modes, however, can always be excited at low temperatures since the dispersion vanishes with k, that is, it is always possible to find a mode k such that $k_B T \approx \hbar c k$. Indeed, these two types of excitations are the most basic ones in condensed matter physics: gapless and gapful. Most of physical properties of solids can be understood on the basis of this classification. Without doing any calculation we can predict the behavior of the thermodynamic functions quite well.

For an acoustical mode at some given temperature T the number of modes available is given by the spherical volume in $\mathbf{k}$-space of radius k at energy $k_B T$ (see Fig.4.3)(a)). In d dimensions this volume is proportional to T^d. Naturally the number of states available at this temperature is proportional to T^d. Thus the specific heat has to behave like T^d. The energy of the states is of order $k_B T$. Therefore the thermal energy of the system, ΔE, $(\Delta E = \bar{E} - E_0)$ has to be proportional to T^{d+1} (in accordance with (4.55) the specific heat is proportional to T^d). This argument is valid as far as the Bose-Einstein occupation number does not give an important contribution. This requires low temperatures (see Fig.4.3(b)). At high temperatures the occupation number gives a contribution of order $k_B T/E$ and therefore the mean energy in (4.58) is just $\bar{E} \approx k_B T \int dE N(E)$ which is linear in the temperature. The specific heat, by its turn, has to be temperature independent. This is known as the *Dulong-Petit law.* But observe that the integral $\int d_E N(E)$ is essentially the total number of states per unit of volume in the system which is $dN/V \propto 1/a^d$ where a is the lattice spacing. Observe that besides the thermal energy $k_B T$ the only other quantities

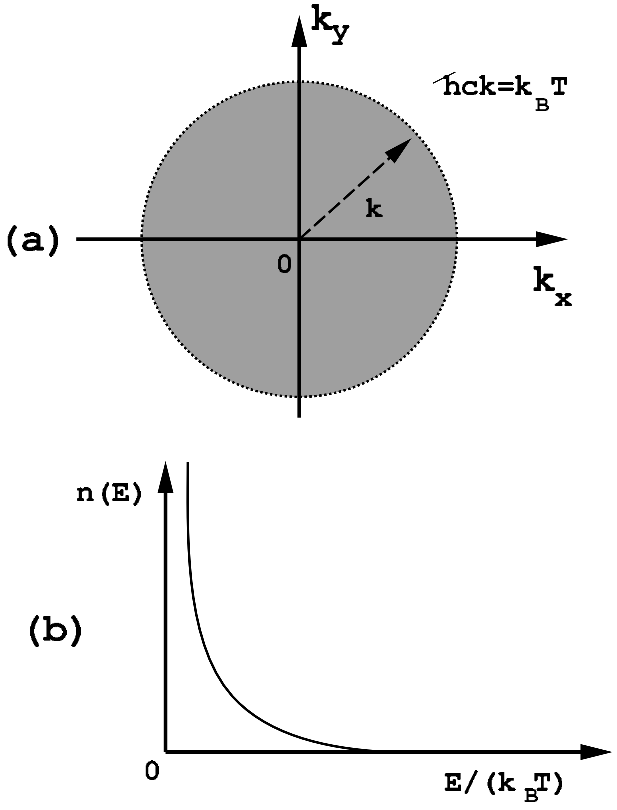

Figure 4.3: *(a) Phase space for phonons in two dimensions; (b) Shape of the Bose-Einstein distribution.*

which can appear in the expression of the energy is the phonon velocity c, the Planck constant $\hbar$ and the lattice spacing a. The only quantity with dimensions of energy that we can construct from these constants is $\hbar c/a$. Since we know that the mean thermal energy is proportional to $(k_BT)^{d+1}$ the only form allowed for the mean energy per unit of volume is

$$\Delta E = \frac{(k_BT)^{d+1}}{(\hbar c/a)^d}\Phi_d\left(\frac{\hbar c/a}{k_BT}\right) \tag{4.59}$$

where $\Phi_d(x)$ is a dimensionless universal function such that for $x >> 1$ it is constant and when $x << 1$ it behaves like x^{d-1} accordingly to the Dulong-Petit law. Eq.(4.59) is called a *scaling form* form of the mean energy because it was only based on dimensional analysis and the study of trivial limits of the problem. This scaling form of the energy is possible because acoustic modes are *critical*, that is, the frequency and momentum scale in a well defined way. In this case we can defined what is called a *dynamical exponent*, z. This can be understood in the following way: suppose the lattice constant of the problem is changed by a constant b, that is, $a \to ba$. Since the momentum is proportional to $1/a$ then it has to change as $k \to k/b$. But the frequency is also proportional to the momentum and therefore $\omega \to \omega/b$. Thus the ratio k/ω is unchanged by any change in the scale of the problem. In this case we say that $z = 1$. In a system where the frequency does not depend linearly with momentum a change in the lattice spacing can lead to a change in the frequency such that $\omega \to \omega/b^z$ and thus the invariant ratio is not k/ω but k^z/ω which defines a generic dynamical exponent. The physical reason for this is due to the *relativistic invariance* of the acoustic problem, that is, the system of acoustic phonons is invariant under a *Lorentz transformation.*

Now that we know the result of the calculation let us consider how a serious calculation would lead to the form (4.59). We approximate the actual frequency by the acoustic relation (4.39). We have to remember, however, that the dispersion is a periodic function of momentum and by replacing the exact dispersion by a linear one we have disregarded wavevectors close to the zone boundary ($k \approx G/2$). We have therefore to cut-off the integrals at some maximum vector, k_D. In order to estimate this wavevector we replace the original unit cell by a spherical

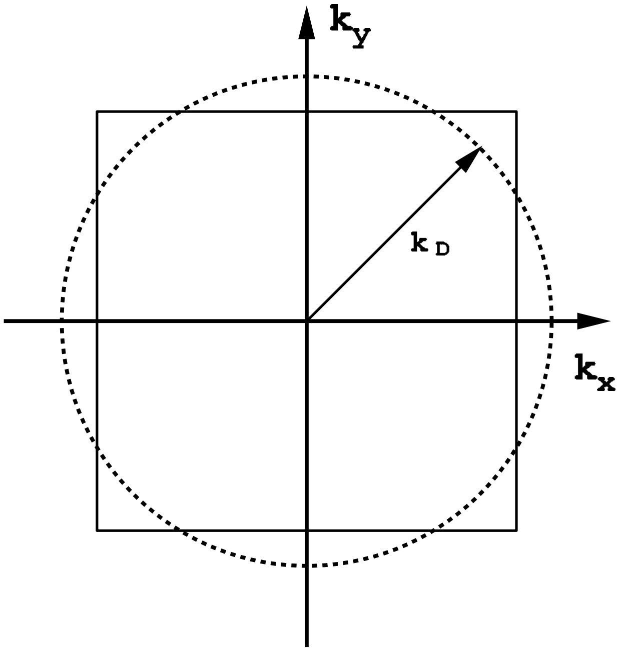

Figure 4.4: *Geometry of the Debye approximation in two dimensions: the square Brillouin zone is replaced by a circle of radius* k_D.

one with radius k_D (see Fig.4.4). The number of states in the original cell is N, the number of atoms in the crystal. Moreover, the volume in k-space per wave vector is $(2\pi)^d/V$ and therefore the number of states is $(2\pi)^d N/V = (2\pi)^d \bar{n}$. In order to preserve the number of states for the spherical problem we require that

$$\begin{aligned} (2\pi)^d \bar{n} &= \int d^d k \; \theta(k_D - k) \\ k_D &= \left(\frac{d(2\pi)^d \bar{n}}{S_d}\right)^{1/d} \end{aligned} \tag{4.60}$$

where $S_d = \int d\Omega$ is the total solid angle in d dimensions ($S_1 = 2$, $S_2 = 2\pi$ and $S_3 = 4\pi$) and $\theta(x) = 1$ if $x > 0$ and vanishes otherwise is a step function. This is called the *Debye model.* Observe that k_D is proportional to $1/a$ and therefore acts as a high energy cut-off for the model. For this model the density of states for acoustical modes is written as

$$\begin{aligned} N_D(E) &= \sum_s \int \frac{d^d k}{(2\pi)^d} \delta\left(E - \hbar c_s(\mathbf{n_k}) k\right) \\ &= \sum_s \int \frac{d\Omega}{(2\pi)^d} \int_0^{k_D} dk k^{d-1} \delta\left(E - \hbar c_s(\mathbf{n_k}) k\right) . \end{aligned} \tag{4.61}$$

We now change the variables as $x = \hbar c_s(\mathbf{n_k}) k$ and write

$$N_D(E) = \frac{d S_d}{(2\pi)^d} \frac{E^{d-1}}{(\hbar c)^d} \theta\left(k_B \Theta_D - E\right) \tag{4.62}$$

where $k_B \Theta_D = \hbar \omega_D = \hbar c k_D \propto \hbar c/a$ is the Debye energy and is the scale of energy that should appear in (4.59). Moreover,

$$\frac{1}{c^d} = \frac{1}{d} \sum_s \int \frac{d\Omega}{S_d} \frac{1}{c_s^d(\mathbf{n_k})} \tag{4.63}$$

gives an estimate of the average phonon velocity. Observe that the density of states is finite only for energies smaller than the Debye energy. By substitution of (4.62) into (4.58) one finds (4.59) with

$$\Phi_d(x) = \frac{d S_d}{(2\pi)^d} \int_0^x dz \frac{z^d}{e^z - 1} . \tag{4.64}$$

Observe that the characteristic energy scale in solids is defined by the Debye temperature. The sound velocity is of order of 10^4 m/s in most solids and since the lattice spacing is of order of $\mathring{A}$ the typical Debye temperatures are of order of hundreds of Kelvin.

The optical modes can be treated in a much simpler way since they are dispersionless and have a gap for excitation of energy $\hbar\omega_0$. It is clear from (4.58) that in this case the physical properties are going to be completely determined by the Bose-Einstein factor which is exponentially small at low temperatures. Thus one expect all the thermal properties of optical modes to decay exponentially with temperature, that is, $e^{-\hbar\omega_0/(k_B T)}$. Since we have $N_b(d-1)$ optical branches in the spectrum we can write that the density of states is simply

$$N_E(E) = \frac{N_b(d-1)N_s}{V}\delta(E - \hbar\omega_0) \tag{4.65}$$

where the prefactor is chosen in such way that the total number of states is correct. Thus, using (4.58), one finds

$$\Delta E = \frac{(d-1)\bar{n}\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1} \tag{4.66}$$

where we have used that $N = N_s N_b$. At low temperatures, as expected, the mean energy vanishes exponentially and at high temperatures one recovers the Dulong-Petit result. This simple model for optical phonons is called *Einstein model*.

4.4 Inelastic scattering

Consider the problem of the scattering of a solid taking into account lattice oscillations, that is, phonons. We assume that the interaction between the probe and the solid is weak and since this is a time dependent problem (the atoms undergo harmonic motion) we are going to use time dependent perturbation theory. The probe (which can be light, neutrons or whatever) is assumed to be initially at some distant time $t_0 \to -\infty$ in a plane wave state $(e^{i\mathbf{p}\cdot\mathbf{r}}/\sqrt{V})$ with wave-vector $\mathbf{p}$ and the solid in a eigenstate of the Hamiltonian H_0 given by $|I\rangle$ with energy E_I. The probe interact with the solid via a potential V and is scattered into a new plane wave state with wave-vector $\mathbf{p}'$ (see Fig.4.5) and the solid is left in another eigenstate $|F\rangle$ with energy E_F at some distant time $t \to \infty$. Observe that the energy must be conserved in the scattering and therefore

$$E_I - E_F = E\,, \tag{4.67}$$

where E is the change in energy of the probe during scattering. Observe that the scattering is inelastic because the probe does not conserve its energy during scattering. The rate of transition is simply given by *Fermi's golden rule*

$$\begin{aligned} T(\mathbf{q},E) &= \frac{2\pi}{\hbar}\sum_F \delta\left(E - E_I + E_F\right) |\langle \mathbf{p}', F|V|\mathbf{p}, I\rangle|^2 \\ &= \frac{2\pi}{\hbar}\sum_F \delta\left(E - E_I + E_F\right) \times \\ &\times \ |\frac{1}{V}\int d^d r e^{i\mathbf{q}\cdot\mathbf{r}} \langle F|V(\mathbf{r})|I\rangle|^2 \end{aligned} \tag{4.68}$$

where $\mathbf{q} = \mathbf{p}' - \mathbf{p}$ is the momentum transfer during scattering.

We will assume as before that the interaction of the probe and the solid is short ranged and can be written as

$$\begin{aligned} V(\mathbf{r}) &= V_0 \sum_{\mathbf{R}} \delta\left(\mathbf{r} - \mathbf{r}(\mathbf{R})\right) \\ V(\mathbf{r}) &= V_0 \sum_{\mathbf{R}} \delta\left(\mathbf{r} - \mathbf{R} - \mathbf{u}(\mathbf{R})\right) \end{aligned} \tag{4.69}$$

where we have used (4.12) and for simplicity of notation we assume one atom per unit cell. Substitution in (4.68) leads to

$$T(\mathbf{q},E) = \frac{2\pi V_0^2}{V^2 \hbar}\sum_F \delta\left(E - E_I + E_F\right) |\sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}} \langle F|e^{i\mathbf{q}\cdot\mathbf{u}(\mathbf{R})}|I\rangle|^2\,. \tag{4.70}$$

The cross-section of the crystal is proportional to the transition rate and this allows us to define the so called *dynamical form factor*, $S(\mathbf{q},\omega)$, which is given by

$$S(\mathbf{q},\omega) = \frac{1}{N}\sum_F \delta\left(\omega + (E_F - E_I)/\hbar\right) |\sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}} \langle F|e^{i\mathbf{q}\cdot\mathbf{u}(\mathbf{R})}|I\rangle|^2\,. \tag{4.71}$$

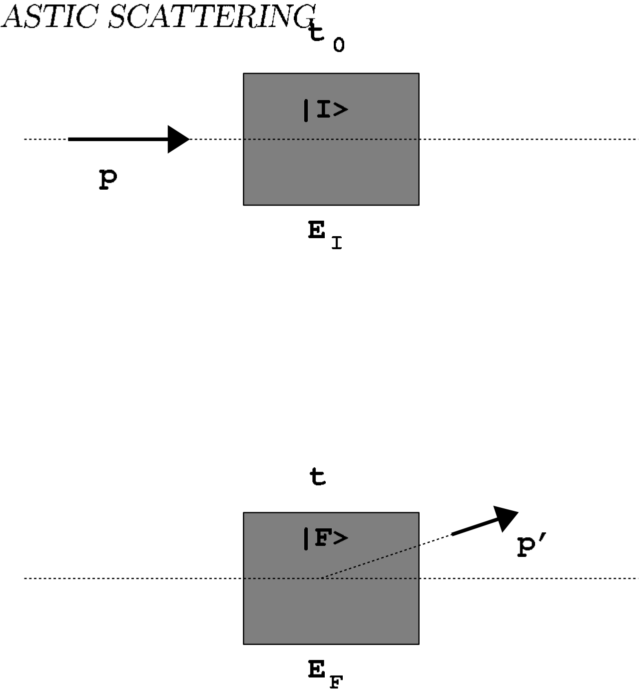

Figure 4.5: *Scattering process.*

which can be Fourier transformed in the frequency domain,

$$S(\mathbf{q},\omega) = \int \frac{dt}{2\pi} e^{i\omega t} S(\mathbf{q},t) \tag{4.72}$$

where

$$\begin{aligned} S(\mathbf{q},t) &= \frac{1}{N}\sum_F e^{i(E_F-E_I)t/\hbar} \sum_{\mathbf{R},\mathbf{R}'} e^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} \langle I|e^{i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')}|F\rangle\langle F|e^{-i\mathbf{q}\cdot\mathbf{u}(\mathbf{R})}|I\rangle \\ &= \frac{1}{N}\sum_F \sum_{\mathbf{R},\mathbf{R}'} e^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} \langle I|e^{i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')}|F\rangle\langle F|e^{iH_0t/\hbar}e^{-i\mathbf{q}\cdot\mathbf{u}(\mathbf{R})}e^{-iH_0t/\hbar}|I\rangle \\ &= \frac{1}{N}\sum_F \sum_{\mathbf{R},\mathbf{R}'} e^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} \langle I|e^{i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')}|F\rangle\langle F|e^{-i\mathbf{q}\cdot\mathbf{u}(\mathbf{R},t)}|I\rangle \\ &= \frac{1}{N}\sum_{\mathbf{R},\mathbf{R}'} e^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} \langle I|e^{i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')}e^{-i\mathbf{q}\cdot\mathbf{u}(\mathbf{R},t)}|I\rangle\,. \end{aligned} \tag{4.73}$$

Where we have used that: (1) $|I\rangle$ and $|F\rangle$ are eigenstates of H_0; (2) the operator identity $Ue^AU^{-1} = e^{UAU^{-1}}$; (3) changed from the

Schrödinger representation to the Heisenberg representation, that is, $e^{iH_0t/\hbar}Ae^{-iH_0t/\hbar} = A(t)$; and (4) that the final states form a complete set $\sum_F |F\rangle\langle F| = 1$. We will assume further that initially the solid is an equilibrium situation at temperature T so that $\langle I|...|I\rangle$ becomes a thermal average. Observe that the dynamical form factor only depends on the properties of the crystal since the probe is already out of the problem. Notice that we can write (4.73) in a simpler form if we use (2.50)

$$S(\mathbf{q}, t) = N\langle I|\rho(-\mathbf{q}, 0)\rho(\mathbf{q}, t)|I\rangle \tag{4.74}$$

is the so-called *density-density correlation function.* Observe that this is a natural result since the probe is coupled to the ion density in (4.69) and therefore the *response* of the solid occurs by creating density fluctuations.

In order to calculate the thermal average in (4.73) we are going to use a result from the appendix which says that if the ground state of the problem is the one for harmonic oscillators and the operators A and B are linear combination of destruction and creation operators we have

$$\langle e^A e^B\rangle = e^{\frac{1}{2}\langle A^2+2AB+B^2\rangle} \tag{4.75}$$

where in our case $A = i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')$ and $B = -i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)$. Thus we have

$$\begin{aligned}\langle e^{i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')}e^{-i\mathbf{q}\cdot\mathbf{u}(\mathbf{R},t)}\rangle &= e^{\frac{1}{2}\langle 2\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')\mathbf{q}\cdot\mathbf{u}(\mathbf{R},t)-(\mathbf{q}\cdot\mathbf{u}(\mathbf{R}'))^2-(\mathbf{q}\cdot\mathbf{u}(\mathbf{R},t))^2\rangle} \\ &= e^{\frac{1}{2}\sum_{\mu,\nu} q^\mu q^\nu C_{\mu,\nu}(\mathbf{R}-\mathbf{R}',t)}\end{aligned} \tag{4.76}$$

where

$$C_{\mu,\nu}(\mathbf{R}-\mathbf{R}', t) = \langle (u^\mu(\mathbf{R}, t) - u^\mu(\mathbf{R}', 0))\,(u^\nu(\mathbf{R}, t) - u^\nu(\mathbf{R}', 0))\rangle \tag{4.77}$$

is the phonon-phonon *correlation function* which depends only on the relative position of the ions. Thus, the dynamic form factor reads

$$S(\mathbf{q}, t) = \sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}}e^{\sum_{\mu,\nu} q^\mu q^\nu C_{\mu,\nu}(\mathbf{R},t)}\,. \tag{4.78}$$

Most of the phenomena in physics can be expressed in terms of correlation function such as (4.77). This is one important example since most of the excitations in solids (even electronic ones) have bosonic character.

The calculation of the correlation function (4.77) is very simple because the u operators are just linear combinations of creation and annihilation operators. We can easily show using (4.43) and the commutation relations between the creation and annihilation operators that

$$C_{\mu,\nu}(\mathbf{R},t) = \sum_s \int \frac{d^dk}{(2\pi)^d} e^\mu_s(\mathbf{k}) e^\nu_s(-\mathbf{k}) \frac{\hbar}{2M\omega_s(\mathbf{k})}$$
$$\left[(1+n_s(\mathbf{k}))\left(e^{-i(\mathbf{k}\cdot\mathbf{R}-\omega_s(\mathbf{k})t)}-1\right)+n_s(\mathbf{k})\left(e^{i(\mathbf{k}\cdot\mathbf{R}-\omega_s(\mathbf{k})t)}-1\right)\right]. \tag{4.79}$$

Notice that the complete evaluation of $S(\mathbf{q},\omega)$ is very complicated. One can however look at some simple limits. Let us study the limit of elastic scattering, that is, when the energy is conserved in the scattering. In this case we have to take the limit of $\omega \to 0$ in (4.72). This is the so-called static limit. Observe that this is equivalent of taking the limit of long times $t \to \infty$ in (4.72) since the exponential term oscillates strongly in this limit and the integral is dominated by small values of the frequency. In this limit the exponential terms in (4.79) also oscillate strongly and give vanishing contribution. The only term left is

$$lim_{t\to\infty}\frac{1}{2}\sum_{\mu,\nu} q^\mu q^\nu C_{\mu,\nu}(\mathbf{R},t) = -2W(T)$$
$$= -\sum_s \int \frac{d^dk}{(2\pi)^d} |\mathbf{q}\cdot\mathbf{e}_s(\mathbf{k})|^2 \frac{\hbar}{2M\omega_s(\mathbf{k})}\left(1+2n_s(\mathbf{k})\right) \tag{4.80}$$

which is the so-called *Debye-Waller factor*. The physical meaning of this factor is clear if we calculate the dynamical form factor from (4.78) and (4.72):

$$S^{(0)}(\mathbf{q},\omega) = e^{-2W(T)}\delta(\omega)N\delta_{\mathbf{q},\mathbf{G}} \tag{4.81}$$

which is the result of elastic scattering obtained before except by the Debye-Waller factor which tells us that virtual transitions induced by the collision of the probe with the crystal at finite temperatures decreases the intensity of the scattering. We have been able, therefore, to reproduce the results of elastic scattering.

The next correction to elastic scattering is obtained by retaining the time dependence on correlation function (4.77). In order to do that we replace the exponent in (4.78) by

$$\begin{aligned} S(\mathbf{q},t) &= \sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}} \exp\left\{\frac{1}{2}\sum_{\mu,\nu} q^{\mu}q^{\nu}\left[lim_{t\to\infty}C_{\mu,\nu}(\mathbf{R},t)+\Delta C_{\mu,\nu}(\mathbf{R},t)\right]\right\} \\ &= \sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}} e^{-2W(T)} \sum_{n=0}^{\infty}\left[\frac{1}{2}\sum_{\mu,\nu} q^{\mu}q^{\nu}\Delta C_{\mu,\nu}(\mathbf{R},t)\right]^{n} \qquad (4.82) \end{aligned}$$

where

$$\Delta C_{\mu,\nu}(\mathbf{R},t) = C_{\mu,\nu}(\mathbf{R},t) - lim_{t\to\infty}C_{\mu,\nu}(\mathbf{R},t)\,. \qquad (4.83)$$

It is possible to show that each power in n in (4.82) is due to the scattering of the probe to n phonons. The first order correction to the static term produces a correction in the dynamic form factor which is given by

$$\begin{aligned} S^{(1)}(\mathbf{q},\omega) &= e^{-2W(T)}\sum_{s}|\mathbf{q}\cdot\mathbf{e}_s(\mathbf{q})|^2\frac{\hbar}{2M\omega_s(\mathbf{q})}\left[(1+n_s(\mathbf{q}))\,\delta\left(\omega+\omega_s(\mathbf{q})\right)\right. \\ &+ \left. n_s(\mathbf{q})\delta\left(\omega-\omega_s(\mathbf{q})\right)\right] \qquad (4.84) \end{aligned}$$

observe that the first term increases the number of phonons by one and therefore is related with the emission of one phonon by the probe. The second process is associated with the absorption of one phonon by the probe. The δ functions guarantee the conservation of energy for each one of these process. Other corrections can be calculated immediately from (4.82). An important property of (4.84) is that the scattering happens when $\omega = E/\hbar = \omega_s(\mathbf{q})$. Thus, by varying the energy of the probe one can map the dispersion relation of the phonons.

4.5 Problems

1. Calculate the commutation relations between $\mathbf{u}_\alpha(\mathbf{k})$ and $\mathbf{P}_\alpha(\mathbf{k})$ starting from (4.16).

2. The group velocity of an excitation is defined as the velocity at which a wave-packet made out of a superposition of plane waves propagate and is given by

$$v_g = \frac{d\omega(k)}{dk} \,.$$

   What is the group velocity of an acoustical wave when $k \to 0$? What is the group velocity of an optical wave when $k \to 0$?

3. Calculate the phonon dispersion and polarizations for an one-dimensional lattice with two atoms with masses M_1 and M_2 as in Fig.4.1(b).

4. What is the sound velocity for the problem in which the chain has two different masses?

5. Assume that a chain is made out of 3 different atoms with different masses. What can you say about the spectrum of the system? Where are gaps located? *Hint: no calculations needed.*

6. Using the commutation relations between $q_s(\mathbf{k})$ and $p_s(\mathbf{k})$ show that the creation and annihilation operators obey the commutation relations (4.45).

7. Here we are going to consider the long wavelength theory of acoustic phonons. Define two new fields,

$$\begin{aligned} \Pi_s(\mathbf{r}) &= \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} p_s(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}} \\ \phi_s(\mathbf{r}) &= \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} q_s(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \end{aligned} \tag{4.85}$$

   which obey canonical commutation relations $[\phi_s(\mathbf{r}), \Pi_{s'}(\mathbf{r}')] = i\hbar\delta(\mathbf{r}-\mathbf{r}')\delta_{s,s'}$. By linearizing the phonon dispersion, $\omega_s(k) = c_s k$

show that Hamiltonian density associated with the acoustic case can be written in terms of these fields as

$$\mathcal{H} = \sum_s \left[\frac{\Pi_s^2(\mathbf{r})}{2\rho} + \frac{c_s^2\rho}{2}\left(\nabla\phi_s(\mathbf{r})\right)^2\right] \tag{4.86}$$

where $\rho = M/a$ is the lattice mass density and a is the lattice spacing. Eq.(4.86) is the Hamiltonian density of a field theory for particles moving with "light" velocity c_s. Observe that in this field theory all the knowledge of the lattice is lost since we assumed that $k << 1/a$ or equivalently that we are looking at wavelengths such that $\lambda >> a$. Show that classical equation of motion for (4.86) is the well-known wave equation:

$$\frac{d^2\phi_s}{dt^2} = c_s^2\nabla^2\phi_s\,. \tag{4.87}$$

8. Prove that the equation (4.64) is correct and obey the scaling properties. Evaluate the low temperature specific heat for the Debye model in $d = 1, 2, 3$.

9. Calculate the specific heat for the Einstein model for phonons with frequency ω_0.

10. Show that the field theory associated with the Einstein model is given by the following Hamiltonian density:

$$\mathcal{H} = \sum_s \left[\frac{\Pi_s^2(\mathbf{r})}{2\rho} + \frac{aM\omega_0^2}{2}\phi_s^2(\mathbf{r})\right]\,. \tag{4.88}$$

11. Prove eq.(4.79).

12. Calculate the Debye-Waller factor in 1, 2 and 3 dimensions at zero temperature for acoustic phonons. What is the physical meaning of your results? This result is related to the famous Mermim-Wagner theorem.

13. Prove that eq.(4.84) is correct.

4.5.1 Appendix: Thermal averages for bosons

Observe that in (4.73) we are interested in calculating an average of exponential of operators. But from (4.43) these operators are linear combinations of harmonic creation and annihilation operators, $\sum_n \left(\alpha_n a_n + \gamma_n a_n^\dagger\right)$, where each mode is independent from each other, that is, $[a_n, a_m^\dagger] = \delta_{n,m}$ (for the phonon case $n = (s, \mathbf{k})$). Since these modes are independent we can look at each mode individually. Let

$$\begin{aligned} A &= \alpha_A a + \gamma_A a^\dagger \\ B &= \alpha_B a + \gamma_B a^\dagger \end{aligned} \tag{4.89}$$

we want to evaluate an average of the form $\langle e^A e^B \rangle$. First we use an operator identity which is valid when the commutator $[A, B]$ is a c-number:

$$e^A e^B = e^{A+B} e^{[A,B]/2} \,. \tag{4.90}$$

Observe that $A + B$ can now be written as

$$A + B = \alpha a + \gamma a^\dagger \tag{4.91}$$

where

$$\begin{aligned} \alpha &= \alpha_A + \alpha_B \\ \gamma &= \gamma_A + \gamma_B \,. \end{aligned} \tag{4.92}$$

Thus we are interested in calculating

$$\begin{aligned} \langle e^{\alpha a + \gamma a^\dagger} \rangle &= e^{-\alpha\gamma/2} \langle e^{\alpha a} e^{\gamma a^\dagger} \rangle \\ &= e^{\alpha\gamma/2} \langle e^{\gamma a^\dagger} e^{\alpha a} \rangle \end{aligned} \tag{4.93}$$

where we have used (4.90). Now we define the function

$$\begin{aligned} f(\alpha) &= \langle e^{\alpha a} e^{\gamma a^\dagger} \rangle \\ &= e^{\alpha\gamma} \langle e^{\gamma a^\dagger} e^{\alpha a} \rangle \,. \end{aligned} \tag{4.94}$$

Now we use the cyclic property of the trace in order to write

$$\begin{aligned}
\langle e^{\gamma a^\dagger} e^{\alpha a}\rangle &= tr\left[e^{-\beta H} e^{\gamma a^\dagger} e^{\alpha a}\right]/Z \\
&= tr\left[e^{\alpha a} e^{-\beta H} e^{\gamma a^\dagger}\right]/Z \\
&= tr\left[e^{-\beta H} e^{\beta H} e^{\alpha a} e^{-\beta H} e^{\gamma a^\dagger}\right]/Z \\
&= \langle e^{\beta H} e^{\alpha a} e^{-\beta H} e^{\gamma a^\dagger}\rangle\,. \qquad (4.95)
\end{aligned}$$

The Hamiltonian for the problem is simply $H = \hbar\omega(a^\dagger a + 1/2)$ and if we use the operator identity $Ue^A U^{-1} = e^{UAU^{-1}}$ and

$$e^{xa^\dagger a} a e^{-xa^\dagger a} = e^x a \qquad (4.96)$$

we obtain from (4.95):

$$\begin{aligned}
\langle e^{\gamma a^\dagger} e^{\alpha a}\rangle &= \langle e^{\alpha e^{-\hbar\omega\beta} a} e^{\gamma a^\dagger}\rangle \\
&= f(\alpha e^{-\hbar\omega\beta}) \qquad (4.97)
\end{aligned}$$

where we have used the definition of f. Now, from (4.94) we find

$$f(\alpha) = e^{\gamma\alpha} f(\alpha e^{-\hbar\omega\beta}) \qquad (4.98)$$

which can be solved by iteration, that is,

$$f(\alpha) = e^{\gamma\alpha(1+e^{-\hbar\omega\beta})} f(\alpha e^{-2\hbar\omega\beta}) = e^{\gamma\alpha(1+e^{-\hbar\omega\beta}+e^{-2\hbar\omega\beta})} f(\alpha e^{-3\hbar\omega\beta}) \qquad (4.99)$$

and so on. If we do this process an infinite number of times we find

$$f(\alpha) = e^{\gamma\alpha/(1-e^{-\hbar\omega\beta})} f(0) \qquad (4.100)$$

where we have used the result of a geometric series $\sum_0^\infty x^n = 1/(1-x)$. Observe however that

$$f(0) = \langle e^{\gamma a^\dagger}\rangle = \sum_n e^{-\beta\hbar\omega n}\langle n|e^{\gamma a^\dagger}|n\rangle = 1 \qquad (4.101)$$

and therefore

$$f(\alpha) = e^{\gamma\alpha/(1-e^{-\hbar\omega\beta})}\,. \qquad (4.102)$$

We now observe that the Bose-Einstein factor is

$$\bar{n} = \frac{1}{e^{\hbar\omega\beta} - 1} \tag{4.103}$$

and therefore

$$f(\alpha) = e^{\gamma\alpha(1+\bar{n})}\,. \tag{4.104}$$

With this result at hand we can rewrite

$$\langle e^{\alpha a + \gamma a^\dagger} \rangle = e^{\frac{1}{2}\gamma\alpha(1+2\bar{n})} \tag{4.105}$$

and finally

$$\begin{aligned} \langle e^A e^B \rangle &= \exp\left\{ \frac{1}{2}\left[\alpha_A\gamma_B - \gamma_A\alpha_B + (\gamma_A+\gamma_B)(\alpha_A+\alpha_B)(1+2\bar{n})\right]\right\} \\ &= \exp\left\{\frac{1}{2}\langle A^2 + 2AB + B^2\rangle\right\} \end{aligned} \tag{4.106}$$

which can be obtained directly from the definition of A and B, the commutation relation $[a, a^\dagger] = 1$, the definition $\bar{n} = \langle a^\dagger a\rangle$ and that $\langle a^2\rangle = \langle \left(a^\dagger\right)^2 \rangle = 0$.

Chapter 5

Electrons in Solids

5.1 Introduction

We have seen that the difference in the mass of the electrons and ions allow us to separate their time (or energy) scales. This introduces a major simplification since we can treat electrons and ions separately. We have investigated the problem of the coupling between ions and showed that the ion problem has *elementary excitations* which are called phonons. The short range character of the interaction between ions and the fact that they form a lattice makes their theoretical treatment quite simple. The same thing does not happen with electrons. This can be seen clearly from the experimental fact that electronic properties of solids can vary wildly, that is, we can have metals, insulators, magnetic systems, superconductors, etc, with properties which depend only on the way the electrons interact among themselves.

In this chapter we are going to study the interaction between the electrons and the atoms in a crystal. We are going to explore the fact that in a crystal the potential felt by the electrons has to be periodic due to the periodic arrangement of the atoms. We are going to consider first the case of a linear chain of atoms since the mathematical treatment is quite simple and it is relevant for the experimental case of one-dimensional systems such as organic conductors, polymers and other low dimensional systems. The treatment of the higher dimensional problem is completely analogous and we will generalize the one-dimensional results to higher dimensions.

5.2 The linear chain

Let us consider now a problem where a symmetry helps us to solve the problem entirely. Consider a ring of N identical atoms which are separated from each other by an angle $2\pi/N$ as shown on Fig.natom. We label the states of the electron localized in each one of these atoms by ψ_n with $n = 1, ..., N$. Observe that this problem has rotational invariance, that is, if we rotate the system by $2\pi/N$ we should not notice any difference. In the limit where $R \to \infty$ and $N \to \infty$ but N/R is a constant (which is just the linear density of the chain) the problem goes into a linear chain of atoms with *periodic boundary conditions*, that is, the atom $N+1$ is simply atom 1. If we had no atoms on the ring and we allow an electron to move along the ring then the system has *translational* invariance, that is, we could rotate the ring by any angle and the problem should look like the same. The operator that produces translations (or in this case, rotations) is the translation operator

$$R(l) = e^{i\hat{p}l/\hbar} \tag{5.1}$$

where $\hat{p}$ is the momentum operator. In order to understand why this operator generates translations consider the transformation

$$R(l)xR^{-1}(l) = e^{ipl/\hbar}\hat{x}e^{-ipl/\hbar} = \hat{x} + l \tag{5.2}$$

as you can easily shown by using the commutation relations $[\hat{x}, \hat{p}] = i\hbar$. In the absence of the atoms the Hamiltonian of the problem has to commute with $R(l)$ for **any** value of l by translation (rotation) invariance.

In the presence of the atoms this is not true because the electron feels the potential of each atom. The potential $V(x)$ felt by the electron has to be **periodic**, that is, if x is the coordinate along the ring one must have $V(x+a) = V(x)$ where $a = 2\pi R/N$ is the *lattice spacing.* Thus, although the Hamiltonian of the problem does not commute with $R(l)$ for any value of l it has to commute for $l = a$. Thus, the problem does not have a continuous symmetry but a discrete one. Since the

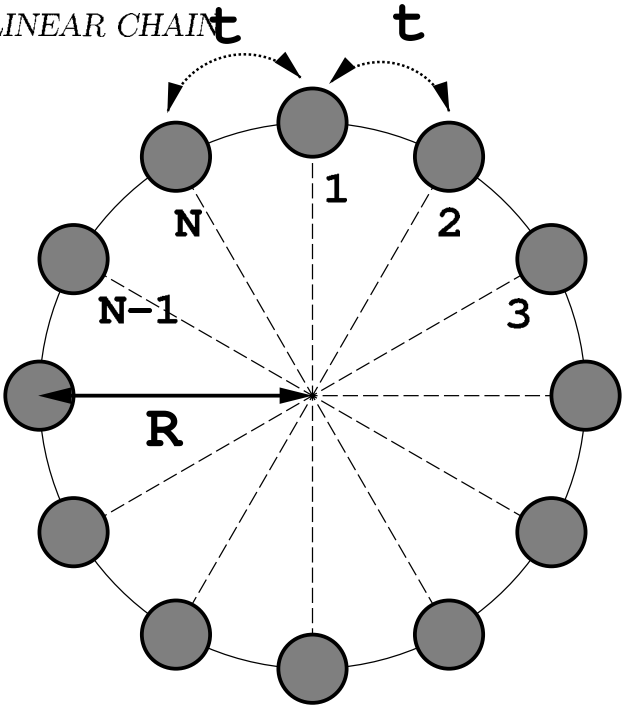

Figure 5.1: *A ring of atoms with radius R and hopping energy t.*

Hamiltonian has to commute with $R(a)$ one knows that H and $R(a)$ share the same eigenvectors. Thus, if we find the eigenvectors of $R(a)$ we will also find the eigenvectors of H. Moreover, because $R(a)$ is written like (5.1) its eigenvalues are related to the eigenvalues of the momentum operator, that is,

$$p|k\rangle = \hbar k|k\rangle \,. \tag{5.3}$$

In this case the eigenvalue problem for $R(a)$ reads

$$R(a)|k\rangle = e^{ika}|k\rangle \,. \tag{5.4}$$

We would like, however, to rewrite the states $|k\rangle$ in terms of the states $|n\rangle$ of the electron localize on atom n. As we used previously this state is essentially a vector with N entries where only the n_{th}

entry is 1 and all the others are zero:

$$|n\rangle \;=\; \begin{pmatrix} 0 \\ 0 \\ 0 \\ \dots \\ 0 \\ 1 \\ 0 \\ \dots \\ 0 \end{pmatrix}. \tag{5.5}$$

We know from basic quantum mechanics that if we have a complete set of orthogonal states any state in the Hilbert space has to be written as a linear combination of these states, in other words, the states $|n\rangle$ span the Hilbert space ($\sum_n |n\rangle\langle n| = 1$)

$$|k\rangle = \sum_n |n\rangle\langle n|k\rangle = \sum_n c_{k,n}|n\rangle \tag{5.6}$$

where $c_{k,n}$ are unknown coefficients. We further know that $R(a)$ has to move the electron one unit in the lattice and therefore

$$\begin{aligned} R(a)|n\rangle &= |n+1\rangle \\ R^{-1}(a)|n\rangle &= |n-1\rangle\,. \end{aligned} \tag{5.7}$$

Applying $R(a)$ to $\psi(k)$ in (5.6) and using the above relation we find

$$R(a)|k\rangle = \sum_n c_{k,n}R(a)|n\rangle = \sum_n c_{k,n}|n+1\rangle = \sum_n c_{k,n-1}|n\rangle\,. \tag{5.8}$$

Using (5.4) together with (5.6) and the fact that the states $|n\rangle$ are orthogonal to each other ($\langle n|m\rangle = \delta_{n,m}$) we see that

$$c_{k,n} = c_{k,n-1}e^{-ika} \tag{5.9}$$

which gives a recursion relation for each $c_{k,n}$ starting from the previous one. Suppose we start from $c_{k,1}$. In this case it is very simple to see that

$$c_{k,n} = c_{k,1}e^{-ikan} \tag{5.10}$$

and thus the expansion (5.6) becomes

$$|k\rangle = c_{k,1} \sum_n e^{-ikan} |n\rangle \tag{5.11}$$

and from the fact that $|k\rangle$ has to be normalized ($\langle k|k\rangle = 1$) we find

$$|c_{k,1}| = \frac{1}{\sqrt{N}} \, . \tag{5.12}$$

We have therefore solved the eigenvalue problem in (5.4).

Because the system has the periodicity generated by $R(a)$ it means that the energy of the system does not change when we translate the system by a, that is, the Hamiltonian commutes with $R(a)$: $[H, R(a)] = 0$. From basic quantum mechanics we know that it implies that the eigenstates of $R(a)$ are also eigenstates of H. This result, however, does not tell us what is the energy of these states. In order to know that we have to use the Hamiltonian itself. Now, let us go back to our original problem of the tunneling of electrons between different atoms. The Hamiltonian can be constructed in exactly the same way as for the case of the other molecules the only difference is that we have a $N \times N$ matrix:

$$H = -t \begin{bmatrix} 0 & 1 & 0 & 0 & ... & 1 \\ 1 & 0 & 1 & 0 & ... & 0 \\ 0 & 1 & 0 & 1 & ... & 0 \\ 0 & 0 & 1 & 0 & ... & 0 \\ 0 & ... & 0 & 1 & 0 & 1 \\ 1 & 0 & ... & 0 & 1 & 0 \end{bmatrix} . \tag{5.13}$$

Observe that if we apply H to a vector like (5.5) we immediately obtain

$$H|n\rangle = -t\left(|n+1\rangle + |n-1\rangle\right) . \tag{5.14}$$

The meaning is rather obvious: the Hamiltonian has only a kinetic term which moves the electron between nearest neighbor sites on the chain.

Since we know that $|k\rangle$ is an eigenstate of the system let us calculate its energy. In order to do that we just have to apply the Hamiltonian the state:

$$
\begin{aligned}
H|k\rangle &= -\frac{t}{\sqrt{N}}\sum_n e^{-ikan}\left(|n+1\rangle + |n-1\rangle\right) \\
&= -\frac{t}{\sqrt{N}}\sum_n \left(e^{-ika(n-1)} + e^{-ika(n+1)}\right)|n\rangle \\
&= -t\left(e^{ika} + e^{-ika}\right)|k\rangle \qquad (5.15)
\end{aligned}
$$

which can be written as

$$H|k\rangle = E_k|k\rangle \qquad (5.16)$$

where

$$E_k = -2t\cos(ka) \qquad (5.17)$$

which gives the spectrum of the problem and is shown as a function of k in Fig.5.2. Observe that the state of lowest energy has $k = 0$ with energy $-2t$. From (5.11) this state is simply given by

$$|k=0\rangle = \frac{1}{\sqrt{N}}\sum_n |n\rangle = \frac{1}{\sqrt{N}}\begin{pmatrix} 1 \\ 1 \\ 1 \\ \ldots \\ 1 \\ 1 \\ 1 \\ \ldots \\ 1 \end{pmatrix} \qquad (5.18)$$

which shows that the probability of finding the electron in any atoms is the same and given by $1/N$, that is, the electron is spread uniformly over the entire chain! That is the way the kinetic energy is maximized.

Observe that we started with N states and therefore we have to end with N states. It means that there are only N allowed values of k! To find out what are these values we have to remember that the ring is periodic and therefore $|n+N\rangle = |n\rangle$. Thus, from (5.10) we must have

$$e^{ikaN} = 1 \qquad (5.19)$$

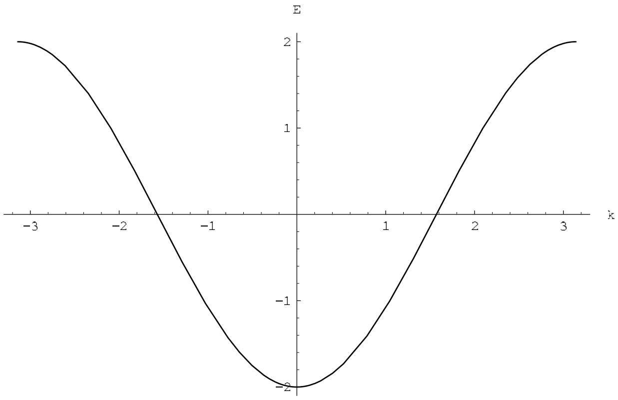

Figure 5.2: *Spectrum for an electron moving on a one-dimensional chain as a function of k.*

which implies that the values of k are quantized and given by

$$k_m = \frac{2\pi m}{Na} \tag{5.20}$$

where $m = 0, \pm 1, ..., \pm(N-1)/2, N/2$ for N even and $m = 0, \pm 1, ..., \pm(N-1)/2$ for N odd produces the required N states. Observe that the available states go from $k = -\pi/a(1-1/N)$ to $k = \pi/a$. In the limit of $N \to \infty$ the "distance" between two states which is just $2\pi/(Na)$ goes to zero and we have $-\pi/a < k \leq \pi/a$ which is called the *Brillouin zone*. Notice that the tunneling between atoms has broken the degeneracy of the original N states into N non-degenerate states for each value of k. Thus if the distance between the atoms is large enough so that $t \to 0$ no tunneling takes place and the electron is stuck in one of the atoms. No motion can occur and the system is an insulator that is highly degenerate. As t increases when we approach the atoms the tunneling grows and the degeneracy is broken as shown in Fig.5.3. The argument here is not only valid for the ground state but for any state of the atom. For instance, we could have electrons coming from other orbitals and going from atom to atom. Thus, each orbital gives rise to what is called a *band* of states which essentially have a dispersion given by (5.17). We also say that each band has a finite *bandwidth*, W, which is the energy difference between the highest and lowest energy state which for (5.17) is just $W = 4t$.

Because the electron is spread over the entire lattice it is very easy to move it around. This is true if the band is not full. This is simple to understand: from the Pauli principle we can only have one electron for each value of k. Suppose we put 1 electron on a lattice of N atoms. The state of lowest energy has $k = 0$ (compare this state with the states we found for the H_2 and the molecule with 3 atoms!). Once this state is occupied we can put another electron on this state but with **opposite** spin. The next state to be occupied is the closest to $k = 0$ since, according to (5.17) (see Fig.5.2) the energy grows with k. Thus, if we put N_e electrons in the system they have to occupy symmetrically the states around $k = 0$. Obviously the band will be full when $N_e = 2N$. In this case there are no more states available! The next state in the system corresponds to an atomic state with larger energy, that is, there is a **gap**, Δ, between bands which in the atomic

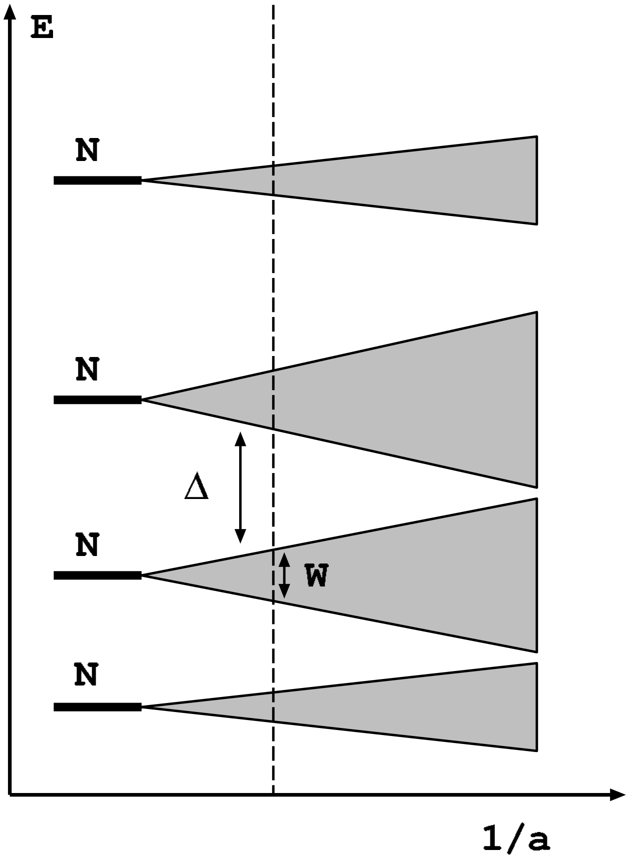

Figure 5.3: *Energy of the system as a function of the distance between atoms.*

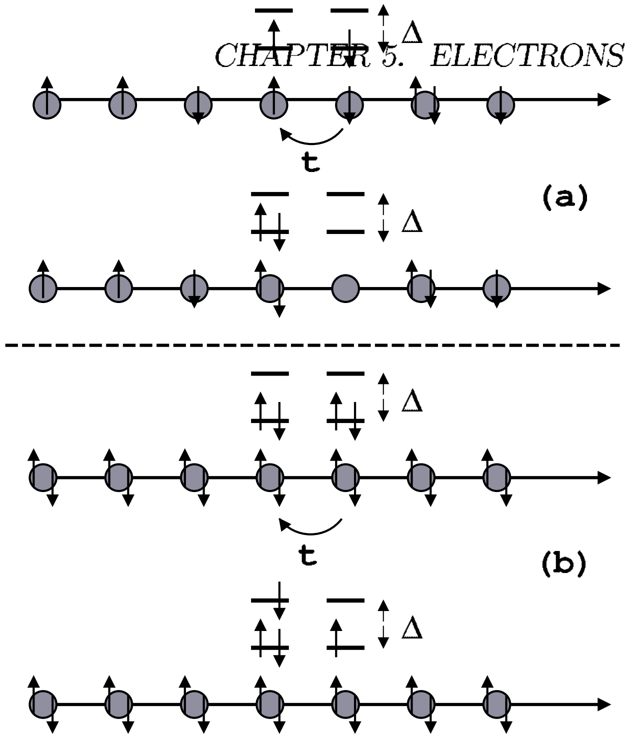

Figure 5.4: *Motion of electron in a periodic array of atoms: (a) band less than filled; (b) filled band.*

picture is just the energy between the discrete states. Thus, in order to make an excitation in the system we have to excite the electron over the gap and this costs energy. Thus, at low temperatures no conduction can happen and the system is a **band insulator**. In real space this is also simple to understand: when $N_e = 2N$ the electrons cannot hop anymore to the same orbital since it is fully occupied (Pauli principle) and therefore it has to hop to another orbital at higher energy, as shown in Fig.5.4.

The scenario that we have been describing here is known as *tight binding* approximation because we assume that the wavefunction on each atom is very close to an atomic wavefunction. This is only true is the tunneling t is small. From Fig. 5.3 one sees that when R decreases the bands can start to overlap and the gap between bands disappear. This implies that the electrons just feel a very weak potential created by the lattice. In this case one can just treat the periodic potential created by the lattice as a perturbation. Let us consider this case in more detail.

In the absence of a periodic potential the electron undergoes free motion in a circle of length L. The Schrödinger equation for this case is simply

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \tag{5.21}$$

which can solved immediately in terms of plane waves:

$$\begin{aligned} \psi_k(x) &= \frac{1}{\sqrt{L}}e^{ikx} \\ E^0_k &= \frac{\hbar^2k^2}{2m}. \end{aligned} \tag{5.22}$$

Observe that the energy is a continuous function of k in complete contrast with the tight binding picture and it is shown on Fig.5.5(a). The question that remains to be answered is what happens when we introduce the periodic potential of the lattice. Observe that because the potential is periodic we have $V(x) = V(x+a)$ and if one expands $V(x)$ in Fourier series

$$V(x) = \sum_k V_k e^{-ikx} \tag{5.23}$$

the condition of periodicity implies that

$$k = \frac{2\pi n}{a} \tag{5.24}$$

where n is an integer. Thus, even without computing the effects of the potential we already know that the momentum is only defined in the Brillouin zone, that is, $-\pi/a < k \leq \pi/a$. Thus, one has to shift the portions of the energy E_k inside of the Brillouin zone as shown in Fig.5.5(b). This is the effect of the pure periodicity of the problem even if $V(x) \to 0$!

When $V(x)$ is finite but small we have to take into account the effect of the potential in the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi_E(x) = E\psi_E(x)\,. \tag{5.25}$$

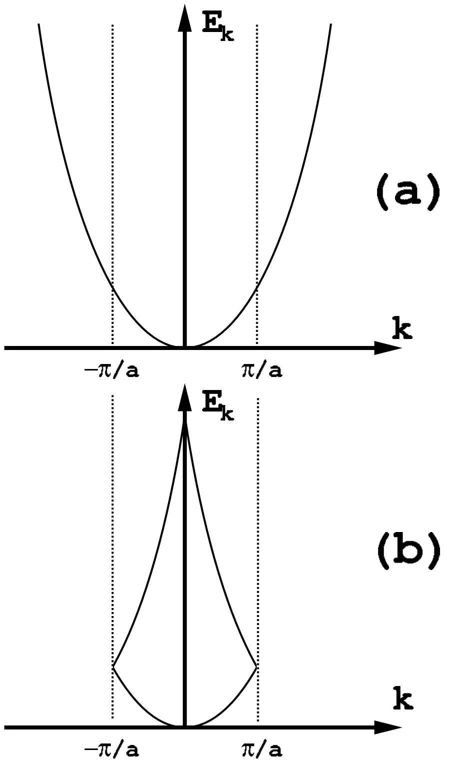

Figure 5.5: *Electron dispersion: (a) in the absence of a periodic potential; (b) in the presence of a periodic potential.*

Let us treat the problem in perturbation theory. Since we know that the problem when $V(x) = 0$ is solved in terms of plane waves we look for a problem of (5.25) which is a linear combination of plane waves

$$\psi_E(x) = \frac{1}{\sqrt{L}} \sum_k c_{k,E} e^{ikx} \tag{5.26}$$

where we would like to know the values of $c_{k,E}$. Because of the periodic boundary conditions, that is, $\psi_E(x+L) = \psi_E(x)$ one has

$$k = \frac{2\pi n}{L} \tag{5.27}$$

where $n = 0, \pm 1, ..., N/2$. We have now to normalize the wavefunction over all space

$$\int_{-L/2}^{L/2} dx |\psi(x)|^2 = 1 \tag{5.28}$$

which can be written as

$$\frac{1}{L} \sum_{k,p} c^*_{k,E} c_{p,E} \int_{-L/2}^{L/2} dx e^{i(k-p)x} = 1\,. \tag{5.29}$$

In order to perform the integral one has to remember that k and p are given by (5.27) which implies that the above integral has the form:

$$\int_{-L/2}^{L/2} dx e^{i(p-k)x} = 2\frac{\sin(p-k)L/2}{(p-x)} = \frac{L}{\pi} \frac{\sin(n-m)\pi}{n-m}\,. \tag{5.30}$$

Observe that the above integral is zero unless $n = m$ (that is, $p = k$) in which case we write

$$\int_{-L/2}^{L/2} dx e^{i(p-k)x} = L\delta_{p,k} \tag{5.31}$$

where $\delta_{p,k}$ is the so-called Kronecker delta which has the properties that $\delta_{p,k} = 1$ if $p = k$ and $\delta p, k = 0$ if $p \neq k$. Thus we conclude that

$$\sum_k |c_{k,E}|^2 = 1 \tag{5.32}$$

gives the normalization of the wavefunction.

If we substitute (5.26) into (5.25) one finds

$$\sum_k \frac{\hbar^2 k^2}{2m} c_{k,E} e^{ikx} + \sum_{k,p} V_k e^{-ikx} c_{p,E} e^{ipx} = \sum_k E c_{k,E} e^{ikx} \tag{5.33}$$

in order to solve this equation we multiply the equation above by e^{-ipx} and integrate over x. We are going to use the following useful integral (5.31) to obtain

$$(E - E^0_p) c_{p,E} = \sum_{p'} V_{p-p'} c_{p',E} \tag{5.34}$$

where

$$V_{k-p} = \frac{1}{L} \int_{-L/2}^{L/2} dx V(x) e^{i(k-p)x} . \tag{5.35}$$

Observe that (5.34) is a matrix equation where $V_{k,p}$ are the matrix elements of the potential and the collection of $c_{k,E}$ for fixed E form a vector. In order to see that let us remember that because of the boundary conditions $k_n = 2\pi n/L$ with $n = 0, \pm 1, ..., N/2$ there are N allowed values of k. Thus, let us number k_m with $m = 1, ..., N$. We will use m to number the eigenstate (which is equivalent to use k in the Brillouin zone). That is, we can rewrite (5.34) as

$$\begin{bmatrix} E - E_{k_1} & 0 & ... & 0 \\ 0 & E - E_{k_2} & ... & 0 \\ ... & ... & ... & ... \\ 0 & ... & E - E_{k_{N-1}} & 0 \\ 0 & ... & 0 & E - E_{k_N} \end{bmatrix} \begin{pmatrix} c_{k_1,E} \\ c_{k_2,E} \\ ... \\ c_{k_{N-1},E} \\ c_{k_N,E} \end{pmatrix}$$

$$= \begin{bmatrix} V_{1,1} & V_{1,2} & ... & V_{1,N} \\ V_{2,1} & V_{2,2} & ... & V_{2,N} \\ ... & ... & ... & ... \\ V_{N-1,1} & ... & V_{N-1,N-1} & V_{N-1,N} \\ V_{N,1} & ... & V_{N,N-1} & V_{N,N} \end{bmatrix} \begin{pmatrix} c_{k_1,E} \\ c_{k_2,E} \\ ... \\ c_{k_{N-1},E} \\ c_{k_N,E} \end{pmatrix} \tag{5.36}$$

which is a $N \times N$ diagonalization problem exactly like in the tight binding problem we solved earlier.

We do not wish at this point to solve (5.34) in its full form but for small values of V, that is, we would like to solve the problem as a power series expansion of the potential. Observe that for $V = 0$ the solution is straightforward, namely, for a given ith eigenvalue we have: if $E = E_{k_i}$ then $c_{k_i,E} = 1$; if $E \neq E_{k_i}$ we have $c_{k_i,E} = 0$. Another way to rewrite this result is to *define* a wave number k such that:

$$E = \frac{\hbar^2 k^2}{2m} \tag{5.37}$$

and rewrite (5.34) as

$$\frac{\hbar^2}{2m}(k^2 - p^2)c_{p,k} = \sum_{p'} V_{p-p'} c_{p',k} \tag{5.38}$$

and therefore the solution for $V = 0$ is: if $p = k$ we have $c_{k,k} = 1$ and if $p \neq k$ $c_{p,k} = 0$. The result can be summarized as

$$c^0_{p,k} = \delta_{p,k} \, . \tag{5.39}$$

The next order correction is obtained if we assume $E = E^0_k + E^{(1)}_k$ and $c_{p,k} = c^0_{p,k} + c^{(1)}_{p,k}$ with $E^{(1)}_k$ and $c^{(1)}_{p,k}$ given in first order in V and substitute on (5.38):

$$\begin{aligned} \left(\frac{\hbar^2}{2m}(k^2 - p^2) + E^{(1)}_k\right)(\delta_{p,k} + c^{(1)}_{p,k}) &= \sum_{p'} V_{p-p'}(\delta_{p',k} + c^{(1)}_{p',k}) \\ E^{(1)}_k \delta_{p,k} + \frac{\hbar^2}{2m}(k^2 - p^2)c^{(1)}_{p,k} &= V_{p-k} \end{aligned} \tag{5.40}$$

where we have kept only terms to first order in V. The solution of this equation is straightforward again: if $k = p$ we find

$$E^{(1)}_k = V_0 \tag{5.41}$$

and if $k \neq p$ we find

$$c^{(1)}_{p,k} = \frac{V_{p-k}}{\frac{\hbar^2}{2m}(k^2 - p^2)} \tag{5.42}$$

which is the first order correction. Notice that $c^{(1)}_{k,k} = 0$! Observe that

$$V_{k-k=0} = \frac{1}{L}\int_{-L/2}^{L/2} dx V(x) = \bar{V} \tag{5.43}$$

is just the mean value of the potential in the system. Thus, we conclude that first correction to the energy is a simple shift in the overall energy of the system. We observe that the wavefunction of the problem at this order in perturbation theory can be written as

$$\psi_k(x) \approx \frac{1}{\sqrt{L}}\left(e^{ikx} + \sum_{p\neq k}\frac{V_{k,p}}{E^0_p - E^0_k}e^{ipx}\right) . \tag{5.44}$$

The normalization condition (5.32) is obeyed to order in V^2.

The second order correction proceeds in the same way, that is, we write $E = E^0_k + E^{(1)}_k + E^{(2)}_k$ and $c_{k,p} = c^0_{k,p} + c^{(1)}_{k,p} + c^{(2)}_{k,p}$ and substitute on (5.38). The first order terms cancel because of (5.40) and the second order equation becomes

$$E^{(2)}_k \delta_{p,k} + E^{(1)}_k c^{(1)}_{p,k} + \frac{\hbar^2}{2m}(k^2 - p^2)c^{(2)}_{p,k} = \sum_{p'} V_{p-p'} c^{(1)}_{p',k} \tag{5.45}$$

which has the solution: if $k = p$ we find

$$E^{(2)}_k = \sum_{p'} V_{k-p'} c^{(1)}_{p',k} = \sum_{p'} \frac{|V_{p'-k}|^2}{\frac{\hbar^2}{2m}(k^2 - (p')^2)} \tag{5.46}$$

where we used (5.42) and the fact that $V_p = V^*_{-p}$. If $k \neq p$ then, from (5.45) we have

$$c^{(2)}_{p,k} = \sum_{p'} \frac{V_{p-p'}V_{p'-k}}{\frac{\hbar^2}{2m}(k^2 - (p')^2)} - \frac{V_0 V_{p-k}}{\frac{\hbar^2}{2m}(k^2 - p^2)} \tag{5.47}$$

which proportional to V^2. In order to calculate the change in the energy we have to calculate the matrix element $V_{k,p}$. From (5.35) and (5.23) one has

$$\begin{aligned} V_{k,p} &= \frac{1}{L}\sum_n V_n \int_{-L/2}^{L/2} dx e^{i(k-p)x} e^{i2\pi nx/a} \\ &= \sum_n V_n \delta_{k,p+2\pi n/a} \end{aligned} \tag{5.48}$$

Thus,

$$E_k^{(2)} = \sum_{n\neq 0} \frac{|V_n|^2}{E_k^0 - E_{k-2\pi n/a}^0}\,. \tag{5.49}$$

Observe that if $k = \pm\pi n/a$ the denominator in the above equation vanishes and perturbation theory fails! Thus, for this particular points something else has to happen and one cannot use non-degenerate perturbation theory. For the other values of k the result (5.49) is fine since no divergences occur.

Thus, let us go back to the original equation (5.34) and try to understand what is going on. For simplicity we are going to assume that $V(x) = V_0\cos(2\pi x/a)$. This implies that we have $V_0 = 0$ and $V_1 = V_{-1} = U_0/2$. Substituting (5.48) into (5.34) one finds

$$(E_k^0 - E)c_{k,E} + \sum_n V_n c_{k-2\pi n/a,E} = 0\,. \tag{5.50}$$

But because of our choice of $V(x)$ this equation simplifies to

$$\left(\frac{\hbar k^2}{2m} - E\right) c_{k,E} + \frac{U_0}{2}\left(c_{k+2\pi/a,E} + c_{k-2\pi/a,E}\right) = 0 \tag{5.51}$$

which again is an infinite matrix problem. The first three terms read

$$\begin{aligned}
\left(\frac{\hbar(k+2\pi/a)^2}{2m} - E\right) c_{k+2\pi/a,E} + \frac{U_0}{2}\left(c_{k+4\pi/a,E} + c_{k,E}\right) &= 0\\
\left(\frac{\hbar k^2}{2m} - E\right) c_{k,E} + \frac{U_0}{2}\left(c_{k+2\pi/a,E} + c_{k-2\pi/a,E}\right) &= 0\\
\left(\frac{\hbar(k-2\pi/a)^2}{2m} - E\right) c_{k-2\pi/a,E} + \frac{U_0}{2}\left(c_{k-4\pi/a,E} + c_{k,E}\right) &= 0
\end{aligned} \tag{5.52}$$

What do we do now? Well our perturbation theory failed for $k = \pi/(2a)$. Thus we will retain in this matrix problem only the values of k and $k - 2\pi/a$ and forget about all the other Fourier components. In this case the problem reduces to

$$\begin{bmatrix} \frac{\hbar k^2}{2m} - E_k & U_0/2 \\ U_0/2 & \frac{\hbar(k-2\pi/a)^2}{2m} - E_k \end{bmatrix} \begin{pmatrix} c_{k,E} \\ c_{k-2\pi/a,E} \end{pmatrix} = 0\,. \tag{5.53}$$

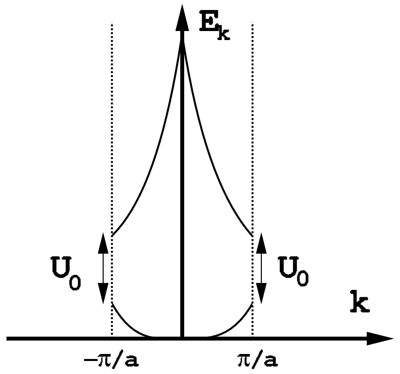

Figure 5.6: *Effect of a periodic potential on a free electron system.*

which can be solved at once

$$E_{k,\pm} = \frac{1}{2}\left\{\left(\frac{\hbar(k-2\pi/a)^2}{2m} + \frac{\hbar k^2}{2m}\right) \pm \sqrt{\left(\frac{\hbar(k-2\pi/a)^2}{2m} - \frac{\hbar k^2}{2m}\right)^2 + U_0^2}\right\} \tag{5.54}$$

Observe that exactly at $k = \pi/a$ we have

$$E_{\pi/a,\pm} = \pm|U_0|/2 \tag{5.55}$$

that is, there is a *gap* in the spectrum with magnitude

$$\Delta_{\pi/a} = E_{\pi/a,+} - E_{\pi/a,-} = |U_0| \tag{5.56}$$

which implies that the two branches in Fig.5.5(b) are now split and there is a gap between them as shown in Fig.5.6.

Moreover, by direct substitution of (5.55) into the matrix equation (5.53) we find

$$\begin{aligned} c_{k,+} &= c_{k-\pi/a,+} \\ c_{k,-} &= -c_{k-\pi/a,-} \end{aligned} \tag{5.57}$$

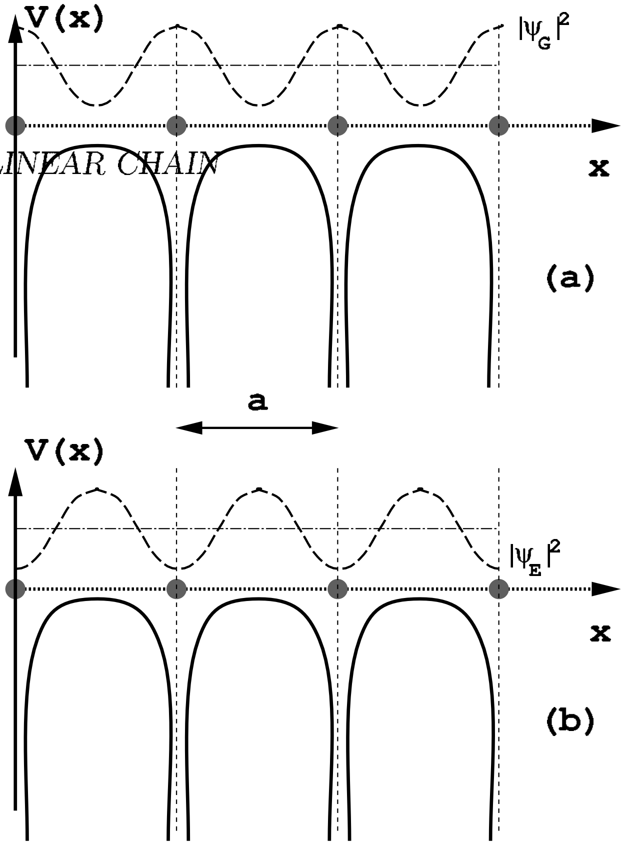

Figure 5.7: *Wavefunctions for an electron in a periodic potential of the ions: (a) ground state; (b) first excited state.*

which implies from (5.26) that

$$\begin{aligned} \psi_{+,k}(x) &\propto \cos(\pi x/a) \\ \psi_{-,k}(x) &\propto \sin(\pi x/a) \end{aligned} \tag{5.58}$$

which have a very simple meaning if we consider a plot of the potential felt by the atoms and the shape of these function as in Fig.5.7. The ground state wavefunction $\psi_G = \psi_-$ has its maximum at the position of the ions while the next excited state $\psi_E = \psi_+$ has its maximum in between the ions. Since the charge of the electron is opposite to the ions the energy is minimized when the electrons have most of the charge on the top of the positive ions as in Fig.5.7(a).

Thus, the appearance of gaps in the spectrum of a free electron system are related to the breaking of the translational symmetry of the system (which now has only discrete translational symmetry). It does not matter from what limit we start, that is, electrons localized on atoms or free electrons. When the *hybridization* between atoms

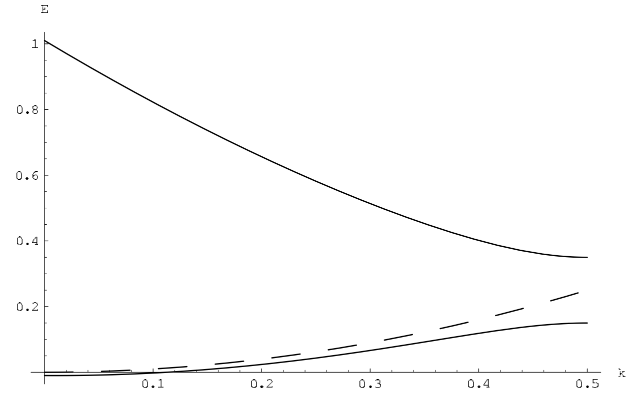

Figure 5.8: *Solution of the problem close to $k = G/2$ and comparison with the free electron result (dashed line).*

is small the system behaves more like isolated atoms and the bands reflect the quantum nature of the atomic states. As the hybridization grows the system behaves more like a free electron gas. Observe that the electron plays a dual role in this dance: it binds atoms together and also gives rise to charge conduction. Depending on the type of system and on the type of orbital that participates on the formation of a solid the properties of the solid can change dramatically as one sees from the simples arguments we have given. In Fig.5.8 we show how the free electron solution compares with the solution close to the Brillouin zone boundary $k = G/2 = \pi/a$. We see that the free electron solution works very well close to the bottom of the band but fails to describe the system at the Brillouin zone boundary.

5.3 $D > 1$

In higher dimensions the situation is very similar to the one dimensional case and we still have to solve the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{5.59}$$

where due to the symmetry we have $V(\mathbf{r}) = V(\mathbf{r}+\mathbf{T})$ where $\mathbf{T} = \sum_{i=1}^{d} n_i \mathbf{a}_i$ is a lattice vector. Because of this symmetry we can write

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \tag{5.60}$$

where $\mathbf{G}$ is a reciprocal lattice vector (notice that $\mathbf{T}\cdot\mathbf{G} = 2\pi n$ which is the Bragg law). The general solution of (5.59) can be written as

$$\psi_E(\mathbf{r}) = \sum_{\mathbf{k}} \psi_{\mathbf{k},E} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{5.61}$$

where the Fourier components obey the equation (by direct substitution of (5.60) and (5.61) into (5.59))

$$\left(\frac{\hbar k^2}{2m} - E\right)\psi_{\mathbf{k},E} + \sum_{\mathbf{G}} V_{\mathbf{G}}\psi_{\mathbf{k}-\mathbf{G},E} = 0 \tag{5.62}$$

which is the higher dimensional analogue of (5.34).

Let us consider now the general properties of (5.62). (5.62) can be thought (as in the case of (5.36)) as a matrix equation for the coefficients $\psi_{\mathbf{k}-\mathbf{G},E}$. For a given eigenvalue E the coefficients $\psi_{\mathbf{k},E}$ have to be linear combinations of other coefficients at wavevectors shifted by $\mathbf{G}$. Thus, if we define again $E = \hbar^2k^2/(2m)$ then we must have accordingly to (5.61):

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \psi_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}}\,. \tag{5.63}$$

We can rewrite this wavefunction in a more interesting way,

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \tag{5.64}$$

where

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \psi_{\mathbf{k}-\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \, . \tag{5.65}$$

Observe that $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{T})$ is a periodic function. Thus, we have shown that in a periodic lattice the wavefunction can be written in a very special form which is *extended* over the whole lattice. This is called *Bloch's theorem*. The result of this demonstration is that the wavefunction can be defined in the Brillouin zone of the material since we can reach any $\mathbf{k}$ outside of the zone by translating by a reciprocal lattice vector, that is, $\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r})$. Moreover, the energy is also a periodic function of the reciprocal lattice since we can always shift the momentum in (5.62) by a reciprocal lattice vector, $E_{\mathbf{k}} = E_{\mathbf{k}+\mathbf{G}}$. This result is completely general and does not depend on the particular form of the potential!

In the limit where the potential is weak, as we have seen previously, we can try perturbation theory. As before we will find that the perturbation theory fails at $k = \pm\mathbf{G}/2$ which is the border of the Brillouin zone. This failure is again related with the opening of a gap in the spectrum due to the Bragg scattering, that is, the energy of the system is only slightly modified in for most wave-vector except when $\epsilon^0_k = \epsilon^0_{\mathbf{k}-\mathbf{G}}$ where perturbation theory gives a divergent contribution. The origin of this divergence can be understood immediately since the condition for the divergence is equivalent to

$$|\mathbf{k}| = |\mathbf{k}-\mathbf{G}| \tag{5.66}$$

which is the Bragg law (see (2.38)). This result makes a lot of sense since electrons are as good waves as any other microscopic particles. Thus when the electron wave-vector is such that the Bragg law (5.66) is obeyed the electron undergoes coherent Bragg diffraction. Observe that this condition is equivalent to say that $\mathbf{k}$ has to lie on the zone boundary in order to undergo Bragg diffraction and this is the point where perturbation theory fails and one has to use the matrix approach described earlier. In this case we obtain the formation of a gap at these points, that is, the gap is a straight consequence of Bragg diffraction. Consider for instance the one dimensional case studied before. Condition (5.66)

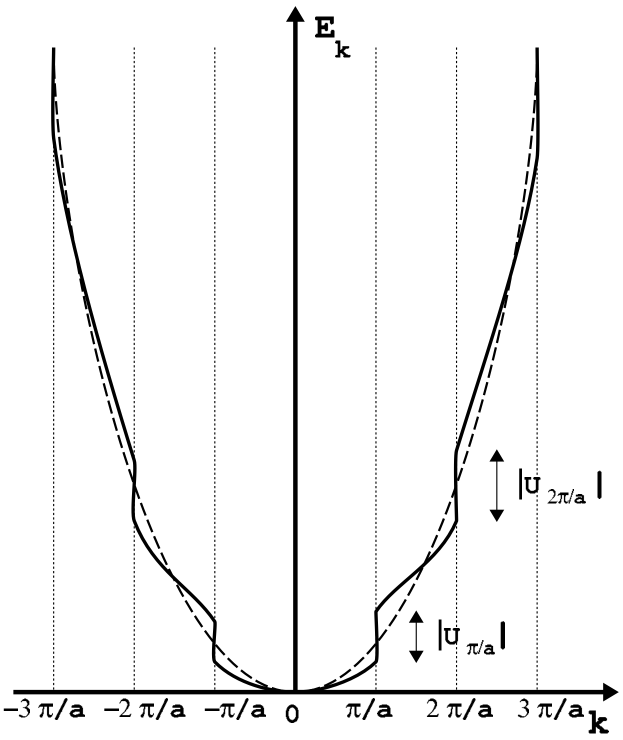

Figure 5.9: *Modification of the free electron dispersion (dashed line) due to the Bragg reflection of the electrons.*

implies that perturbation theory fails for $k = \pm G/2 = \pm n\pi/a$ and one has a sudden jump in the energy at this point. A graphical way to depict this situation is shown in Fig.5.9 where we see that the only substantial difference between the free electron case and the actual case occurs whenever a gap opens at the Bragg points. In order to obtain the bands discussed in previous approach one has just to *fold back* the points back to the Brillouin zone as in Fig.5.8.

This construction can be carried out to higher dimensions where the points where gaps open are still given by the Bragg condition (5.66). Consider for instance the problem of a two dimensional square lattice such as in Fig.5.10. As the momentum varies as shown in Fig.5.10(a) the gaps open as in Fig.5.10(b).

At this point one natural question comes out: how are these results related with the tight binding calculation we have done previously? The answer to that is very straightforward. In the tight binding limit the electrons are tightly bounded to the atoms and therefore the po-

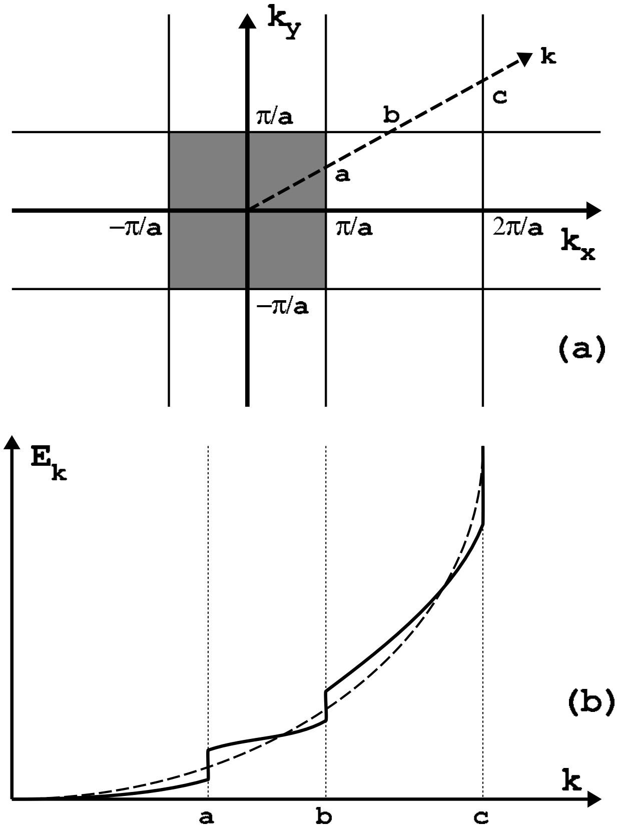

Figure 5.10: *(a) Brillouin zone in k-space (shaded area) and neighboring zones; (b) Electron dispersion along the direction of* **k**.

tential is strong. However, accordingly to Bloch's theorem, (5.64), we should be able to solve the problem in terms of periodic functions. The wavefunction of the problem has to obey Block's theorem which is a statement of the periodicity of the system, nothing more. Observe that from (5.64) and (5.65) the wavefunction of the problem must obey

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi_{\mathbf{k}}(\mathbf{r})\,. \tag{5.67}$$

We would like to construct the wavefunction from localized orbitals instead of the plane waves which are so natural for the weak potential problem. These localized orbitals are the solution of the atomic Schrödinger equation:

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V_A(r)\right)\psi_A(\mathbf{r}) = E_A\psi_A(\mathbf{r}) \tag{5.68}$$

where $V_A(r)$ is the atomic potential and E_A the binding energy of the electron. Let us consider the problem where the atoms are far apart so the tunneling is small. We would like to construct the wavefunction from localized orbitals like the ones given in (5.68) which has this property. Remember that in the case of molecules this can be done by taking linear combinations of localized orbitals (which we called bonding and anti-bonding). A similar idea here is to choose the linear combination

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}}\psi_A(\mathbf{r}-\mathbf{T})\,. \tag{5.69}$$

Observe that this wavefunction obeys (5.67) Moreover, in this approximation each band carries the atomic numbers, that is, for each atomic level we have a band with its quantum numbers.

Observe that (5.69) is a solution of the atomic equation (5.68) but instead we would like to solve the actual Schrödinger equation (5.59). It is clear that this is *not* the actual ground state of the problem. However, in the limit of infinite separation between the atoms it is an eigenstate. Moreover, the spectrum of the problem can be written from (5.59) by using the orthogonality of the wavefunctions as

$$E_{\mathbf{k}} = \int d^dr\ \psi^*_{\mathbf{k}}(\mathbf{r})\left[-\frac{\hbar^2\nabla^2}{2m} + V(r)\right]\psi_{\mathbf{k}}(\mathbf{r}) \tag{5.70}$$

which, as we said before, is periodic on the reciprocal lattice, that is, $E_{\mathbf{k}+\mathbf{G}} = E_{\mathbf{k}}$. Since the energy is periodic on the reciprocal lattice it can be always expand as a Fourier series of the *direct lattice* (remember that the direct lattice is the reciprocal of the reciprocal lattice!) that is,

$$E_{\mathbf{k}} = \sum_{\mathbf{T}} t_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} . \tag{5.71}$$

In order to calculate the coefficients $t_{\mathbf{T}}$ we are going to use (5.70). If we substitute (5.69) into (5.70) we find

$$\begin{aligned} E_{\mathbf{k}} &= \sum_{\mathbf{T},\mathbf{T}'} \frac{e^{i\mathbf{k}\cdot(\mathbf{T}-\mathbf{T}')}}{N} \int d^d r \; \psi_A^*(\mathbf{r}-\mathbf{T}') \left[-\frac{\hbar^2\nabla^2}{2m} + V(r)\right] \psi_A(\mathbf{r}-\mathbf{T}) \\ &= \sum_{\mathbf{T},\mathbf{T}'} \frac{e^{i\mathbf{k}\cdot(\mathbf{T}-\mathbf{T}')}}{N} \int d^d r \; \psi_A^*(\mathbf{r}+\mathbf{T}-\mathbf{T}') \left[-\frac{\hbar^2\nabla^2}{2m} + V(r)\right] \psi_A(\mathbf{r}) \\ &= \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \int d^d r \; \psi_A^*(\mathbf{r}+\mathbf{T}) \left[-\frac{\hbar^2\nabla^2}{2m} + V(r)\right] \psi_A(\mathbf{r}) \end{aligned} \tag{5.72}$$

where we have used the periodicity of the potential $U(\mathbf{r}+\mathbf{T}) = U(\mathbf{r})$. Thus we have shown that (5.71) is correct and that

$$t_{\mathbf{T}} = \int d^d r \; \psi_A^*(\mathbf{r}+\mathbf{T}) \left[-\frac{\hbar^2\nabla^2}{2m} + V(r)\right] \psi_A(\mathbf{r}) \tag{5.73}$$

where the integral runs through the unit cell. We now rewrite $V(r) = V_A(r) + \delta V(r)$ where $\delta V(r) = V(r) - V_A(r)$. In the limit where the distance of the atoms is very large we expect $\delta U \to 0$ and therefore can be treated as a perturbation. In this case, using (5.68) one gets

$$t_{\mathbf{T}} = E_A \int d^d r \; \psi_A^*(\mathbf{r}+\mathbf{T})\psi_A(\mathbf{r}) + \int d^d r \; \psi_A^*(\mathbf{r}+\mathbf{T})\delta V(r)\psi_A(\mathbf{r}) . \tag{5.74}$$

Observe now that the atomic wavefunction decays exponentially with distance ($\psi_A(r) \propto e^{-r/a_o}$ where a_0 is the Bohr radius) and therefore the *overlap integrals* above will be very small for $\mathbf{T} \neq 0$. In this case it is a good approximation to use the *on-site* ($\mathbf{T} = 0$) and *nearest neighbor* contributions since the integrals will decay exponentially with distance. This is known as the *tight binding approximation.* In this approximation we write

$$t_{\mathbf{T}} \approx E_A \delta_{\mathbf{T},0} - t_A \sum_{\vec{\delta}} \delta_{\mathbf{T},\vec{\delta}} \tag{5.75}$$

where $\vec{\delta}$ represent the nearest neighbors sites and t_A is the overlap given in (5.74) for nearest neighbors. Substitution of the above expression into (5.71) leads to

$$E_{\mathbf{k}} \approx E_A - t_A \sum_{\vec{\delta}} e^{i\mathbf{k}\cdot\vec{\delta}}. \tag{5.76}$$

Observe that corrections to the tight binding approximation can be computed directly from (5.73).

As an example consider the one-dimensional case. In this case we have just two nearest neighbors which correspond to $\delta = \pm a$ where a is the lattice spacing. In this case the energy becomes,

$$E_k = E_A - 2t_A \cos(ka) \tag{5.77}$$

and has the shape shown in Fig.5.2. For a cubic system in d dimensions the tight binding model predicts a dispersion

$$E_{\mathbf{k}} = E_A - 2t_A \sum_{i=1}^{d} \cos(k_i a) \tag{5.78}$$

which has its minimum value at $E_A - 2dt_A$ and its maximum at $E_A + 2dt_A$. Thus, we say that the system has a *bandwidth* $W = 4dt_A$. In the atomic limit $t_A \to 0$ and the bandwidth vanishes while as the tunneling between atoms increases the bandwidth increases proportionally to the hopping t_A as in Fig.5.3. Observe that gaps that we have computed in the free electron gas just represent the difference in energy between the atomic levels that decreases as the tunneling between atoms increases. When the energy levels start to overlap we are back to the nearly free electron gas.

Notice that at long wavelengths $ka << 1$ we can approximate the problem by expanding the exponential in (5.76) to second order in ka,

$$E_{\mathbf{k}} \approx E_A - Zt_A + \frac{t_A}{2} \sum_{\vec{\delta}} (\mathbf{k} \cdot \vec{\delta})^2 \tag{5.79}$$

where Z is the number of nearest neighbor sites ($Z = 2d$ for a cubic system) and we have used that $\sum_{\vec{\delta}} \mathbf{k} \cdot \vec{\delta} = 0$ by inversion symmetry. We can now use that

$$\vec{\delta} = \sum_{i=1}^{d} a\mathbf{n}_i \tag{5.80}$$

where a is the lattice spacing and $\mathbf{n}_i$ is the unit vector along the main crystal axis. In this case we rewrite (5.79) as

$$E_{\mathbf{k}} \approx E_A - Zt_A + \sum_{i=1}^{d} \frac{\hbar^2 k_i^2}{2m_A^*} \tag{5.81}$$

which has the form of a free electron dispersion where

$$m_A^* = \frac{\hbar^2}{2t_A a^2} \tag{5.82}$$

is the so-called *effective mass* of the electrons. Observe that this mass can be very different from the free electron mass since its physical meaning is completely different of that one. The effective mass measures the *static dragging* of the lattice by the electron motion since the electron interacts with the atomic cores. This can be easily understood if we take a *semi-classical* approach. As we have seen the electrons are described by a dispersion $\epsilon_{\mathbf{k}}$. From this dispersion we can define the velocity by

$$\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar} \nabla \epsilon_{\mathbf{k}} \tag{5.83}$$

which can be checked to be correct for the free electron case where $\epsilon_{\mathbf{k}} = \hbar^2 k^2/(2m)$ and $\mathbf{v}_{\mathbf{k}} = \hbar\mathbf{k}/m$. Suppose an electrical field $\mathbf{E}$ is applied to the system. This electric field will cause the electrons to accelerate. It turns out that the electrons deep inside the Fermi sea cannot accelerate since they would have to make transitions to already occupied states. This is forbidden by Pauli's principle. The electrons at the Fermi surface, however, can be accelerated freely. If we imagine this electrons to behave like wavepackets (that is, like classical particles) then the acceleration is given by

$$\frac{d\mathbf{v}_{\mathbf{k}}}{dt} = \frac{1}{\hbar} \frac{d}{dt} \sum_{i=1}^{d} \frac{\partial \epsilon_{\mathbf{k}}}{\partial k_i} \mathbf{n}_i$$

$$= \frac{1}{\hbar} \sum_{i,j=1}^{d} \frac{\partial^2 \epsilon_{\mathbf{k}}}{\partial k_j \partial k_j} \frac{dk_j}{dt} \mathbf{n}_i \tag{5.84}$$

which is valid for $\mathbf{k} \approx \mathbf{k}_F$ and where we used the chain rule and $\mathbf{n}_i$ is the unit vector in the i-direction. Observe that the momentum of the electron is simply $\hbar\mathbf{k}$ and therefore by Newton's equation of motion in an external field we have

$$\hbar \frac{d\mathbf{k}}{dt} = e\mathbf{E} \tag{5.85}$$

which substituted in (5.84) leads to

$$\frac{d\mathbf{v}_{\mathbf{k}}}{dt} = \frac{e}{\hbar^2} \sum_{i,j=1}^{d} \frac{\partial^2 \epsilon_{\mathbf{k}}}{\partial k_j \partial k_j} E_j \mathbf{n}_i \,. \tag{5.86}$$

Observe that (5.84) is very similar to the classical equation

$$\frac{d\mathbf{v}}{dt} = \frac{e\mathbf{E}}{m} \,. \tag{5.87}$$

This similarity allows us to define the *effective mass tensor*

$$m_{ij}^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon_{\mathbf{k}}}{\partial k_j \partial k_j} \,. \tag{5.88}$$

Observe that for a cubic system with dispersion given by (5.78) in the limit where $k_F a << 1$ we obtain (5.82) as expected.

In this picture the difference between metals and band insulators is very simple to understand. At band fillings smaller than one there is *in average* less than two electron per site as in Fig.5.4(a). Thus the electrons can move freely since electrons with opposite spin can hop from site to site. When the band becomes full (that is we have two electrons per site) the Pauli principle does not allow motion as shown in Fig.5.4(b). In order to move an electron one has to excite the electron to an unfilled atomic state and therefore one has to pay an energy price which is the gap energy.

5.4 Problems

1. Prove eq.(5.62).

2. Show that (5.69) obeys (5.67).

3. Show that a band insulator always has an *even* number of electrons per atom. Also argue that the opposite is not true, that is, solids with an even number of electrons per atom can be metallic.

4. In the free electron gas the mass of the electron is just m. In the tight binding case the mass of the electron is defined as

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2 E_k}{dk^2}\,.$$

   (1) What is the mass of the electron as a function of the momentum? Why is this mass different from m? (2) What is the mass of the electron when the band is empty? What happens to this mass when the tunneling between atoms goes to zero? Give a physical interpretation for your result.

5. In these notes we have used the so-called *reduced zone scheme* in which the momentum is plotted only in the first Brillouin zone $-\pi/a < k \leq \pi/a$. Another possible scheme is to plot the energy-momentum relation over all momentum space in which case we do not fold the energy in the Brillouin zone. Starting from the free electron problem (parabolic band) make a qualitative plot of the energy of a particle in a periodic potential as a function of k from $-4\pi/a$ to $4\pi/a$. What are the positions of the gaps in momentum space? What are the values of the gaps in terms of the Fourier components of the periodic potential? *Hint: no calculations needed.*

6. Solve exactly the matrix problem in (1.52) for the case where $c_{k\pm 4pi/a,E} = 0$. Make a plot of the energy bands you get from the solution. What is the value of the gaps in the spectrum?

7. Show that for a cubic system we have:

$$m_{ij}^{-1} = \frac{\cos(k_i a)}{m^*}\delta_{i,j}\,.$$

Chapter 6

The Free Electron Gas

6.1 Introduction

In the last chapter we have seen that the main difference between metals and band insulators is that in insulators the bands are full and therefore the electron has to pay an energy equal to the gap in order to be excited from one band to another. Thus in a metal an electric field can excite electrons from one momentum state to another with almost no energy cost while in an insulator this is not possible because of the gap. In this chapter we are going to discuss the physics of metals based on the picture of the last section, that is, the picture that the electrons do not interact among each other but only fill energy states accordingly to the Pauli principle. This is called the electron gas approximation.

The Pauli principle asserts that the ground state of the problem is obtained filling up all the states with lowest energy. We observe that the properties of the system depend strongly on the way we fill up the bands, that is, the so called *filling factor*. Suppose we assume periodic boundary conditions. The allowed vectors k are

$$k_i = \frac{2\pi n_i}{N_i a} \tag{6.1}$$

where $i = x, y, z$ where we have written the size $L_i = N_i a$. Observe that maximum allowed value of n_i is $N_i/2$ since at this point we reach the boundary of the Brillouin zone, $G_i/2 = \pi/a$. Thus, the number of states available is $N = N_x N_y N_z$ which is the number of primitive

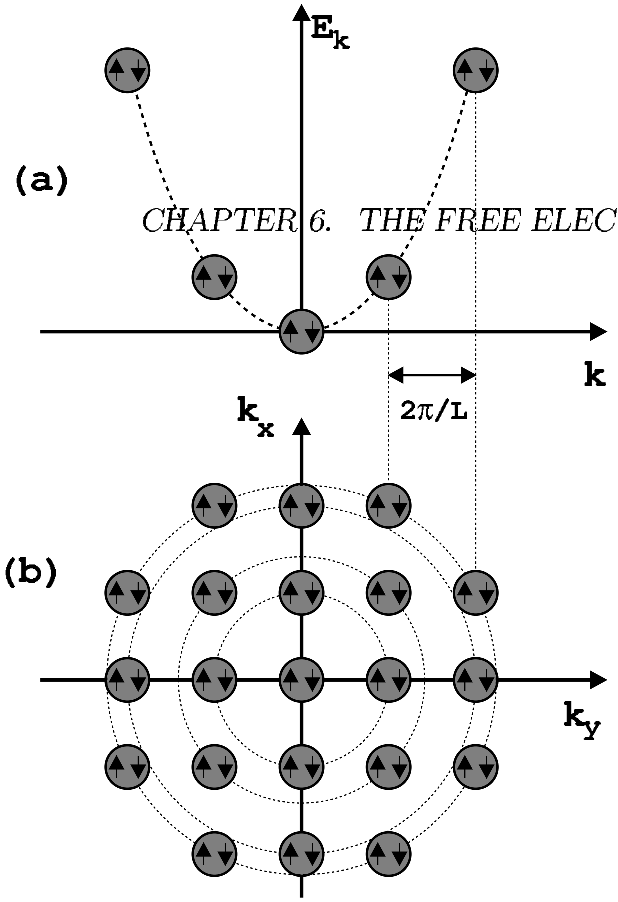

Figure 6.1: *(a) Ground state of a free Fermi gas as a function of energy; (b) Ground state in momentum space showing the lines of equal energy (circles).*

cells. If we take into account the spin we have $2N$ independent orbitals in each energy band. If the atom contributes with just one electron (we say that the atom has valence one) the band can be half filled with electrons. If each atom contributes with two electrons (valence two) the band will be completely filled. The state of lowest energy is obtained by filling up the spectrum starting with the $k = 0$ as in Fig.6.1(a). For each $\mathbf{k}$ we can have two electrons with opposite spins. In momentum space this is equivalent of filling up all the states symmetrically up to the largest value which depend on the total number of electrons as in Fig.6.1(b).

We are interested in the so-called *thermodynamic limit*, that is, the limit that $N \to \infty$ and $L \to \infty$ but $\bar{n} = N/L^d$ is finite. In this limit the distance between the states goes to zero and therefore we fill densely the momentum space. It is clear that the number of electrons in the system can be written as

$$N = 2\sum_{\mathbf{k}} \theta(k_F - k) \tag{6.2}$$

where k_F is the largest possible momentum and the factor 2 comes from the two spin projections. In the thermodynamic limit we use our old trick

$$\sum_{\mathbf{k}} \to \frac{L^d}{(2\pi)^d}\int d^dk \tag{6.3}$$

and find

$$\begin{aligned} \bar{n} &= \frac{N}{L^d} = 2\int \frac{d^dk}{(2\pi)^d}\theta(k_F - k) = \frac{2S_d}{(2\pi)^d}\int_0^{k_F} dk k^{d-1} \\ &= \frac{2S_d k_F^d}{d(2\pi)^d} \end{aligned} \tag{6.4}$$

which defines the so-called *Fermi momentum*,

$$k_F = \left(\frac{d(2\pi)^d\bar{n}}{2S_d}\right)^{1/d} \tag{6.5}$$

which depends only on the electron density and the dimensionality of the system. Associated with this Fermi momentum there is the so-called *Fermi energy* which is the energy of the highest energy state,

$$E_F = \frac{\hbar^2 k_F^2}{2m}\,. \tag{6.6}$$

Thus, in this case, the finite size spectrum of Fig.6.1 becomes the one in Fig.6.2. The points in momentum space, $\mathbf{k}_F$, such that

$$\epsilon_{\mathbf{k}_F} = E_F \tag{6.7}$$

defines the *Fermi surface*. Observe, also, that this system is highly degenerated since we have a large number of states for a given energy. The magnitude of this degeneracy is again defined in terms of a density

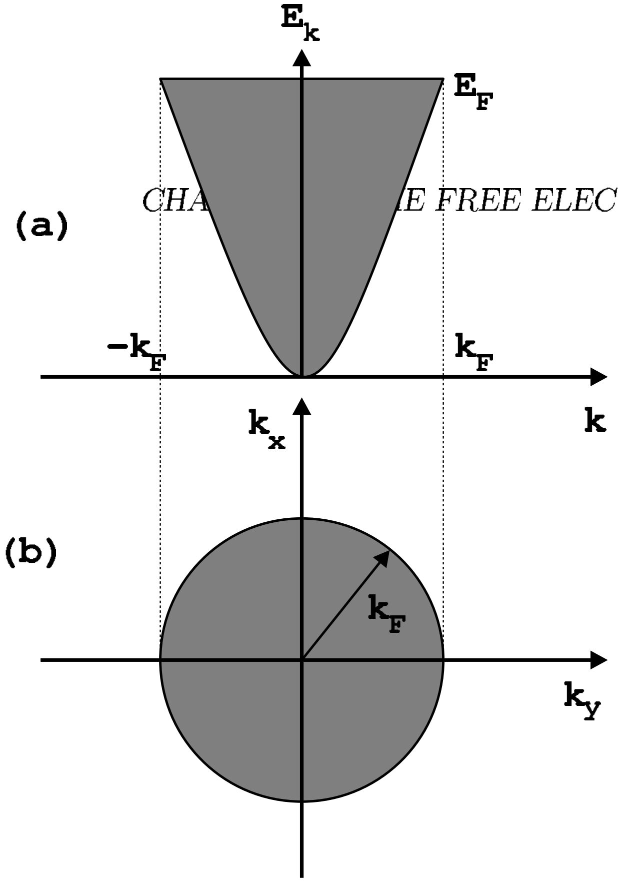

Figure 6.2: *(a) Ground state of the free Fermi gas; (b) Ground state in momentum space.*

of states which is defined exactly like in the phonon problem, that is, Eq.(4.56). For the free electron problem one has

$$\begin{aligned} N(E) &= \frac{2}{V}\sum_{\mathbf{k}}\delta(E-\epsilon_k) = 2\int \frac{d^dk}{(2\pi)^d}\delta(E-\epsilon_k) \\ &= \frac{2S_d}{(2\pi)^d}\int_0^\infty dkk^{d-1}\delta\left(E-\frac{\hbar^2k^2}{2m}\right) = \frac{S_d}{(2\pi)^d}\left(\frac{2m}{\hbar^2}\right)^{d/2}E^{\frac{d-2}{2}} \\ &= \frac{d\bar{n}}{2E_F}\left(\frac{E}{E_F}\right)^{\frac{d-2}{2}} \end{aligned} \qquad (6.8)$$

where we have used (6.5) and (6.6).

The concept of a Fermi surface is one of the most important concepts in the physics of electrons in solids and this is easy to understand why when we look at the characteristic energies involved here. In a solid of density $\bar{n}$ the volume occupied by one electron is, in average, $S_d r_0^d/d$

and therefore the mean distance between electrons is of order of

$$r_0 = \left(\frac{d}{S_d \bar{n}}\right)^{1/d} . \tag{6.9}$$

Since we are talking about atomic scales it is convenient to use the *Bohr radius*, $a_0 = \hbar^2/(me^2)$, as a distance scale. Thus, the number,

$$r_s = \frac{r_0}{a_0} \tag{6.10}$$

gives us an idea of the density of the solid relative to the atomic volume of the atom. In this unit the Fermi energy (6.6) can be rewritten using (6.5) as

$$E_F = \left(\frac{d^2(2\pi)^d}{2S_d^2}\right)^{2/d} \frac{me^4}{2\hbar^2}\frac{1}{r_s^2} . \tag{6.11}$$

Observe that apart from the geometric factors the Fermi energy is proportional to the ionization energy of the Hydrogen atom $E_I = me^4/(2\hbar^2) \approx 13.6$ eV. In most metals (3 dimensions) r_s is of order of one (the distance between electrons is of the order of the distance between atoms). In this case it is easy to see that the Fermi energy is of order of eV, that is, of order of $10,000$ K! The ground state energy can now be easily calculated:

$$\begin{aligned} E_0 &= \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} \theta(k_F - k) \\ \frac{E_0}{N} &= \frac{d}{d+2} E_F . \end{aligned} \tag{6.12}$$

6.2 Elementary excitations

Consider now the *elementary excitation* of a Fermi gas. The lowest energy excitation corresponds to take an electron with momentum $k < k_F$ and transfer it to a state with momentum $k' > k_F$. In this case a *hole* is left behind (see Fig.6.3).

The momentum of this *particle-hole excitation* is

$$\mathbf{q} = \mathbf{k}' - \mathbf{k} \tag{6.13}$$

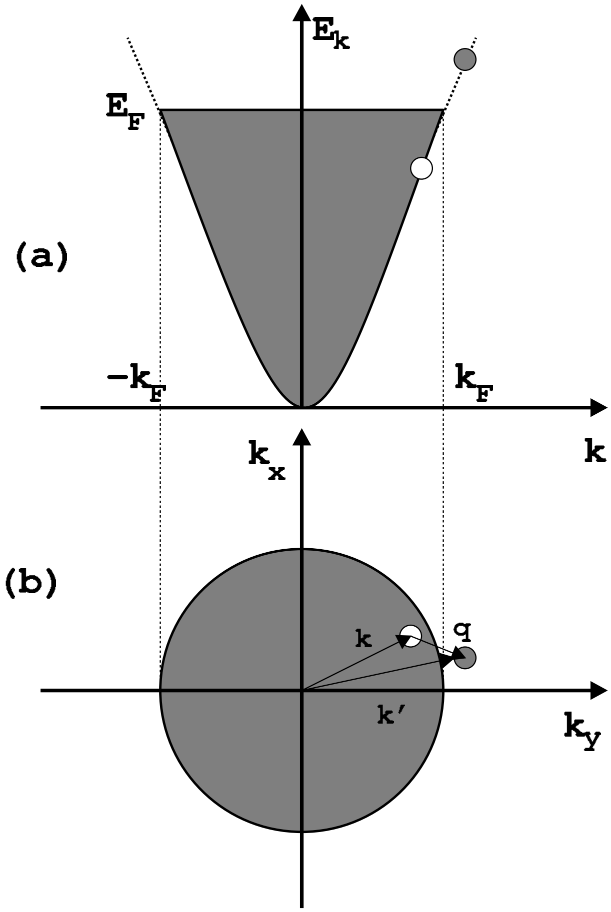

Figure 6.3: *(a) Particle-hole excitation across the Fermi surface; (b) Particle-hole excitation in momentum space.*

and has a characteristic energy

$$\hbar\omega(\mathbf{q},\mathbf{k}) = \frac{\hbar^2(\mathbf{k}-\mathbf{q})^2}{2m} - \frac{\hbar^2\mathbf{k}^2}{2m} = \frac{\hbar^2}{2m}(2\mathbf{q}\cdot\mathbf{k}-\mathbf{q}^2)\,. \tag{6.14}$$

At some temperature T all particle-hole pairs such that $\hbar\omega(\mathbf{q},\mathbf{k}) \leq k_B T$ can be excited. At low temperatures only a region of energy $k_B T$ can be excited around the Fermi surface. This is clear contrast with the phonon problem where any phonon state can be excited with any number of phonons. The fact that the *phase space* for excitations in the electronic system is much smaller than in the phonon problem is a pure consequence of Pauli's principle since we cannot occupy states which are already occupied. Obviously the excitation with lowest energy has $|\mathbf{k}| = k_F$ and $q \to 0$. In this limit the excitation energy reduces to

$$\omega(q_{||}) \approx v_F q_{||} \tag{6.15}$$

where $q_{||}$ is the component of $\mathbf{q}$ in the direction of $\mathbf{k}_F$ and

$$v_F = \frac{\hbar k_F}{m} \tag{6.16}$$

is the *Fermi velocity.* The striking discovery here is that the dispersion relation for particle-hole excitations is very similar to the one of acoustic phonons (see 4.39)). Observe that what we actually have done is the *linearization* of the dispersion of the electrons close to k_F as shown in Fig.6.4.The fact that at low energies look like acoustic phonons is not a mere coincidence. It turns out that the *elementary excitations* of Fermi systems have bosonic character. Particle-hole excitations are the main gapless excitations of Fermi systems. We will come back to this interesting issue later but now we are going to consider another important excitation of Fermi systems.

Let us go back to our original problem of electrons on a box of size L in *three dimensions.* Suppose we displace the whole electron gas through a distance x with respect to background of charge produced by the ions. In this case we will have an excess of positive charge on one side of the box and an excess of negative charge on the opposite side of the box (see Fig.6.5). This effect will create an electric field across the box. By Gauss law the electric field is simply $E = 4\pi\sigma$ where σ

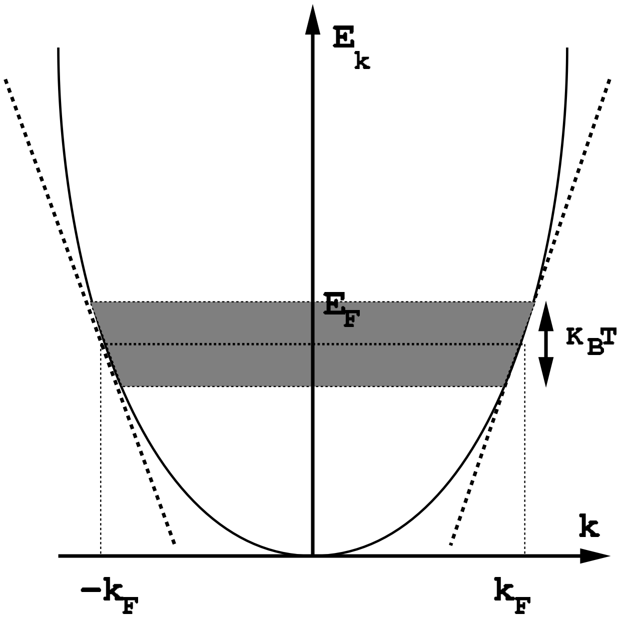

Figure 6.4: *Linearization of the electron dispersion close to the Fermi surface.*

is the charge density on the wall of the box. This density is simply $\sigma = e\bar{n}x$. Of course this field will act on the electrons in such a way to move the displaced charge density back to its original place so charge neutrality is obtained again. Mathematically this come from the fact that the force applied on the charge on the opposite side of the box is $F = -NeE = -Ne4\pi\sigma = -4\pi\bar{n}e^2Nx$. Thus the equation of motion for the displaced density is

$$\begin{aligned}(Nm)\frac{d^2x}{dt^2} &= -4\pi\bar{n}e^2Nx(t)\\ \frac{d^2x}{dt^2} &= -\omega_p^2x(t)\end{aligned} \tag{6.17}$$

where

$$\omega_p^2 = \frac{4\pi\bar{n}e^2}{m} \tag{6.18}$$

is the so-called *plasma frequency* of the electron system. Observe that (6.17) predicts that the displaced charge undergoes harmonic motion with the plasma frequency. Since the plasma frequency is associated with the displacement of the whole electron system it has a characteristic wave-vector $q = 0$. Thus this simple argument shows that the electron gas, besides the particle-hole excitations described by (6.15), also has a *collective mode* called the *plasmon* which has dispersion

$$\omega(q) \approx \omega_p \tag{6.19}$$

at small wavelengths. Again, we have a similarity between the optical phonon problem and the electron gas. These similarities do not stop here. Observe that the plasmon is a high energy excitation since we need temperatures of the order of $\hbar\omega_p$ in order to excite this mode. The plasmon is a *massive* or *gapful* excitation. Using the equations given before we can show that

$$\hbar\omega_p \approx 41.7r_s^{-3/2} \tag{6.20}$$

in eV. Thus, for metallic densities the plasma frequency is of order of the order of 40 eV or 40,000 K. Thus, in order to excite a plasmon in a

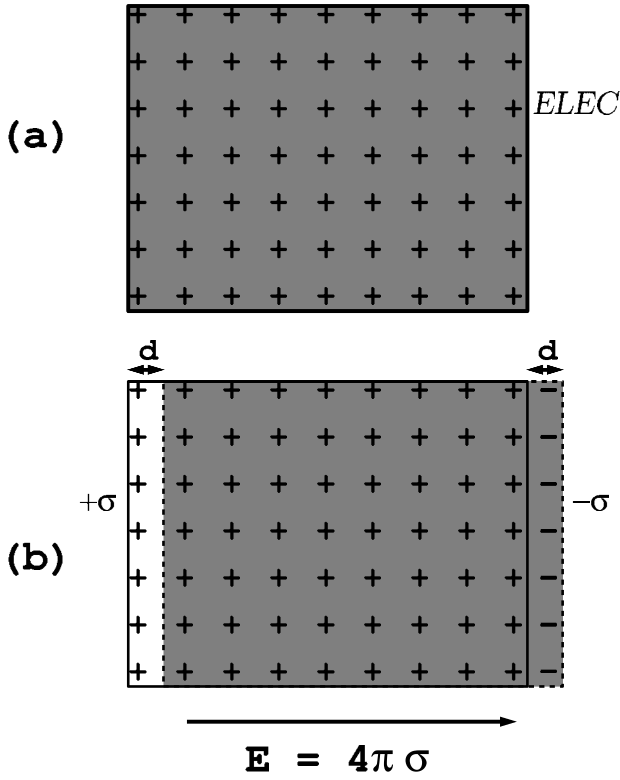

Figure 6.5: *Formation of a plasmon in a non-interacting electron gas: (a) uniform positive background plus electron gas; (b) displaced electron gas relative to background.*

metal one has to use high energy probes such as X-rays or high energy electrons. Like in the phonon problem where acoustic phonons describe the the low temperature properties of ion vibration the particle-hole excitations dominate the behavior of Fermi liquids at low temperatures. Observe that all the *elementary excitations* we are discussing here have a counterpart in the physics of elementary physics. In order to create a particle from the vacuum one has to pay an energy price which is twice the rest energy of the particle. Thus optical phonons and plasmons behave like actual particles although they are *collective modes* which are born out of the interaction between ions and electrons. The result for the plasmon frequency is only valid for three dimensional solids. In lower dimensions the situation is more complicated because the electric field is not the one created by a capacitor plate but by a line of charge! In this case we can show that the plasmon dispersion and the plasmon mode becomes gapless.

6.3 Free electron gas in a magnetic field

A simple way to probe the properties of an electron gas is to subject it to external fields and look at its behavior. One way is to attach it to a battery and look at the current produced by the application of difference of potential. For a free electron gas the field will accelerate the electron freely producing an infinite current. This, of course, never happens since the electrons collide with impurities and among themselves so that the current is always finite. We will discuss these issues in detail later. Another important properties of an electron gas can be measured by applying a magnetic field. Since the electron has a spin and a charge the magnetic field will couple to the electron in two different ways. The first and most simple coupling is to the electronic spin since the magnetic field will tend to align the spin. This is the *Zeeman effect* that you probably have seen in the study of the Hydrogen atom. The second effect is due to the *Lorentz force* that the electron feels when it is in motion. These are relativistic effects but they have different origins. While the Lorentz force can be applied to classical particles the Zeeman effect is a pure quantum mechanical effect. We are going to study each effect separately.

6.3.1 Zeeman effect and Pauli susceptibility

Consider a magnetic field $\mathbf{B}$ applied to a free electron gas. The Zeeman shift in energy due to the magnetic field is just

$$H_Z = -\mathbf{m}_e \cdot \mathbf{B} \tag{6.21}$$

where $\mathbf{m}_e$ is the electron magnetic moment. For the electron spin $\mathbf{S}$ the magnetic moment is written as

$$\mathbf{m}_e = \mu_e \frac{\mathbf{S}}{\hbar} \tag{6.22}$$

where

$$\mu_e = g_s \mu_B \approx 1.16 \times 10^{-8} \tag{6.23}$$

in units of eV/Gauss. Here $g_s \approx 2$ is the *g-factor* and $\mu_B = e\hbar/(2mc)$ is the *Bohr magneton.* In order to study the Zeeman effect we have to add the new term (6.21) to the free electron Hamiltonian. Without any loss of generality we choose the magnetic field to be along the z axis. Thus, it is clear the problem can be completely diagonalized in the basis $|\mathbf{k}, \sigma\rangle$ where $\sigma =\uparrow, \downarrow$ where $\uparrow$ means that the spin is parallel to the field and $\downarrow$ that the spin is anti-parallel to the field ($S_z|\uparrow\rangle = (\hbar/2)|\uparrow\rangle$ and $S_z|\downarrow\rangle = -(\hbar/2)|\downarrow\rangle$). The eigenenergies of the problem can now be written as

$$\begin{aligned} E_{k,\uparrow} &= \frac{\hbar^2 k^2}{2m} - \mu_B B \\ E_{k,\downarrow} &= \frac{\hbar^2 k^2}{2m} + \mu_B B \,. \end{aligned} \tag{6.24}$$

Thus, the dispersion of each mode is shifted relative to each other by a quantity $2\mu_B B$. The ground state of the system is obtained by filling up the states starting from the lowest energy state up to the Fermi energy, E_F, as shown in Fig.6.6. Since the up and down spins are in equilibrium with each other it means that the chemical potential is the same, that is, the field does not change the Fermi energy of the system but only the number of species of electron as depicted in Fig.6.6. Thus, in the presence of a magnetic field the number of $\uparrow$ spins, $n_\uparrow$, is different from the number of $\downarrow$ spins, $n_\downarrow$. This implies the system has been magnetized with a *magnetization*

$$M = \mu_B (n_\uparrow - n_\downarrow) \,. \tag{6.25}$$

Observe that the change in the number of the two species of electrons is equivalent to a change in the Fermi momentum of them. Thus we can define two new Fermi momenta, $k_{F,\downarrow}$ and $k_{F,\uparrow}$ which are related to the number of fermions as in (6.4):

$$n_\sigma = \frac{S_d}{d(2\pi)^d} k^d_{F,\sigma} \,. \tag{6.26}$$

Since the total number of electrons is conserved in the presence of the magnetic field we have a constraint that

$$\begin{aligned} n_\uparrow + n_\downarrow &= \bar{n} \\ k^d_{F,\uparrow} + k^d_{F,\downarrow} &= \frac{d(2\pi)^d \bar{n}}{S_d} \,. \end{aligned} \tag{6.27}$$

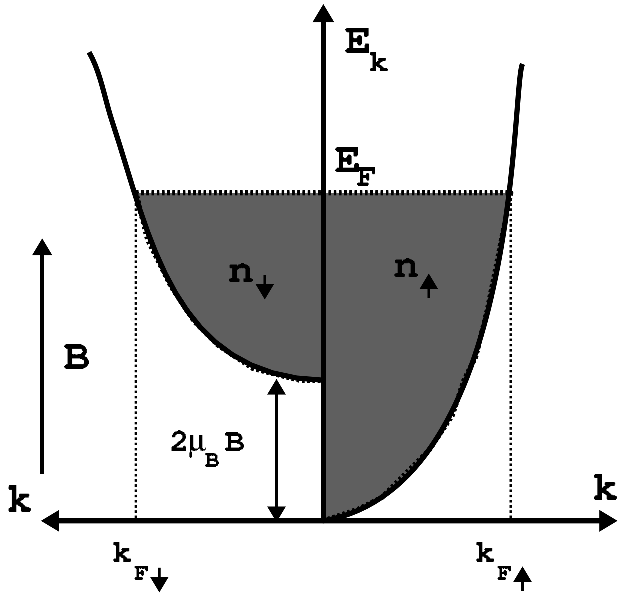

Figure 6.6: *Magnetization in a free Fermi gas.*

The other constraint that we discussed before is that the chemical potential is the same which implies

$$\begin{aligned} E_F = \frac{\hbar k_{F,\uparrow}^2}{2m} - \mu_B B &= \frac{\hbar k_{F,\downarrow}^2}{2m} + \mu_B B \\ k_{F,\uparrow}^2 - k_{F,\downarrow}^2 &= \frac{4m\mu_B B}{\hbar^2} \,. \end{aligned} \tag{6.28}$$

Equations (6.27) and (6.28) have to be solved at the same time. It is useful to parameterize the unknowns as

$$\begin{aligned} k_{F,\uparrow} &= k_0 \cosh\theta \\ k_{F,\downarrow} &= k_0 \sinh\theta \end{aligned} \tag{6.29}$$

so that (6.28) is solved at once:

$$k_0 = \sqrt{\frac{4m\mu_B B}{\hbar^2}} \tag{6.30}$$

since $\cosh^2\theta - \sinh^2\theta = 1$. Substituting (6.29) on (6.27) one gets

$$\cosh^d\theta + \sinh^d\theta = \frac{d(2\pi)^d\bar{n}}{k_0^d S_d} \tag{6.31}$$

which is a very complicated equation for θ. The quantity we are after is the magnetization of the system which is given in (6.25) which can be written as

$$M = \frac{S_d \mu_B k_0^d}{d(2\pi)^d}\left(\cosh^d\theta - \sinh^d\theta\right) . \tag{6.32}$$

Instead of the general solution of this problem we are going to look at the limit of very weak magnetic field. In this limit ($B \to 0$) we see that from (6.30) that $k_0 \to 0$ and therefore the right hand side of (6.31) diverges. It implies that $\theta \to \infty$. In this case we can approximate $\cosh\theta \approx \sinh\theta \approx e^\theta/2$ and we find

$$e^\theta = \left(\frac{2^{d-1}d(2\pi)^d\bar{n}}{S_d}\right)^{1/d}\frac{1}{k_0} \tag{6.33}$$

In this approximation we can write (6.32) as

$$\begin{aligned} M &\approx \frac{\mu_B 2^{1-d} S_d k_0^d}{(2\pi)^d} e^{(d-2)\theta} \\ &\approx \mu_B^2 N(E_F) B \end{aligned} \tag{6.34}$$

where $N(E_F)$ is the density of states at the Fermi energy which is given in (6.8). Notice that the magnetization is directly proportional to the density of states at the Fermi surface. The *magnetic susceptibility* of the system is given by

$$\chi_P(T) = \lim_{B\to 0}\frac{\partial M}{\partial B} = \mu_B^2 N(E_F) \tag{6.35}$$

is called the *Pauli susceptibility* and it is an exact result since only the linear term in the magnetic field contributes. Thus, the measurement of the magnetic susceptibility of a free electron gas is a direct measurement of its density of states at the Fermi energy.

Let us consider now a simple case of the general problem discussed here. Let us consider $d = 2$. In this case one can calculate the magnetization exactly from (6.32) and (6.30),

$$M = \frac{m\mu_B^2 B}{\hbar^2 \pi} \tag{6.36}$$

which is strictly linear with the magnetic field. In this case (6.34) is not approximate but exact.

Finally we observe that by increasing the field one can fully polarize the electron gas (that is, $n_\uparrow = \bar{n}$). As we can see from Fig.6.6 this happens at a critical field, B_c, given by

$$B_c = \frac{E_F}{2\mu_B} \, . \tag{6.37}$$

For a metallic system this will happen at fields of the order of 10^8 G or 10^4 Tesla (1 Tesla= 10^4 Gauss). These are incredibly large fields.

6.3.2 Landau levels and de Hass-van Alphen effect

After discussing the spin part of the magnetic field problem we will consider the orbital part, that is, the effect of the Lorentz force on the electron which is given by $e\mathbf{v} \times \mathbf{B}/c$. Classically it is easy to show that in the plane perpendicular to the field the electrons undergo circular motion. This motion is a result of the centripetal force mv^2/R where R is the classical radius of the orbit. It is clear that the velocity of the electron on its orbit is $v = 2\pi R/T = \omega_c R$ where T is the period of the orbital motion and $\omega_c = 2\pi/T$ is the cyclotron frequency. The cyclotron frequency can be obtained immediately from the classical equation of motion

$$\begin{aligned} evB/c &= mv^2/R \\ \omega_c &= \frac{eB}{mc} \, . \end{aligned} \tag{6.38}$$

Classically the radius of the orbit depends on the velocity of the electron. This is not entirely correct in quantum mechanics. In quantum mechanics the angular momentum is always quantized in units of $\hbar$.

For the circular motion the angular momentum is just pR. Thus, from the quantization of the angular momentum we find

$$\begin{aligned} pR &= n\hbar \\ R_n &= \sqrt{n} l_0 \end{aligned} \tag{6.39}$$

where

$$l_0 = \sqrt{\frac{c\hbar}{eB}} \tag{6.40}$$

is the so-called *cyclotron radius* which gives an idea of the size of the electron wavefunction in the presence of an external magnetic field. Observe that apart from the magnetic field the cyclotron radius only depends on universal quantities. If we choose the magnetic field to be in Tesla the cyclotron radius can be written as

$$l_0 = \frac{250}{\sqrt{B}} \mathring{A}\,. \tag{6.41}$$

We see, therefore, that the cyclotron radius will be usually much larger than the typical separation between atoms in a solid. In order for l_0 to be of order of $1\mathring{A}$ one needs fields of the order of 6×10^4 T. These are incredibly large fields. As we saw previously at these fields the electron gas is completely spin polarized.

As you already know the Hamiltonian for a charged particle in a magnetic field is

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 \tag{6.42}$$

where $\mathbf{A}(\mathbf{r})$ is the vector potential which is related to the magnetic field via $\mathbf{B} = \nabla \times \mathbf{A}$. Assume for simplicity that the field points in the z direction, that is $\mathbf{B} = B\mathbf{z}$. As you know the problem of a particle in an electromagnetic field has what is called *gauge invariance*, that is, we can replace the vector potential by $\mathbf{A} \to \mathbf{A} + \nabla\phi$ (where $\phi(\mathbf{r})$ is an arbitrary function) without changing the value of the actual magnetic field since $\nabla \times \nabla\phi = 0$ is a mathematical identity. This gauge invariance allows us to choose any form of $\mathbf{A}(\mathbf{r})$ such that $\mathbf{B} = B\mathbf{z}$ holds. Here we will choose the so-called *Landau gauge* in which

$$\mathbf{A} = -By\mathbf{x}\,. \tag{6.43}$$

Substitution of (6.43) directly into (6.42) leads to

$$H = \frac{1}{2m}\left(p_x + \frac{eB}{c}y\right)^2 + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}\,. \tag{6.44}$$

Observe that the Hamiltonian does not depend explicitly on x and z. Therefore, in the x and z direction one has free motion. In this case the wavefunction of the problem can be written as

$$\Psi_{k_x,k_z}(\mathbf{r}) = e^{i(k_x x + k_z z)}\psi(y) \tag{6.45}$$

where $\psi(y)$ is unknown. In this case the Hamiltonian of the problem reduces to

$$H = \frac{1}{2m}\left(\hbar k_x + \frac{eB}{c}y\right)^2 + \frac{p_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m}\,. \tag{6.46}$$

A simple redefinition of variables helps a lot

$$\begin{aligned} \delta y &= y + y_0 \\ y_0 &= \frac{\hbar k_x}{m\omega_c} \end{aligned} \tag{6.47}$$

and the Hamiltonian of the problem becomes

$$H = \frac{p_y^2}{2m} + \frac{m\omega_c^2}{2}(\delta y)^2 + \frac{\hbar k_z^2}{2m} \tag{6.48}$$

which is the Hamiltonian for a harmonic oscillator plus a free particle part. We have therefore solved the problem entirely. The wavefunction is given by (6.45) with $\psi(y) \propto H_n(y - y_0)$ is a Hermite polynomial of order n.

Since we have mapped the problem into the harmonic oscillator the spectrum is giving by

$$E_n(k_z) = \hbar\omega_c\left(n + \frac{1}{2}\right) + \frac{\hbar^2 k_z^2}{2m} \tag{6.49}$$

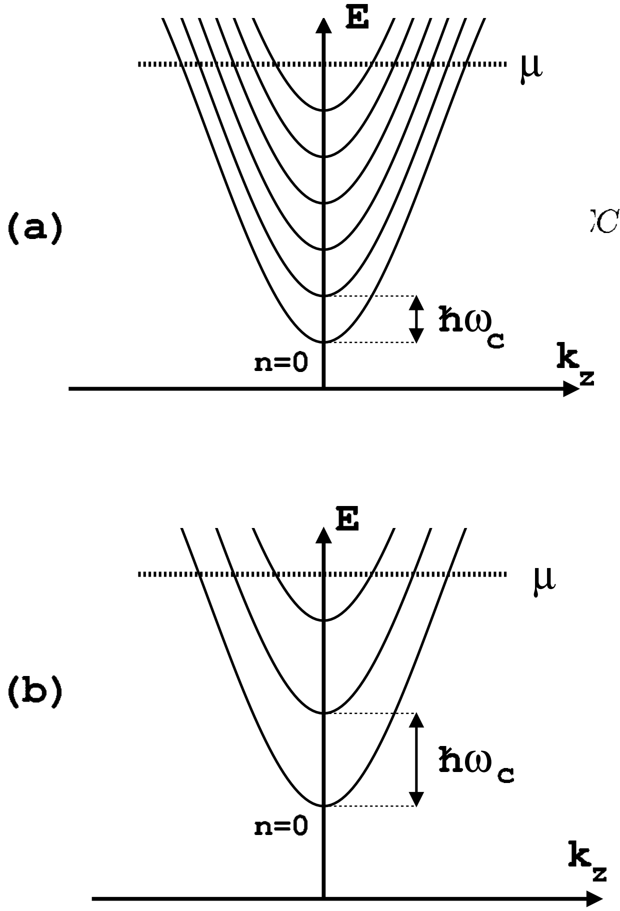

Figure 6.7: *Landau levels of a free Fermi gas: in (b) the field is larger than in (a).*

and is shown in Fig.6.7. The physics here is straightforward: the electron undergoes circular motion in the plane perpendicular to the field (due to the Lorentz force) and free motion along the direction of the field (since the Lorentz force vanishes). Circular motion is essentially harmonic motion in the x and y coordinates. Furthermore, we are going to be interested in the physical quantities such as the magnetization of the system. Notice that when we change the magnetic field by an infinitesimal amount δB the internal energy of the system changes by $\delta U = -M\delta B$. Thus, the magnetization is simply

$$M(B) = -\frac{\partial U}{\partial B} \,. \tag{6.50}$$

Observe, however, that the energy does not depend on k_x and therefore the problem is highly degenerate. The reason for this degeneracy can be understood by looking into (6.47). Observe that the wavefunction of the electron is centered at y_0 which is called the *center of orbit.* The energy of the problem is invariant if we shift the center of the orbit in the plane perpendicular to the field because the field is homogeneous in the perpendicular plane. Physically one has to impose the condition that $0 \leq y_0 \leq L_y$. It implies from (6.47) that the momentum in the x direction is bounded by

$$0 \leq k_x \leq m\omega_c L_y/\hbar \, . \tag{6.51}$$

But from the periodic boundary conditions we require that $k_x = 2\pi n_x/L_x$ and therefore the number of states in k space for fixed k_z is simply

$$N_\phi = \frac{m\omega_c L_x L_y}{2\pi\hbar} = \frac{\Phi}{\phi_0} \tag{6.52}$$

where $\Phi = BL_xL_y$ is the total magnetic flux through the plane perpendicular to $\mathbf{B}$ and

$$\phi_0 = \frac{ch}{e} \approx 4 \times 10^{-7} \tag{6.53}$$

in Gauss-cm^2 is the so-called *flux quanta.*

As we have seen so far the interesting part of the electron motion happens at the plane perpendicular to the field. It is possible to build artificial semiconducting structures such that the electrons are confined to a very thin layer of thickness L_z. In this case $k_z = 2\pi n_z/L_z$ is quantized. From now on we will focus on the two-dimensional electron gas and forget about the motion in the third direction. It is easy to generalize our discussion here to the three dimensional situation in ordinary solids. From now on we just forget the k_z dependence in (6.49) (as you can easily convince yourself all we are going to do here is equivalent to work with fixed k_z). The energy levels are shown in Fig.6.8. Each level can comport N_ϕ electrons (we will forget spin for the moment being). If there are a total of N_e electrons in the system the ground state is obtained by filling up the lowest energy states. Observe that the number of states per electron is simply

$$\frac{1}{\nu} = \frac{N_\phi}{N_e} = \frac{B}{\sigma\phi_0} \tag{6.54}$$

where

$$\sigma = \frac{N_e}{L_xL_y} \tag{6.55}$$

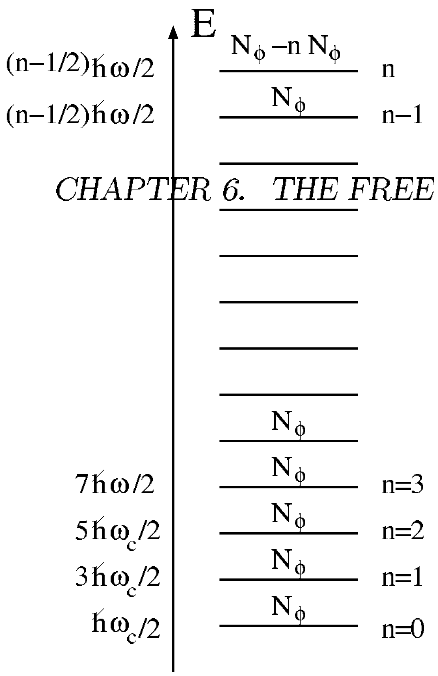

Figure 6.8: *Landau levels of a two dimensional free Fermi gas.*

is the planar density of electrons.

Consider initially the case where $N_\phi > N_e$, that is, only the first Landau levels has electrons $(0 < \nu < 1)$. Clearly it implies very strong magnetic fields or small electronic densities since we must have from (6.54) that $B > \sigma\phi_0$. In semiconductors we have ordinarily $\sigma \approx 10^{11}$ cm^{-2} which implies $B > 4 \times 10^4$ G (or $B > 4$ Tesla). In this case the total energy of the system is simply

$$\begin{aligned} E_0 &= N\frac{\hbar\omega_c}{2} \\ \frac{E_0}{N} &= \frac{\hbar e B}{2mc}. \end{aligned} \tag{6.56}$$

From (6.50) we find

$$\frac{M(B)}{N} = -\mu_e = -\frac{\hbar e}{2mc} \tag{6.57}$$

is the electronic magnetic moment (notice that $2\mu_e B = \hbar\omega_c$). Observe that this magnetization is constant as far as $N_\phi > N$ or $\nu < 1$. Suppose we decrease the magnetic field in the system with fixed number of electrons. Then the fractional occupation ν increases and the distance between Landau levels decreases. When $\nu = 1$ the first Landau level is fully occupied if we reduce the magnetic field even further $N_\phi < N_e <$

$2N_\phi$ (or $1 < \nu < 2$) and some of the electrons, say, $\delta N = N_e - N_\phi$ have to occupy the second Landau level. In this situation the energy of the system is

$$\begin{aligned} E_1 &= N_\phi \frac{\hbar\omega_c}{2} + \delta N \frac{3\hbar\omega_c}{2} \\ \frac{E_1}{N} &= \hbar\omega_c \left(\frac{3}{2} - \frac{1}{\nu}\right) \end{aligned} \tag{6.58}$$

and the magnetization is

$$\frac{M_1}{N} = \mu_e \left(-3 + \frac{4}{\nu}\right) . \tag{6.59}$$

Observe that something drastic happened because at $\nu = 1$ there is a jump in the magnetization from $-\mu_e$ to $+\mu_e$. This jump occurred because the electrons in the lowest levels move to higher Landau levels as the field decreases. Observe that this effect will occur every time ν is an integer number, that is, each time a Landau level is fully occupied. The generalization of the above argument is simple. Assume that the last fully occupied Landau level is $n-1$ so that n is occupied by $N - nN_\phi$ electrons (see Fig.6.8). In this case $n < \nu < n+1$ and the total energy of the system is

$$\begin{aligned} E_n &= N_\phi \sum_{m=0}^{n-1} \hbar\omega_c \left(m + \frac{1}{2}\right) + (N - nN_\phi)\hbar\omega_c \left(n + \frac{1}{2}\right) \\ \frac{E_n}{N} &= \hbar\omega_c \left(n + \frac{1}{2} - \frac{n(n+1)}{2\nu}\right) \end{aligned} \tag{6.60}$$

and the magnetization

$$\frac{M_n}{N} = 2\mu_e \left(\frac{n(n+1)}{\nu} - n - \frac{1}{2}\right) \tag{6.61}$$

which is shown in Fig.6.9 as a function of ν. Notice that the magnetization of the system is a periodic function of ν for $\nu > 1$. Thus the magnetization of the electron gas is a periodic function of $1/B$ as we see from (6.54). This effect is observed experimentally in the magnetization of solids and it is known as the *de Haas-van Alphen* effect.

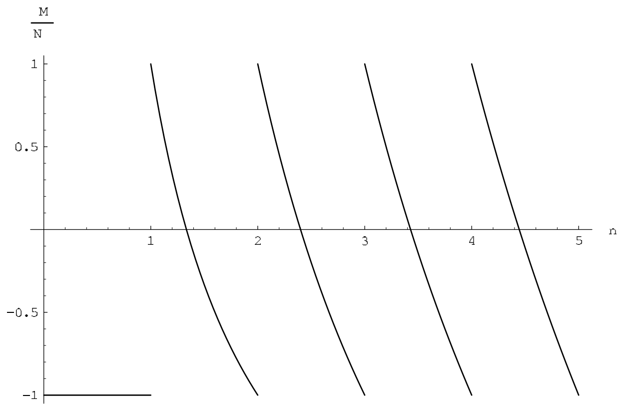

Figure 6.9: *Magnetization of a Fermi gas as a function of ν.*

6.3.3 Flux quantization

In our discussion of the Landau levels we defined a quantity called the flux quanta $\phi_0 = hc/e$ but we gave no interpretation for it or even why it is called a *quanta*. In order to understand why the magnetic flux is quantized we have to study the effect of the magnetic field in the electron wave function. Consider the problem of a two dimensional electron gas in a plane where an infinite solenoid is put perpendicular to it. The solenoid has area S and an internal magnetic field B. The magnetic field outside the solenoid is zero. The magnetic field is given by the usual relation $\mathbf{B} = \nabla \times \mathbf{A}$. Although the magnetic field is zero outside of the solenoid the vector potential is still finite. As a consequence we must have

$$\mathbf{A}(\mathbf{r}) = \nabla\Omega(\mathbf{r}) \tag{6.62}$$

outside of the solenoid since $\nabla \times \mathbf{A} = \nabla \times \nabla\Omega = 0$. Moreover, the magnetic flux through the plane is given by

$$\Phi = \int_A \mathbf{B} \cdot d\mathbf{S} = \int_C \mathbf{A} \cdot d\mathbf{l} = \int_C \nabla\Omega \cdot d\mathbf{l} = \Delta\Omega \tag{6.63}$$

where A is the area of the solenoid, C is a closed curve outside of the solenoid and $\mathbf{l}$ is a vector that parameterizes this curve. Observe that the flux through the plane depends only on the change of the function Ω around a closed curve.

The Schrödinger equation for this problem is

$$\begin{aligned} \frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}\mathbf{A}(\mathbf{r})\right)^2 \psi(\mathbf{r}) &= E\psi(\mathbf{r}) \\ -\frac{\hbar^2}{2m}\left(\nabla + \frac{ie}{c\hbar}\mathbf{A}(\mathbf{r})\right)^2 \psi(\mathbf{r}) &= E\psi(\mathbf{r})\,. \end{aligned} \tag{6.64}$$

For the region outside the solenoid we can use (6.62) and rewrite the above equation as

$$-\frac{\hbar^2}{2m}\left(\nabla + \frac{ie}{c\hbar}\nabla\Omega(\mathbf{r})\right)^2 \psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{6.65}$$

and a simple inspection of this equation leads to the conclusion that the wavefunction has the form

$$\psi(\mathbf{r}) = e^{-\frac{ie}{c\hbar}\Omega(\mathbf{r})}\phi(\mathbf{r}) \tag{6.66}$$

where

$$-\frac{\hbar^2}{2m}\nabla^2\phi(\mathbf{r}) = E\phi(\mathbf{r}) \tag{6.67}$$

obeys the free particle problem. As expected by *gauge invariance* the spectrum of the problem does not depend on the magnetic field (since there is none) but the wavefunction now has a new phase factor which depends on the magnetic field. This result has amazing consequences and one of them is the so-called *Bohm-Aharonov effect.* Since there is no field outside the solenoid we must require that the wavefunction is invariant under closed curves that circulate the solenoid. Suppose the

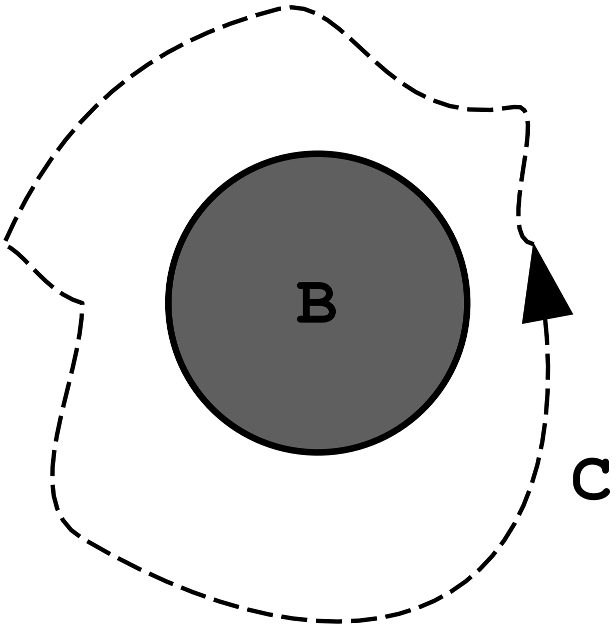

Figure 6.10: *Geometry of the Bohm-Aharonov effect.*

electron starts at a point $\mathbf{R}$ with a wavefunction $\Psi_B(\mathbf{R})$ and returns to the same point after going around the solenoid as in Fig.6.10

From (6.66) the wavefunction of the electron after the closed curve is

$$\Psi_A(\mathbf{R}) = e^{-\frac{ie}{c\hbar}\Delta\Omega}\Psi_B(\mathbf{R}) \tag{6.68}$$

but since $\Psi_A(\mathbf{R}) = \Psi_B(\mathbf{R})$ we must require

$$\frac{e}{c\hbar}\Delta\Omega = 2\pi n \tag{6.69}$$

where n is an integer. Using (6.63) we obtain that

$$\Phi = n\phi_0 \tag{6.70}$$

where $\phi_0 = hc/e$ is the flux quantum. Our argument shows therefore that for a free electron moving in a closed orbit around the solenoid the magnetic flux through the orbit must be quantized. The relevance of this result for the Landau level problem comes from the fact that the

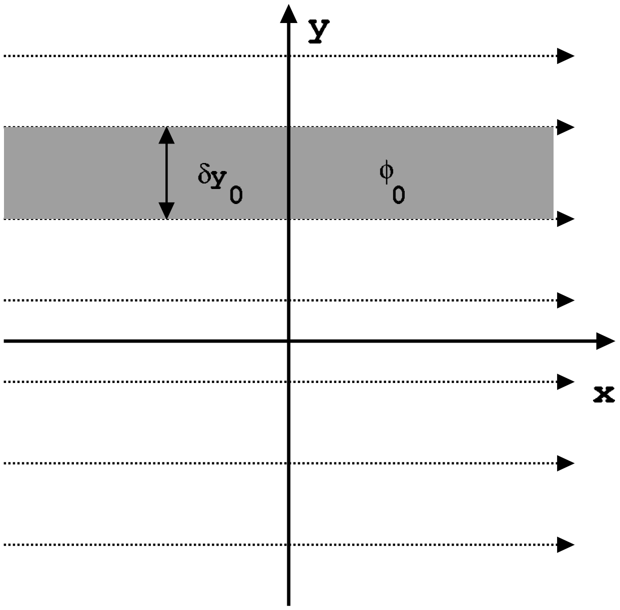

Figure 6.11: *Quantization of the magnetic flux in the Landau gauge.*

degeneracy of each Landau level is the total magnetic flux measured in units of the flux quantum, (6.52). Physically, this can be understood if we recall that in the Landau gauge the electron motion in the x direction is free while in the y direction we have harmonic motion as shown in Fig.6.11. Observe that the wavefunction in the y direction is peaked around y_0 and because $k_x = 2\pi n_x/L_x$ is quantized the values of y_0 from (6.47) are also quantized as $y_0(n_x) = (\phi_0/BL_x)n_x$. Thus, the magnetic flux through a strip of size δy_0 is simply, $B\delta y_0 L_x = \phi_0$. Thus, exactly one flux quantum goes through the strip.

6.4 Free electrons at finite temperature

We have talked only about what happens to the electron gas at zero temperature. As we said before if we increase the temperature we can excite electrons to states out of the Fermi surface producing particle-hole excitations. In order to talk about finite temperature effect one has to discuss first the concept of *chemical potential.* The chemical potential is the energy required in order to change the number of particles in the system by 1, that is, if $E(N)$ is the free energy of the system with N electrons than the chemical potential, μ, is defined as

$$\begin{aligned} \mu &= E(N+1) - E(N) \\ &= \frac{\partial E}{\partial N} \end{aligned} \tag{6.71}$$

where the last line is valid if $N \gg 1$ which is the case under consideration here. At zero temperature, in the free Fermi gas, the energy required to put on electron more in the system is essentially the Fermi energy, E_F since as we put one extra electron it has to go to an unoccupied state at the Fermi surface. In the phonon problem the chemical potential is zero since phonons can be produced with infinitesimally small energies. We observe that in the Fermi gas the excitations occur close to the Fermi surface, or chemical potential, thus it is convenient to measure all the energies relative to it since it is the natural energy scale. Observe that one usually calculates the total energy of the system assuming a fixed number of particles. It turns out, however, that for most calculations at finite temperature it is more convenient to work with fixed chemical potential. Moreover, one actually have the systems of interest in contact with reservoir of particles (such as batteries, for instance) which keep the chemical potential constant and allow the number of particles fluctuate. In the *thermodynamic limit*, $N \to \infty$, these fluctuations are of order $\sqrt{N}$ and therefore irrelevant compared to N itself. Thus we define the *free energy*, F, of the system as

$$F = E - \mu N \,, \tag{6.72}$$

which is known as the *Legendre transformation* of the thermodynamic potential. Thus, using (6.71), we find $dF = dE - \mu dN - N d\mu = -N d\mu$, that is

$$N = -\frac{\partial F}{\partial \mu} \tag{6.73}$$

which gives the average number of particles as a function of the chemical potential.

Let us consider here the simple problem of the N non-interacting electrons described by a Hamiltonian H with single energies ϵ_α. By the

Pauli principle we know that the occupation n_α of each state can be only 0 or 1. A state Ψ_n of the system is described by the occupation of each single particle state, that is, each state is represented by a set of numbers $\Psi_n = (n_1, n_2, n_3, ...)$. The total number of electrons in the system is

$$N = \sum_\alpha n_\alpha \,, \tag{6.74}$$

while the total energy of a particular state Ψ_n is

$$E_n = \sum_\alpha n_\alpha \epsilon_\alpha \,. \tag{6.75}$$

The partition function of the problem is defined as

$$\begin{aligned} Z &= e^{-\beta F} = \sum_n \langle n | e^{-\beta(H-\mu N)} | n \rangle \\ &= \sum_{n_\alpha=0}^{1} e^{-\beta \sum_\alpha n_\alpha(\epsilon_\alpha-\mu)} \\ &= \prod_\alpha \sum_{n_\alpha=0}^{1} e^{-\beta(\epsilon_\alpha-\mu)n_\alpha} \\ &= \prod_\alpha \left(1 + e^{-\beta(\epsilon_\alpha-\mu)}\right) \end{aligned} \tag{6.76}$$

and the free energy is

$$F = -\frac{1}{\beta} \sum_\alpha \ln\left(1 + e^{-\beta(\epsilon_\alpha-\mu)}\right) \,. \tag{6.77}$$

Therefore, using (6.73), one finds

$$N = \sum_\alpha \frac{1}{e^{\beta(\epsilon_\alpha-\mu)} + 1} \tag{6.78}$$

which by comparison with (6.74) allows us to define the mean occupation per state α as

$$\bar{n}_\alpha = \frac{1}{e^{\beta(\epsilon_\alpha-\mu)} + 1} \tag{6.79}$$

which is the so-called *Fermi-Dirac* occupation number. Naturally the average energy density of the system in simply

$$\bar{E} = \frac{1}{V}\sum_{\alpha} \epsilon_\alpha n_\alpha \tag{6.80}$$

and other physical quantities can be calculated as well. As in the phonon case we define the density of states

$$N(E) = \frac{1}{V}\sum_{\alpha} \delta\left(E - \epsilon_\alpha\right) \tag{6.81}$$

and transform all the sums into integrals, in particular, the mean energy density is

$$\bar{E} = \int dE\, N(E)\, E\, \bar{n}(E)\,. \tag{6.82}$$

Observe that the Fermi-Dirac distribution has the properties one expects for electrons. For instance, consider the zero temperature limit, that is, $\beta \to \infty$. If $E > \mu$ the exponent in the exponential in (6.79) is positive and therefore when $\beta \to \infty$ the Fermi-Dirac occupation vanishes. If $E < \mu$ the exponent is negative and at zero temperature it vanishes leading to $\bar{n} = 1$. The conclusion is that at $T = 0$ we have a step function

$$\bar{n}(E) = \theta(\mu - E) \tag{6.83}$$

as in Fig.6.12(a) and no state are occupied below the chemical potential, as expected. At low temperatures $k_B T << \mu$ only states in a region of width $k_B T$ with energy close to μ is affected as shown in Fig.6.12(b).

These properties of the Fermi-Dirac distribution are very useful if we use the fact that the derivative of a theta function is a Dirac delta function, that is,

$$\frac{\partial \bar{n}}{\partial E} = -\delta(\mu - E)\,. \tag{6.84}$$

At finite temperatures the delta function is broadened by $k_B T$ as expected. In order to explore the usefulness of the properties of the

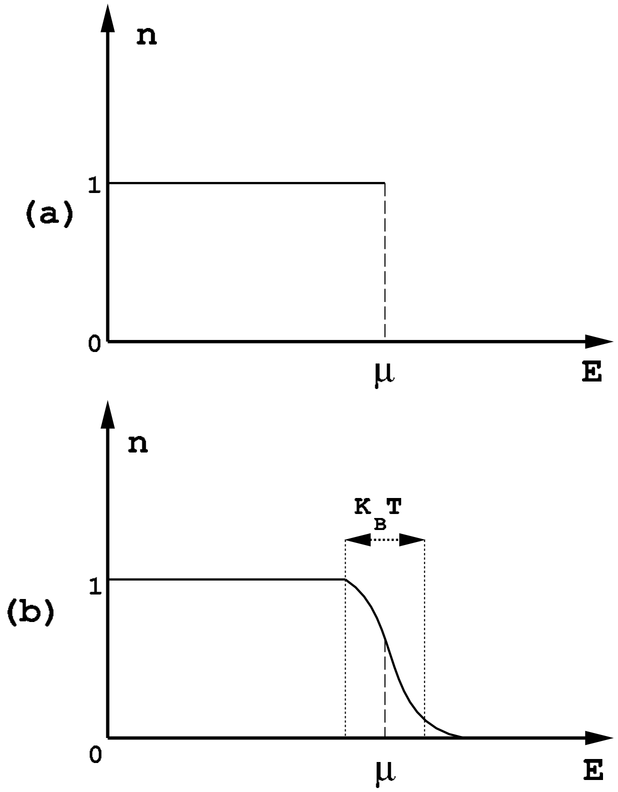

Figure 6.12: *Fermi-Dirac distribution: (a) zero temperature; (b) finite temperature.*

Fermi-Dirac distribution consider a typical integral of the distribution with an arbitrary function $f(E)$

$$\begin{aligned} I(\mu,T) &= \int_{-\infty}^{+\infty} dE f(E) n(E) \\ &= \int_{-\infty}^{+\infty} dE \frac{dF}{dE} n(E) \\ &= -\int_{-\infty}^{+\infty} dE F(E) \frac{\partial \bar{n}}{\partial E} \end{aligned} \tag{6.85}$$

where we have defined as

$$F(E) = \int_{-\infty}^{E} dE' f(E') \,. \tag{6.86}$$

Observe that the last line was obtained by integration by parts which is correct if $F(E)$ diverges slower than an exponential. Moreover, we assume that in doing the integral by parts the integrand vanishes in the $E \to -\infty$ limit. This is going to be true in general because the integrand in the thermodynamic quantities involves the density of states which always vanishes in this limit. Now we observe that the derivative of the Fermi-Dirac distribution at low temperatures is highly peaked around $E = \mu$ and assuming that $F(E)$ is a smooth function close to this point we make a series expansion

$$F(E) = F(\mu) + \sum_{n=1}^{\infty} \frac{F^{(n)}(\mu)}{n!} (E-\mu)^n \tag{6.87}$$

where $F^{(n)}(\mu)$ is the n^{th} derivative of the function at $E = \mu$. We further observe that

$$\int_{-\infty}^{+\infty} dE \left(-\frac{\partial \bar{n}}{\partial E} \right) = 1 \tag{6.88}$$

and that the Fermi-Dirac function is an even function of $E - \mu$. By direct substitution of (6.87) into (6.85) we obtain

$$I(\mu,T) = \int_{-\infty}^{\mu} f(E) dE + \sum_{n=1}^{\infty} \frac{f^{(2n-1)}(\mu)}{(2n)!} \int_{-\infty}^{+\infty} dE (E-\mu)^{2n} \left(-\frac{\partial \bar{n}}{\partial E} \right) \tag{6.89}$$

which can be further simplified if we change variables $x = \beta(E - \mu)$ in order to obtain

$$I(\mu, T) = \int_{-\infty}^{\mu} f(E)dE + \sum_{n=1}^{\infty} f_n(\mu)(k_B T)^{2n} \tag{6.90}$$

where

$$f_n = \frac{f^{(2n-1)}(\mu)}{(2n)!} \left(2 - 2^{2(1-n)}\right) \zeta(2n) \tag{6.91}$$

where $\zeta(n)$ is a Riemann zeta function. Equation (6.90) gives the finite temperature correction to the zero temperature result in powers of T. This is called the *Sommerfeld expansion.* Moreover, we observe that the corrections to the zero temperature results are even powers of the temperature. In particular, at low temperatures the first correction will always be of order T^2, thus, the first term in (6.90) can be replaced by

$$\begin{aligned} \int_{-\infty}^{\mu} f(E)dE &= \int_{-\infty}^{E_F} f(E)dE + \int_{E_F}^{\mu} f(E)dE \\ &\approx \int_{-\infty}^{E_F} f(E)dE + (\mu - E_F) f(E_F)\,. \end{aligned} \tag{6.92}$$

6.4.1 Specific heat

Let us apply this result for the case of the free electron gas. From (6.80) we have $f(E) = EN(E)$ and

$$\begin{aligned} \bar{E} &\approx \int_0^{E_F} EN(E)dE \\ &+ E_F(\mu - E_F)N(E_F) + \frac{\pi^2}{6}\left(E_F N'(E_F) + N(E_F)\right)(k_B T)^2 \end{aligned} \tag{6.93}$$

and the mean density is

$$\bar{n} \approx \int_0^{E_F} N(E)dE + (\mu - E_F)N(E_F) + \frac{\pi^2}{6} N'(E)(k_B T)^2\,. \tag{6.94}$$

Notice that number of particles is the same as at zero temperature and therefore from (6.94) we get

$$\mu \approx E_F - \frac{\pi^2}{6}\frac{N'(E_F)}{N(E_F)}(k_B T)^2 \tag{6.95}$$

which when substituted in (6.93) gives

$$\bar{E} \approx \frac{E_0}{V} + \frac{\pi^2}{6} N(E_F)(k_B T)^2 \tag{6.96}$$

Finally, from (6.96), we obtain the electronic contribution for the specific heat

$$\frac{C_V}{V} = \frac{\partial \bar{E}}{\partial T} = \frac{\pi^2}{3} N(E_F) k_B^2 T \tag{6.97}$$

independent of the dimensionality of the problem which only appears through the density of states which for the case of free electrons is given in (6.8).

This last result could have been obtained without all this mathematical workout if we have used the physical meaning of the specific heat which is the number of excitations in the system. Obviously in the case of a system with a Fermi surface the number of excitations available is proportional to the $k_B T$ times the number of states per unit of energy which is simply $N(E_F)$ which gives the correct order of magnitude of the specific heat. Since the average energy of the particle-holes is $k_B T$ the excitation energy will be $N(E_F)(k_B T)^2$ which misses the correct value by a factor $\pi^2/6$. Another way to calculate the specific heat is to use the analogy we made before between the particle-hole excitations and acoustic phonons. As we showed in (6.15) the particle-hole excitations have a dispersion relation of one-dimensional acoustic phonons since it depends only on the component of the momentum perpendicular to the Fermi surface. The specific heat of one dimensional phonons, according to (4.59), indeed behave like T. In order to show that this is more than a coincidence let us calculate the specific heat of these particle-hole excitations. First we observe that the density of states at the Fermi surface of a Fermi gas can be written as in (6.8)

$$N(E_F) = 2 \int \frac{d^d k}{(2\pi)^d} \delta(E_F - \epsilon_k) \, . \tag{6.98}$$

Observe that only states at the Fermi surface, that is, with k such $E_F = \epsilon_k$ contribute to the integral. Thus we make a simple change of variables

$$\mathbf{k} = \mathbf{k}_F + \mathbf{q} \tag{6.99}$$

and therefore

$$\begin{aligned}\epsilon_k &\approx E_F + \mathbf{q}\cdot\nabla\epsilon_{k_F} \\ &= E_F + q_{||}v_F \end{aligned} \tag{6.100}$$

where we have used (6.16). As expected only the component of $\mathbf{q}$ normal to the Fermi surface appears in the energy in agreement with (6.15). Therefore it is natural to rewrite

$$\mathbf{q} = q_{||}\frac{\mathbf{k}_F}{k_F} + \mathbf{q}_\perp \tag{6.101}$$

where $\mathbf{q}_\perp$ is *tangent* to the Fermi surface. Observe that the density of states at the Fermi energy can be written as

$$\begin{aligned}N(E_F) &= 2\int \frac{dq_{||}d^{d-1}q_\perp}{(2\pi)^d}\frac{\delta(q_{||})}{v_F} \\ &= 2\int \frac{d^{d-1}q_\perp}{(2\pi)^d}\frac{1}{v_F}\end{aligned} \tag{6.102}$$

involves only the component of $\mathbf{q}$ perpendicular to the Fermi surface. Now *assume* for the moment being that the particle-hole excitations have bosonic character. Then the partition function for these bosons is the same one as the acoustic phonons case, (4.52)

$$Z = e^{-\beta F} = \prod_{\mathbf{q}} \left[\sinh(\beta v_F q_{||}/2)\right]^{-1} . \tag{6.103}$$

The specific heat is simply

$$\begin{aligned}\frac{C_V}{V} &= \frac{\partial F}{\partial T} = \frac{\beta^2}{4}\int \frac{dq_{||}d^{d-1}q_\perp}{(2\pi)^d}\frac{(v_F q_{||})^2}{\sinh^2(\beta v_F q_{||}/2)} \\ &= \frac{N(E_F)v_F\beta^2}{4}\int_{-\infty}^{\infty} dq_{||}\frac{(v_F q_{||})^2}{\sinh^2(\beta v_F q_{||}/2)} \\ &= 2\frac{\pi^2}{3}N(E_F)T\end{aligned} \tag{6.104}$$

where we have used (6.102). Observe that this is twice than the expected result (6.97). This happened because we have double counted the number of particle-hole excitations. The mapping of the particle-hole problem into bosons has an extra requirement that $q_{||} \geq 0$, that is, we count only the excitations outside the Fermi surface. If we take this into account we get the correct result. The connection between the particle-hole excitations of an electron system goes beyond what has been discussed here. We can show that in dense Fermi systems there is an operator identity between fermions and bosons. This identity is called *bosonization* for obvious reasons.

6.4.2 Correction to the Pauli susceptibility

Another interesting application of this effect is the temperature correction to the Pauli susceptibility discussed in the last section. In the presence of a magnetic field the Zeeman energy will shift the energy of the up spins by $-\mu_B B$ while the down spins are shifted by $+\mu_B B$. Therefore the density of states of each species can be directly obtained by the density of states of the unpolarized case, $N(E)$. Indeed, by definition,

$$\begin{aligned} N_{\uparrow}(E) &= \frac{1}{V}\sum_{\mathbf{k}} \delta(E - \epsilon_k + \mu_B B) \\ N_{\downarrow}(E) &= \frac{1}{V}\sum_{\mathbf{k}} \delta(E - \epsilon_k - \mu_B B) \end{aligned} \tag{6.105}$$

but from definition (6.8)

$$\begin{aligned} N_{\uparrow}(E) &= \frac{1}{2}N(E + \mu_B B) \\ N_{\downarrow}(E) &= \frac{1}{2}N(E - \mu_B B)\,. \end{aligned} \tag{6.106}$$

The magnetization is given by

$$M = \frac{\mu_B}{2}\int_{-\infty}^{\infty} dE\, \bar{n}(E)\; (N(E + \mu_B B) - N(E - \mu_B B)) \tag{6.107}$$

and the magnetic susceptibility is simply

$$\chi(T) = lim_{B\to 0}\frac{\partial M}{\partial B} = \mu_B^2 \int dE \bar{n}(E)\frac{dN}{dE}\,. \tag{6.108}$$

Using the Sommerfeld expansion one finds

$$\chi(T) = \mu_B^2 N(E_F)\left(1 + \frac{\pi^2}{6}[\ln(N(E_F))]^{(2)}(k_B T)^2\right) \tag{6.109}$$

which gives the correction to the Pauli susceptibility.

6.4.3 Landau diamagnetism

Finally let us consider the problem of a two dimensional electron gas in a magnetic field. Since the levels are quantized the density of states is not a smooth function of the energy but has delta functions at the energy of each Landau level

$$N(E) = 2N_\phi \sum_{n=0}^{\infty} \delta\left(E - \hbar\omega_c(n+1/2)\right) \tag{6.110}$$

where N_ϕ gives the degeneracy of each level and the factor of 2 account for the two spin orientations.. Thus there is no advantage of substituting the summations by integrals. In particular the free energy of the system is given in (6.77)

$$F = -\frac{2N_\phi}{\beta}\sum_{n=0}^{\infty} \ln\left(1 + e^{\beta(\mu - \hbar\omega_c(n+1/2))}\right) \tag{6.111}$$

It is very hard to perform this sum. Since we will be interested on the susceptibility of the electron gas we just have to evaluate the free energy at very small fields, that is, $k_B T >> \hbar\omega_c$. In this case we rewrite the sum as

$$\frac{F}{S} = -\frac{2B}{\beta\phi_0}\sum_{n=0}^{\infty} \ln\left(1 + e^{\beta(\mu - \hbar\omega_c/2)}e^{-x_n}\right) \tag{6.112}$$

where $S = L_x L_y$ is the total area and

$$x_n = \frac{n}{k_B T/(\hbar\omega_c)} = (\beta\hbar\omega_c)n\,. \tag{6.113}$$

Thus, when $k_B T >> \hbar\omega_c(\beta\hbar\omega_c << 1)$ the separation between the allowed values of x_n is very small and we can replace the sum by an integral. However, we are not interested in strictly zero magnetic field and we have to keep the first correction. This is done with the help of the so-called *Euler-MacLaurin* formula,

$$\begin{aligned}\sum_{n=0}^{r} f(x_n) &= \frac{1}{h}\int_{x_0}^{x_r} dx f(x) + \frac{1}{2}\left(f(x_0) + f(x_r)\right) \\ &+ \sum_{n=1}^{\infty} \frac{B_{2n}h^{2n-1}}{(2n)!}\left(f^{(2n-1)}(x_r) - f^{(2n-1)}(x_0)\right) \end{aligned} \tag{6.114}$$

where $x_n = x_0 + nh$ and B_n is a Bernoulli number. Application to this formula to (6.112) leads to

$$\frac{F}{S} = -\frac{2B}{\beta\phi_0}\int_0^{\infty} dx \ln\left(1 + z\, e^{-\beta\hbar\omega_c x}\right) + \frac{e^2B^2}{24\pi mc^2}\frac{z}{z+1} \tag{6.115}$$

where

$$z = e^{\beta\mu} \tag{6.116}$$

is called the *fugacity* of the metal. Observe that all the dependence of the free energy on the chemical potential can be obtained from the fugacity. Thus any derivative in respect to the chemical potential can be replaced by a derivative with respect to the fugacity, in particular, from (6.73) one has

$$N = -\frac{\partial F}{\partial \mu} = -\beta z\frac{\partial F}{\partial z}\,. \tag{6.117}$$

A simple change of variables $y = -ze^{-\beta\hbar\omega_c x}$ in (6.115) leads to

$$\frac{F}{S} = \frac{m}{\pi\beta^2\hbar^2}Li_2(-z) + \frac{e^2B^2}{24\pi mc^2}\frac{z}{z+1} \tag{6.118}$$

where

$$Li_2(x) = \int_x^0 dy\frac{\ln(1-y)}{y} = \sum_{n=1}^{\infty}\frac{x^n}{n^2} \tag{6.119}$$

is a polylogarithmic function of second degree.

The total number of electrons is obtained from (6.73)

$$\sigma = \frac{N}{S} = \frac{m}{\pi\beta\hbar^2}\ln(1+z) + \frac{e^2B^2\beta}{24\pi mc^2}\frac{z}{(z+1)^2} \tag{6.120}$$

which is a transcendental equation which gives z as a function of σ. Let us first consider the $B = 0$ case, then

$$1 + z_0 = e^{\beta E_F} \tag{6.121}$$

where we have used (6.4). Since we are interested in the low density limit it is clear that corrections to z_0 are going to be very small. We therefore write $z \approx z_0 >> 1$. Substituting this result in (6.118) we find

$$\frac{F}{S} \approx E_0 + \frac{e^2B^2}{24\pi mc^2} \tag{6.122}$$

where E_0 is the ground state energy of the system in the absence of an external field. Finally the magnetization density is given by (6.50),

$$\frac{M}{S} = -\frac{e^2B}{12\pi mc^2} = -\frac{N(E_F)\mu_B^2 B}{3} \tag{6.123}$$

where $N(E_F) = m/(\pi\hbar^2)$ is the density of states of a two dimensional electron gas (see (6.8) with $d = 2$) and $\mu_B = \hbar e/(2mc)$. Therefore, the susceptibility is

$$\chi_L = -\frac{N(E_F)\mu_B^2}{3} = -\frac{\chi_P}{3} \tag{6.124}$$

where we have used the result (6.35). Observe that the sign is negative implying that the magnetization is contrary to the direction of the field in accord with *Lenz's law.* This susceptibility was originally derived by *Landau* and carries his name. Observe therefore that the total susceptibility of an electron gas is

$$\chi_T = \chi_P + \chi_L = \frac{2}{3}\chi_P\,. \tag{6.125}$$

6.5 Problems

1. Prove eq.(6.11) and calculate for Al ($r_s \approx 2$) and Cs ($r_s \approx 5.5$) their respective Fermi energies. Show that in 3 dimensions we have:

   $$E_F = \frac{50.1}{r_s^2}$$

   where the energy is measured in eV.

2. Prove (6.12).

3. Calculate the Fermi velocity in d dimensions and show that in 3 dimensions we can write:

   $$v_F = \frac{4.2 \times 10^6}{r_s}$$

   where the velocity is measured in m/s. What is the value of the Fermi velocity for Al and Cs?

4. Prove (6.20).

5. Prove eq.(6.34).

6. Calculate the exact expression for the magnetization of a electron gas for $d = 1$ and $d = 2$.

7. What happens with the magnetization of a free electron gas for $B > B_c$?

8. Prove (6.39).

9. Show that the mean square deviation $\langle(\delta y)^2\rangle$ is proportional to the cyclotron length squared, that is, l_0^2.

10. Solve the problem of an electron in a magnetic field in the symmetric gauge: $\mathbf{A} = B(-y\mathbf{x} + x\mathbf{y})/2$.

11. Prove eq. (6.60).

12. Calculate the jump in the magnetization ν and $\nu + 1$ for a two dimensional electron gas.

13. Prove (6.109).

Chapter 7

Introduction to disordered systems

Up to this point we have only discussed the physics of perfectly ordered systems, that is, crystals. We have seen that in a periodic potential the momentum **k** is still a good quantum number and that the wavefunction of the electrons looks very much like plane waves, that is, it is delocalized over the entire crystal. As a consequence a crystal can conduct current without any loss since the electrons, accordingly to (5.86) can be accelerated indefinitely. Real life is not that easy. Real materials always contains imperfections like impurities, dislocations, etc. We have seen, for instance, that even for entropic reasons there are always vacancies in real crystals. Thus, in the presence of an electrical field the electrons will be scattered. As electrons move through the system they will exchange momentum with the lattice and undergo Brownian motion as shown in Fig.7.1.

When the number of imperfections is small the electrons will move ballistic between impurities. This is called the weakly disordered limit. If however the number of impurities is large then new effects can arise since there is going to be a destructive interference of the electron wavefunction due to disorder. We are going to briefly discuss these two extreme limits.

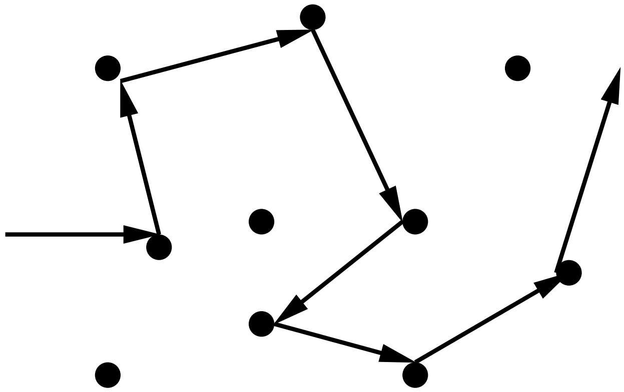

Figure 7.1: *Motion of an electron in the presence of scattering centers.*

7.1 Weak scattering

Let us consider the influence of an electrical field **E** in the motion of electrons in a solid when the electrons collide with impurities. We are going to assume the simple model of elastic scattering (no phonons are created for the moment being). In this case the electrons when they collide with the impurities they transfer momentum. After many collisions the velocity of the electrons decreases as a consequence of the collisions. A simple model for this process is to assume that there is a mean-time τ between collisions so that in between collisions the motion is purely ballistic. The ordered case is obtained when $\tau \to \infty$, that is, it takes a large amount of time between collisions. Let us rewrite the semiclassical equation of motion (5.86) for a cubic symmetry as

$$\frac{d\mathbf{v}_{\mathbf{k}}}{dt} = \frac{e\mathbf{E}}{m^*} - \frac{1}{\tau}\mathbf{v}_{\mathbf{k}} \tag{7.1}$$

which is known as the *Langevin equation* which describes the motion of a particle in a viscous environment. Observe that in principle τ depends on the momentum **k** but as explained before we are going to calculate τ always at the Fermi surface. Observe that this equation leads to an exponential decay of the velocity with time in a time scale given by τ. If we wait long enough we obtain the steady state condition, that is, the electron reach a final velocity

$$\langle \mathbf{v}_{\mathbf{k}} \rangle = \frac{e\tau}{m^*}\mathbf{E} \tag{7.2}$$

which allows us to define the *electron mobility*, μ, as

$$\langle \mathbf{v}_{\mathbf{k}} \rangle = \mu \mathbf{E} \tag{7.3}$$

where

$$\mu = \frac{e\tau}{m^*}\,. \tag{7.4}$$

Notice that $\langle \mathbf{v}_{\mathbf{k}} \rangle$ has nothing to do with the actual velocity (that is, the Fermi velocity) of the electron. This velocity is the net effect of the collisions. In between impurities indeed the electron move with the Fermi velocity but because the direction of motion of the electron is changing all the time its velocity *along* the electric field is smaller than its velocity in between collisions.

The steady state current in the system is just

$$\mathbf{J} = e\bar{n}\langle \mathbf{v}_{\mathbf{k}} \rangle \tag{7.5}$$

where $\bar{n}$ is the average electronic density. Using (7.2) and (7.5) we can write

$$\mathbf{J} = \sigma \mathbf{E} \tag{7.6}$$

where

$$\sigma = \frac{e^2\bar{n}\tau}{m^*} \tag{7.7}$$

is the *electric conductivity of the system.* The *resistivity* is defined as its inverse, namely,

$$\rho = \frac{1}{\sigma} = \frac{m^*}{e^2\bar{n}\tau}\,. \tag{7.8}$$

Since we are talking about electrons at the Fermi surface with a Fermi velocity it is clear that in a time period τ the electrons will move a distance ℓ such that

$$\ell = v_F \tau \tag{7.9}$$

which is called the *mean free path* of the electrons. Equation (7.7) is known as the *relaxation time approximation.*

At this point the main element of the theory, namely, the relaxation time τ is a phenomenological parameter. We can calculate however its value from microscopics if we assume that the number of impurities is very small so that single impurity scattering dominates the relaxation mechanism. Consider the scattering of an electron from a state $|\mathbf{k}\rangle$ to a state $|\mathbf{k}'\rangle$ in the presence of an impurity potential V. In this case we just use Fermi Golden's rule tells us that the scattering rate is giving by

$$W_{\mathbf{k},\mathbf{k}'} = \frac{2\pi N_i}{\hbar}\delta(\epsilon_k - \epsilon_{k'})|\langle\mathbf{k}|V|\mathbf{k}'\rangle|^2 \tag{7.10}$$

where N_i is the number of impurities. The total scattering rate is obtained by integrating (7.10) over all final states $|\mathbf{k}'\rangle$. We have to remember, however, that not all the states contribute. In Fig.7.2 we show the actual situation in which the electric field is applies in some arbitrary direction. Observe that only the component of the momentum in the direction out of the field contributes to the relaxation. Forward scattering events in the direction of the field cannot contribute since the electron retains its momentum in this direction. Thus, the important fact is not that the electron is scattered but the amount that the component of its momentum along the electric field is changed in the process. If we take this effect into account we can write the expression for the relaxation time as

$$\frac{1}{\tau} = \sum_{\mathbf{k}'} W_{\mathbf{k},\mathbf{k}'}\left[1 - \cos\left(\theta_{\mathbf{k},\mathbf{k}'}\right)\right] \tag{7.11}$$

where $\theta_{\mathbf{k},\mathbf{k}'}$ is the angle between the two states.

Equation (7.10) is valid only in the Born approximation. A better approximation can be obtained if we observe that in the Born approximation the scattering amplitude $f_k(\theta_{\mathbf{k},\mathbf{k}'})$ is given by

$$f_k(\theta_{\mathbf{k},\mathbf{k}'}) \approx -\frac{m^*V}{2\pi\hbar^2}\langle\mathbf{k}|V|\mathbf{k}'\rangle\,. \tag{7.12}$$

But in general the differential cross-section is given by

$$\sigma(\theta) = |f_k(\theta)|^2 \tag{7.13}$$

which allows us to rewrite (7.10) in a more general way, that is,

$$W_{\mathbf{k},\mathbf{k}'} = \frac{(2\pi\hbar)^3 N_i}{(Vm^*)^2}\delta(\epsilon_k - \epsilon_{k'})\sigma(\theta_{\mathbf{k},\mathbf{k}'})\,. \tag{7.14}$$

It is a simple calculation to show that the (7.11) reduces to

$$\frac{1}{\tau} = 2\pi c v_F \int_0^\pi d\theta \sin\theta(1-\cos\theta)\sigma(\theta) \tag{7.15}$$

where $c = N_i/V$ is the impurity concentration. From the knowledge of the differential cross section of the impurity we can calculate the relaxation time from (7.15).

We can get further insight into (7.15) if use the partial wave expansion of the wavefunction in the presence of the impurity. As we know from elementary quantum mechanics the asymptotic value of the wavefunction of the electron due a central potential at the origin can be written as

$$\psi_k(r,\theta) \approx \sum_{l=0}^{\infty}(2l+1)i^l e^{i\delta_l(k)}\frac{\sin(kr - l\pi/2 + \delta_l(k))}{kr}P_l(\cos(\theta)) \tag{7.16}$$

where $\delta_l(k)$ is the *phase shift* of the electron wavefunction in the presence of the potential (obviously, $\delta_l(k) = 0$ if $V = 0$). From (7.16) one can obtain the scattering amplitude in terms of the phase shifts,

$$f_k(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)e^{i\delta_l(k)}\sin(\delta_l(k))P_l(\cos\theta) \tag{7.17}$$

and the differential cross-section is given in (7.13). By direct substitution of (7.17) into (7.15) one finds

$$\frac{1}{\tau} = \frac{4\pi c v_F}{k_F^2}\sum_{l=1}^{\infty} l\sin^2(\delta_{l-1}(k_F) - \delta_l(k_F)) \tag{7.18}$$

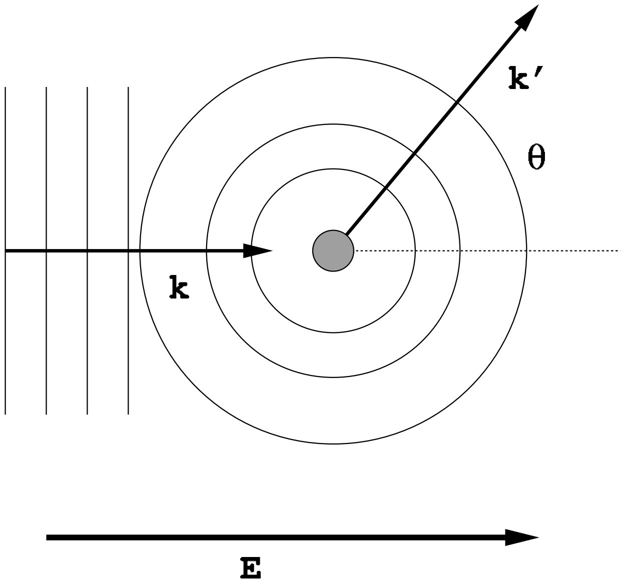

Figure 7.2: *Scattering of an electron wave by an impurity in the presence of the field.*

It is now interesting to investigate the effect of the impurity on the spectrum of the system. Assume that the impurity is at the center of radius R which is of the order of the size of the system. We impose the condition that the wavefunction vanishes at the surface, that is, $\psi_k(R, \theta) = 0$. Then, from (7.16), we find

$$k_{n,l} = \frac{\pi\left(n - \frac{\delta_l(k)}{\pi} + \frac{l}{2}\right)}{R} \tag{7.19}$$

where n is an integer. In the absence of the impurity ($\delta_l(k) = 0$) we easily see that $k_{n,l} = \pi(n + l/2)/R$ and therefore, for fixed l, the distance between two allowed values of k is π/R. In the presence of the impurity this energy levels are shifted by δ_l/R. Consider first the case without impurities. Suppose we fill up all the states up to the Fermi momentum $k_F = \pi(N_{max} + l/2)/R$ where N_{max} is the label of the last occupied state. In the presence of the impurity we will have $k_F = \pi(N'_{max} - \delta_l(k_F)/\pi + l/2)/R$. Since the density of the system is kept constant the Fermi momentum cannot change. Thus we must require that $N'_{max} = N_{max} + \delta_l(k_F)/\pi$ which implies that the number of available states has changed. Taking into account that the degeneracy of each state is $2(2l+1)$ (the factor of 2 comes from the spin component) the total number of *new* electrons required to fill up the levels to the same wave-vector k_F is

$$Z = \sum_{l=0}^{\infty} 2(2l+1)\frac{\delta_l(k_F)}{\pi} \, . \tag{7.20}$$

Observe that in the presence of the impurity we have an extra amount of charge Z in the system. So, in order for the system to be neutral we have to require that Z equals the amount of electrons given by the impurity to the system, that is, the valence difference between the impurity and the host metal. Of course an impurity with $Z = 0$ cannot be distinguished from the metal itself. This is the so-called *Friedel sum rule* and behind it hides the idea of charge neutrality: the electric charge of the impurity must be neutralized by an excess of electrons in its vicinity. Of course, far away from the impurity the the system relaxes to the case without impurities where k_F is given by the value of the density.

Observe that this sum rule is very useful since it relates the phase shift to the valence of the impurity. Suppose for simplicity that only s-wave scattering is important ($l = 0$) and $Z = 1$ (notice that if $Z > 1$ then s-wave scattering alone cannot account for the phase shift). Then from (7.20) one has

$$\delta_0 = \frac{\pi}{2} \tag{7.21}$$

which is the value of the phase shift at a resonance. That is, the impurity is *resonant* with the Fermi system. From (7.18) we have

$$\frac{1}{\tau} = \frac{4\pi c v_F}{k_F^2} . \tag{7.22}$$

Thus under these conditions the resistivity is given by

$$\begin{aligned} \rho &= \frac{4\pi c}{e^2 \bar{n} k_F} \\ &= 4\left(\frac{\pi}{3}\right)^{1/3} \frac{c}{e^2 \bar{n}} \end{aligned} \tag{7.23}$$

where in the last line we used the free electron result (6.5). For typical electronic densities one has $\rho/c \approx 4\mu\Omega$ cm.

7.2 Strong scattering

You now should be wondering in what conditions our result (7.18) is valid. The condition, of course, is that the electron moves freely between collisions. If the mean free time between collisions becomes too short we cannot describe the electron system as free. In order to estimate the validity of the theory we have to remember that τ gives an estimate of the mean free time that the electron stays in a state with well defined momentum $\mathbf{k}$ and energy approximately given by E_F. That is, τ is the *lifetime* of the state. Thus, from the uncertainty principle point of view, the description we gave will only be valid if

$$\tau \gg \frac{\hbar}{E_F} \tag{7.24}$$

which, by using $E_F = \hbar^2 k_F^2/(2m^*)$ and $\tau = \ell/v_F$ implies that

$$k_F \ell \gg 2 \tag{7.25}$$

which implies that the wavelength of the electron $\lambda_F = 2\pi/k_F$ has to be larger than the mean free path. This is nothing but the condition of ballistic motion. Condition (7.25) can also be written in a different form if we realize that the Fermi wave-vector, given in (6.5) is approximately given by π/a where a is the lattice spacing. Therefore, we have the condition that $\ell \gg a$ which implies that the mean distance between impurities has to be much larger than the lattice spacing.

The question that comes to mind is: what happens when $k_F\ell \approx 1$ or $\ell \approx a$? It is clear that in this case we have in average one impurity per unit cell, that is, $c \approx 1/a^3$. Let us assume that the impurity potential is short range and can be described by

$$V(r) = V_0 \frac{e^{-r/a}}{r/a} \,. \tag{7.26}$$

Using the simplest Born approximation (7.10) we find that the differential cross section can be written as

$$\sigma(\theta) \approx \frac{4(m^*)^2 a^6 V_0^2}{\hbar^4} \tag{7.27}$$

in the limit where $a \to 0$ (that is $ka << 1$). Substituting (7.27) into (7.18) and using (5.82), (7.9) and $c = 1/a^3$ one finds

$$\frac{1}{\ell} = \frac{16\pi a^3 V_0^2 (m^*)^2}{\hbar^4} = \frac{4\pi}{a}\left(\frac{V_0}{t}\right)^2 \tag{7.28}$$

and observe that the condition of $\ell < a$ implies $V_0 \approx t$, that is, the strength of the disordered potential is of order of the kinetic energy. It is clear that in this limit it is *wrong* to do perturbation theory around the plane wave state!

So, if the plane wave state is incorrect what is the nature of the ground state? In order to solve the problem let us consider the one-dimensional potential of Fig.7.3(a). As we have seen the solution for this problem is a Bloch wavefunction which in the atomic limit can be

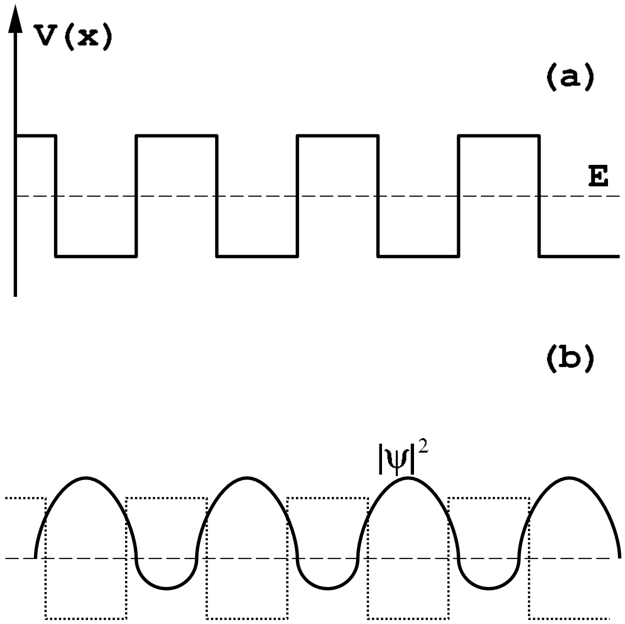

Figure 7.3: *(a) Ordered potential; (b) Module square of the Bloch wavefunction.*

well described by (5.69) and is depicted on Fig.7.3(b). Suppose we now have a potential like the in Fig.7.4(a) where the heights of the potential wells fluctuate around some mean value $\bar{V}$ and with variance V_0. What we are going to argue is that the wavefunction looks like Fig.7.4(b), that is, the wavefunction is *localized* around some site in the lattice. That is, the wavefunction instead of (5.69) will look like

$$\psi(\mathbf{r}) = \frac{e^{-r/\xi}}{\sqrt{N}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \psi_A(\mathbf{r}-\mathbf{T})\,. \tag{7.29}$$

where ξ is the so-called *localization length* and gives the envelope of the function in Fig.7.4(b).

In order to understand how localization arises in this problem consider our familiar problem of the molecule with two atoms. We now have only two sites 1 and 2 and the state of the electron localized on site 1 (2) is $|1\rangle$ ($|2\rangle$). We now generalize the Hamiltonian (1.44) in order to allow the two states to have different energies and the tunneling is

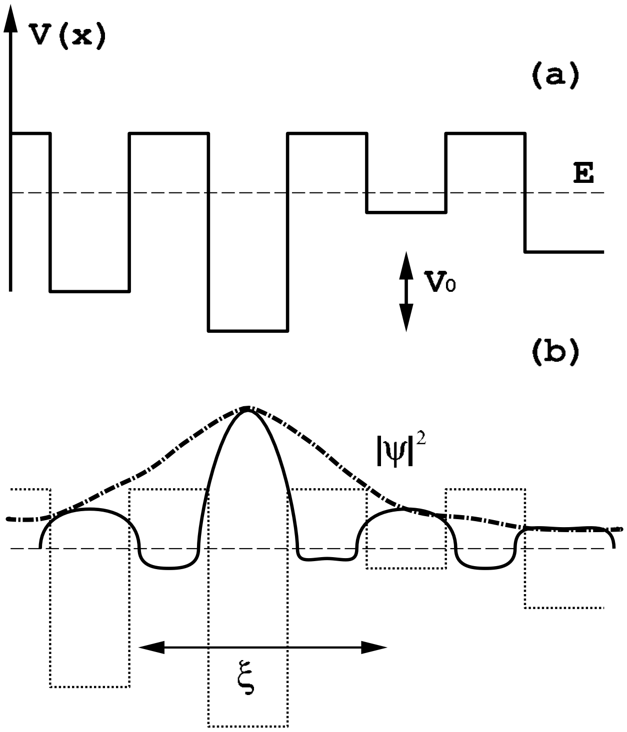

Figure 7.4: *(a) Disordered potential; (b) Module square of the wave function.*

still described by (1.46), that is, the complete Hamiltonian reads

$$H = \bar{V}|1\rangle\langle 1| + (\bar{V} + V_0)|2\rangle\langle 2| + t\,(|1\rangle\langle 2| + |2\rangle\langle 1|)\ . \tag{7.30}$$

which is our toy model for the disordered problem. Since $\bar{V}$ is just a shift in the energy of the problem we just set it to zero. This problem can be solved exactly as before by writing linear combinations of the states $|1\rangle$ and $|2\rangle$

$$\begin{aligned} |B\rangle &= \alpha|1\rangle + \beta|2\rangle \\ |A\rangle &= \alpha|2\rangle - \beta|1\rangle \end{aligned} \tag{7.31}$$

which are the analogue of the bonding and anti-bonding states. In this new basis the Hamiltonian is diagonalized and it looks like

$$H = E_A|A\rangle\langle A| + E_B|B\rangle\langle B|\,. \tag{7.32}$$

The coefficients α, β, E_A and E_B depend on the parameters t and V_0 and are left for you to calculate.

Let us consider the extreme cases where our physical intuition can work for us. The perfect lattice happens when the two potential wells are the same, that is, $V_0 = 0$. If $V_0 << t$ we have $\alpha \approx \beta \approx 1/\sqrt{2}$ and $E_B - E_A \approx 2t$ which is the case we discussed previously. In this case the two wave-functions for the bonding and anti-bonding states have equal weight in the two wells. This is the case equivalent to the Bloch state where the electron, by tunneling between atoms, is extended over the crystal. Consider however the opposite case in which $V_0 \gg t$. In this case you can show that

$$\frac{\alpha}{\beta} \approx \frac{V_0}{2t} \gg 1 \tag{7.33}$$

which means that the probability of finding the particle in the site 1 is much larger than the probability of finding the particle in site 2, that is, the particle is trapped inside of the well. If we now turn to the infinite crystal this argument suggests that there should be not only fluctuations in the phase of the wavefunction as we go from site to site but also fluctuations in the amplitude! These fluctuations become larger as the ration V_0/t increases. If V_0/t is very large we expect that the wavefunction of the electron on that particular site is very little affected by the presence of the other sites in its neighborhood and therefore should decay exponentially away from the site as the wavefunction (7.29) implies. Thus, our expectation is that for a given electron energy there must be a minimum value of V_0/t for which the electron becomes *localized.* This is the so-called *Anderson localization transition.* The critical value of V_0/t is a non-universal number which depends on the type of lattice, dimensionality and type of disorder in the material. In particular, it has been shown that in one dimension all the electronic states are localized. The fact that the localization depends on the energy of the electron is clear from Fig.7.4 since electrons with large energies do not care for the disordered potential but electrons with low energies will feel the bottom of the wells. Thus, for a given value of V_0/t above the critical value where localization happens, there is also a minimal energy E_C, below which all the states are localized and above which the states are extended. This is the so-called *mobility edge.* If we make a plot of the density of states of a such material it will look like the one on Fig.7.5. Below the mobility edge the states are localized and above it they are extended.

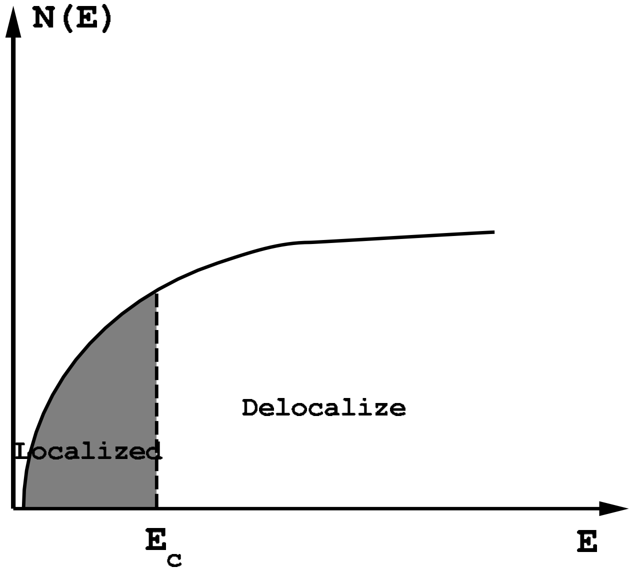

Figure 7.5: *Density of states for a disordered system.*

7.3 Problems

1. Using (7.11) and (7.14) and assuming $\epsilon_k = \hbar^2 k^2/(2m^*)$ prove (7.15).

2. Prove that in the Born approximation the scattering amplitude for the potential (7.26) is given by:

$$f_k(\theta) = -\frac{2m^* V_0 a^3/\hbar^2}{4(ka)^2 \sin^2(\theta/2) + 1}.$$

   Calculate the differential scattering cross-section and compare with (7.27).

3. Diagonalize the Hamiltonian (7.30) exactly and calculate α, β, E_A and E_B.

Chapter 8

Semiconductor Physics

8.1 Introduction

As we have seen in the previous chapters we can classify non-interacting electron systems as metals or insulators depending if they have a non-filled or filled band, respectively. Metals do not have a gap in the charge spectrum and can conduct electricity very well, insulators, however, cannot conduct charge if the temperature is much smaller than the gap E_g. When $K_B T$ at room temperature is of order of E_g then we can promote electrons from the lower band to the upper band and conduction is possible. In this case these systems are called semiconductors. It is quite amazing that the electronic revolution of the 20^{th} century was not driven by the development of metals but by the progress in the understanding of semiconductors. These are the basic elements for the production of transistors and other electronic elements in modern computers. It is therefore of interest to understand the physics of these systems.

The lower band in a semiconductor is called the *valence* band while the upper band is called the *conduction* band. Here we are going only to consider the case where the conduction band and the valence band can be described by:

$$E_k^c = E_c + \frac{\hbar^2 k^2}{2m_c}$$

$$E_k^c = E_v - \frac{\hbar^2 k^2}{2m_v} \tag{8.1}$$

where m_c and m_v represent the different curvatures of the conduction and valence band, respectively (notice that in terms of our definition of the effective mass the valence band has *negative* mass while the conduction band has positive mass. The bands described in (8.1) are not generic because many times the top of the valence band is not at the same point as the bottom of the conduction band. Many times they will be shifted by a finite momentum $\mathbf{Q}$. However, there are some systems where the two edges are at the same point in momentum space which facilitates their description. It is in fact very simple to generalize what we are going to describe here if this is not the case. Another simplification in (8.1) is that we are using infinite parabolic bands. As we know this approximation is only good if we are considering states at close to the edge of the bands. If the temperature becomes too large one starts to excite particles at higher energy states and the deviation from parabolicity becomes a serious factor. Here, however, we are going always to consider cases where $k_B T \leq E_g = E_c - E_v$ in which case we constrain ourselves to states close to the edges of the bands. For simplicity, from now on we are going to set $E_v = 0$ so that $E_g = E_c$.

It is a very simple exercise to calculate the density of states of a semiconductor as a function of energy. Using the results of the previous sections we find that for $E \geq E_g$:

$$N_c(E) = \frac{1}{2\pi^2}\left(\frac{2m_c}{\hbar^2}\right)^{3/2}\sqrt{E - E_g} \tag{8.2}$$

is the density of states for the conduction band and for $E \leq 0$ we have

$$N_v(E) = \frac{1}{2\pi^2}\left(\frac{2m_v}{\hbar^2}\right)^{3/2}\sqrt{-E} \tag{8.3}$$

is the density of states for the valence band. Observe that the density of states is zero everywhere in the gap, $0 < E < E_g$.

When an electron with momentum $\mathbf{k}_e$ is excited from the valence band to the conduction band it lives a hole behind in the valence band. Since the number of electrons do not change ewe can either describe the problem in terms of electrons or holes. The total momentum of the system before and after the transition is the same which implies that the momentum of the hole, $\mathbf{k}_h$, has to be $-\mathbf{k}_e$. Moreover, in describing the system in terms of holes the energy of the holes is obtained by inverting the valence band so that $E_h(\mathbf{k}_h) = -E(\mathbf{k}_e)$ which implies that the mass of the hole is given by $m_h = m_v$. Because the properties of semiconductors depend strongly on the number of electrons and holes we will be always talking about the number of such carriers in the system.

Let us calculate the number of electrons in the conduction band, n_c, and holes in the valence band, p_v, at a fixed temperature T. It is clear that

$$n_c = \int_{E_g}^{\infty} dE N_c(E) f(E) \tag{8.4}$$

and

$$p_v = \int_{-\infty}^{0} dE N_v(E) f(E) \tag{8.5}$$

where

$$f(E) = \frac{1}{e^{\beta(E-\mu)} + 1} \tag{8.6}$$

is the Fermi-Dirac distribution function ($\beta = 1/(k_B T)$). In what follows we are going to assume that the temperature is such that

$$\begin{aligned} E_g - \mu &\gg k_B T \\ \mu &\gg k_B T \end{aligned} \tag{8.7}$$

so that the Fermi-Dirac distribution function (8.6) can be replaced by

$$f(E) \approx e^{-\beta(E-\mu)} . \tag{8.8}$$

Because the chemical potential μ depends on the amount of charge in the system these conditions can only be checked *a posteriori*. We are going to see that this is indeed the case of interest.

Using (8.8) we can write (8.4) as

$$\begin{aligned} n_c &\approx \frac{1}{2\pi^2}\left(\frac{2m_c}{\hbar^2}\right)^{3/2} \int_{E_g}^{\infty} dE \sqrt{E - E_g} e^{-\beta(E-\mu)} \\ &= N_c(T) e^{-\beta(E_g-\mu)} \end{aligned} \tag{8.9}$$

where

$$N_c(T) = \frac{1}{2\pi^2}\left(\frac{2m_c k_B T}{\hbar^2}\right)^{3/2} \tag{8.10}$$

that should not be confused with the density of states (8.2). By the same token we can show that

$$p_v = P_v(T)e^{-\beta\mu} \tag{8.11}$$

where

$$P_v(T) = \frac{1}{2\pi^2}\left(\frac{2m_v k_B T}{\hbar^2}\right)^{3/2} . \tag{8.12}$$

Equations (8.9) and (8.11) give the density of electrons at the conduction band and holes in the valence band. Observe, however, that these expressions still depend on the chemical potential μ which is undefined. However, if we multiply (8.9) and (8.11) we find that

$$n_c p_v = N_c P_v e^{-\beta E_g} \tag{8.13}$$

which is independent on the chemical potential. This expression is very important in the theory of semiconductors.

8.1.1 Intrinsic Semiconductors

In intrinsic semiconductors the number of impurities is minimum. This implies that all the holes in the valence band are due to the excitation of electrons from the valence band to the conduction band. In this case it is obvious that:

$$n_c = p_v = n_i \tag{8.14}$$

where n_i is the intrinsic density of a semiconductor and can be obtained directly from (8.13):

$$n_i = \sqrt{N_c P_v} e^{-\beta E_g/2} . \tag{8.15}$$

This result implies that at finite temperatures the number of electrons in the conduction band or holes in the valence band is exponentially small with temperature.

Using (8.14) and (8.15) in (8.9) we can immediately obtain the value of the chemical potential;

$$\mu = \frac{E_g}{2} + \frac{3k_BT}{4}\ln\left(\frac{m_v}{m_c}\right) \tag{8.16}$$

which shows that at low temperatures the chemical potential is essentially at the center of the gap. Observe that in this case the conditions (8.7) are obeyed as long as

$$k_BT \ll E_g/2 \tag{8.17}$$

which is obeyed in most semiconductors where the energy gap is of order of a few electron volts.

8.2 Extrinsic Semiconductors

In the presence of external atoms the physics of a semiconductor can change profoundly. Imagine that we dope a semiconductor with another atom that has a valence +1 larger than the host atom (it gives up one electron more to the conduction band). In this case we can think of the external atom as simply the host atom with one electron and on proton more. This kind of atoms are called *donors*. At first sight this is equivalent to add a Hydrogen atom to the host material. If this was the case the extra electron would be strongly bound to the impurity atom with an energy of the order of $E_b = -me^4/\hbar^2 \approx -13.6$ eV. One has to remember, however, that a Hydrogen atom on a host material is not the same as a Hydrogen atom in vacuum. The properties of the motion of the electron are changed by the presence of other atoms and other electrons. A first consequence of the fact that there are other atoms in the system implies that the electron is moving in the external periodic potential of the lattice. Thus, the mass of the electron is not its bare mass but its effective mass, m_c, which can be much smaller than the bare mass (usually, $m_c \approx 0.1m$). This implies that the binding energy is decreased already by one order of magnitude. However, the biggest effect is not due to electron-ion interactions but due to the electron-electron interactions.

In a metal (a system with no gap) charges can move freely and therefore an external charge can be easily shielded (or screened) by a local change in the electron density. Thus, in a metal the potential seen by the extra electron would be essentially zero far away from the impurity and the electron would be free to go to the conduction band. In an perfect insulator at zero temperature charges cannot move freely because there is a gap in the charge spectrum and it requires a large amount of energy to move electrons around. This implies that in an insulator the potential seen by the electron is essentially the bare potential (Hydrogen atom) and it would be strongly bounded as discussed previously. However, in a semiconductor the situation is middle way between a metal and an insulator: there is charge motion because there are n_i electrons in the conduction band (see (8.15)) that can screen partially the potential generated by the external impurity. So the binding energy is neither as small as in a metal or large as in a insulator.

A way to quantify the amount of screening in a semiconductor is via the dielectric constant ϵ of the system. The effective potential seen by an electron due to an external charge $+e$ is given by

$$V(r) = -\frac{1}{\epsilon}\frac{e^2}{r} . \tag{8.18}$$

In semiconductors we can find $\epsilon \approx 20 - 100$. The consequence of (8.18) is that we can replace e^2 by e^2/ϵ. Putting together the effects of the electron-ion interaction and the electron-electron interactions we see that the binding energy of an electron by an impurity is of order:

$$E_b = -\frac{m_c}{m}\frac{1}{\epsilon^2}\frac{me^4}{\hbar^2} \tag{8.19}$$

which can be 10^{-4} times smaller than the biding energy of an electron in the Hydrogen atom! In fact for a host of Ga atoms (valence +4) with As impurities (valence +5) it is found that the binding energy is of order of 0.013 eV. For this reason, the radius of motion of the electrons is also increase from a few Bohr radius, a_0, to

$$r_0 = \frac{m}{m^*}\epsilon a_0 . \tag{8.20}$$

Thus, the conclusion is that in a semiconductor the impurity levels are weakly bound to the impurities and can be easily ionized. In other words, at $T = 0$ the impurity level is occupied by a single electron which can be promoted to the conduction band at finite temperatures. Because these are bound states of electrons they are localized just below the bottom of the conduction band by an amount given by E_b. We call $E_d = E_g + E_b$ the donor energy in a semiconductor and to a donor doped semiconductor we call it as *n-type*.

As we can dope electrons in a semiconductor we can also dope holes. We just have to choose an impurity atom that has a valence -1 relative to the host. In this case we are taking one proton and one electron from the host. The situation here is one of a localized negative charge with a hole bounded to it. For the same reasons described above this will lead to a bound state of holes above the top of the valence band. These are called *acceptor* states and the semiconductor is said to be *p-type*. Observe that the ionization of a acceptor state is equivalent to a hole going to the valence band or an electron moving from the valence band to the impurity level. At $T = 0$ the acceptor state has one hole but at finite temperatures such that $k_B T = E_a = -E_b$ (where m_c is replaced by m_v in (8.19)) an electron can be promoted to the acceptor state while a hole goes to the valence band.

Because the donor and acceptor states are such that $E_d, E_a \ll E_g$ one can easily dope the conduction or the valence bands with external charges. In this case the n_c and p_v as defined previously will change by an amount δn, that, is:

$$\delta n = n_c - p_v \tag{8.21}$$

which is equivalent to a change in the chemical potential of the system. Independent of this change the condition (8.13) is still valid. Using the definition of n_i given in (8.15) we can rewrite (8.13) as

$$n_c p_v = n_i^2 \,. \tag{8.22}$$

Solving (8.21) and (8.22) for n_c and p_v we find

$$n_c = \sqrt{\left(\frac{\delta n}{2}\right)^2 + n_i^2} + \frac{\delta n}{2}$$

$$p_v = \sqrt{\left(\frac{\delta n}{2}\right)^2 + n_i^2} - \frac{\delta n}{2} \qquad (8.23)$$

which gives the number of electrons and holes as functions of the intrinsic density and the extrinsic density of impurities. When $\delta n > 0$ there are more donors than acceptors and the system is n-type. If $\delta n < 0$ we have the opposite situation and the system is p-type.

In order to calculate the value of δn we need to know how many electrons (holes) are ionized and go to the conduction (valence) band and how many remain bounded to the impurity atoms. Let us call the density of donors N_d, the density of acceptors N_a, density of electrons bounded in the donor states n_d and the density of holes bounded in acceptor states p_a. From the fact that the total number of electrons and holes has to be conserved it is easy to see that:

$$\delta n = n_c - p_v = N_d - N_a - (n_d - p_a)\,. \qquad (8.24)$$

Since N_d and N_a are fixed for a given semiconductor we are left with the calculation of n_d and n_a.

Let us consider the problem of the donor levels first. The occupation N_j of the donor level can be $N_0 = 0$ (no electrons), $N_1 = 1$ (spin up or down) or $N_2 = 2$ (one electron with spin up and another with spin down). The doubly occupied state requires the donor state to be charged relative to the host and therefore is energetically not stable. We therefore disregard double occupancy. The donor state with zero electrons makes no contribution to the energy and therefore $E_0 = 0$. The donor state with one electron costs energy $E_1 = E_d$. Thus, in thermal equilibrium the average number of electrons in donor sites will be

$$\begin{aligned} n_d &= N_d \frac{\sum_j N_j e^{-\beta(E_j-\mu)}}{sum_j e^{-\beta(E_j-\mu)}} \\ &= N_d \frac{2e^{-\beta(E_d-\mu)}}{1+2e^{-\beta(E_d-\mu)}} \\ &= \frac{N_d}{\frac{e^{-\beta(E_d-\mu)}}{2}+1}\,. \qquad (8.25) \end{aligned}$$

Observe that because $E_d \approx E_g$ we expect that for $k_B T \gg E_g - E_d$ we must have $n_d \ll N_d$, that is, almost all the donor levels are ionized the electrons are in the conduction band.

In the case of acceptors the situation changes. The occupation N_j can be 0 holes (or two electrons $N_j = 2$), 1 hole (or one electron with either spin up or down, $N_j = 1$), or 2 holes (that is, zero electrons $N_j = 0$). The state with two holes is again stable because it is positively charged relative to the host. The energy of the state with one hole has energy zero, $E_1 = 0$, while the state with no holes costs energy E_a (this is the energy cost to take one electron from the valence band and put in the acceptor level, in this case, the hole that was bound in the acceptor level goes into the valence band). In this case, the number of *electrons* in the acceptor level can be calculated as before:

$$\begin{aligned} < n > &= \frac{2e^{-\beta(E_a-\mu)} + 2e^{\beta\mu}}{e^{-\beta(E_a-\mu)} + 2e^{\beta\mu}} \\ &= \frac{e^{\beta(\mu-E_a)} + 1}{\frac{e^{\beta(\mu-E_a)}}{2} + 1} . \end{aligned} \tag{8.26}$$

Since the maximum occupation of the acceptor level is 2, the average number of holes in an acceptor level is:

$$p_a = N_a(2 - < n >) = \frac{N_a}{\frac{e^{\beta(\mu-E_a)}}{2} + 1} . \tag{8.27}$$

Since we expect $E_a \ll k_B T \ll E_g$ we expect the acceptor levels to be fully ionized at room temperature. In this case the holes will be all essentially in the valence band.

The conclusion of these calculations is that we can approximate (8.24) by

$$\delta n \approx N_d - N_a \tag{8.28}$$

at room temperature. Substitution of (8.28) in (8.23) allows us to give a better definition to intrinsic and extrinsic semiconductor. The intrinsic semiconductor is the one in which $n_i \gg |N_d - N_a|$ and therefore

$$\begin{aligned} n_c &\approx n_i + \frac{N_d - N_a}{2} \\ p_v &\approx n_i - \frac{N_d - N_a}{2} \end{aligned} \tag{8.29}$$

and the number of electrons in the conduction band and holes in the valence band only change by a small amount. An extrinsic semiconductor is one such that $n_i \ll |N_d - N_a|$ so that

$$\begin{aligned} n_c &\approx N_d - N_a \\ p_v &\approx \frac{n_i^2}{N_d - N_a} \end{aligned} \tag{8.30}$$

for $N_d > N_a$ and

$$\begin{aligned} p_v &\approx N_a - N_d \\ n_c &\approx \frac{n_i^2}{N_a - N_d} \end{aligned} \tag{8.31}$$

for $N_d < N_a$. Thus, in an extrinsic semiconductor there is large difference between the number of charge carriers. It is exactly the flexibility in controlling the number of charge carriers that makes semiconductors so attractive for making devices.

8.3 The p-n junction

Let us consider the problem of a junction between two identical semiconductors with energy gap E_g so that one of them has N_a acceptors and the other has N_d donors. While the p-type semiconductor has free holes, the n-type has free electrons. Thus, when these two semiconductors are put in contact through an interface (or junction) we expect electrons and holes to flow between them and establish chemical equilibrium across the junction, that is, the chemical potential becomes the same in both sides of the junction. In order words, when these two different systems are put in contact a potential $\phi(x)$ appears in the system so the system remains in equilibrium. Here we are going to assume that the junction is an infinite plane and that the potential only varies in the x direction.

The first assumption of our description of the junction is that the potential varies smoothly across the junction and is such that very far away from the junction it vanishes. Consider, for instance, the p-type semiconductor to be at $x < 0$ and the n-type to be at $x > 0$. For

$x = -\infty$ the p-type semiconductor can be described as in the previous sections and there are N_a acceptors which neutralize the extra holes in the system. At $x = +\infty$, deep inside of the n-type semiconductor, there are N_d donors that neutralize the extra electrons in the system. Consider the potential $\phi(x)$ built up by the junction in the system. The energy of electrons (holes) can be rewritten as

$$\begin{aligned} E_d(x) &= E_d - e\phi(x) \\ E_a(x) &= E_a - e\phi(x) \end{aligned} \tag{8.32}$$

by the same token the edges of the conduction band, E_c, and the valence band, E_v, also change with $\phi(x)$ so that the chemical potential μ is the same in both sides of the junction:

$$\begin{aligned} E_c(x) &= E_g - e\phi(x) \\ E_v(x) &= -e\phi(x) \,. \end{aligned} \tag{8.33}$$

Because of this change in the energies of electrons and holes, their densities will also change. In fact, we can write:

$$\begin{aligned} n_c(x) &= N_c e^{-\beta(E_g - e\phi(x) - \mu)} \\ p_v(x) &= P_v e^{-\beta(\mu + e\phi(x))} \,. \end{aligned} \tag{8.34}$$

Thus, far away from the junction we can write:

$$\begin{aligned} n_c(x \to +\infty) &= N_d = N_c e^{-\beta(E_g - e\phi(+\infty) - \mu)} \\ p_v(x \to -\infty) &= N_a = P_v e^{-\beta(\mu + e\phi(-\infty))} \end{aligned} \tag{8.35}$$

and if we multiply the two equations we get:

$$\begin{aligned} N_a N_d &= N_c P_v e^{-\beta(E_g - e\delta\phi)} \\ \delta\phi &= \phi(+\infty) - \phi(-\infty) \end{aligned} \tag{8.36}$$

which can also be written as:

$$e\,\delta\phi = E_g + k_B T \ln\left(\frac{N_d N_a}{N_c P_v}\right) \tag{8.37}$$

which gives the total drop of the potential across the junction. Observe that because usually $E_g \gg k_B T$ the drop is essentially given by the gap in the semiconductor. Observe that the actual values of $\phi(\pm\infty)$ do not have especial physical significance because we can fix one of them to be zero. Only the difference of potential has physical meaning. Using (8.35) we can rewrite (8.34) as

$$\begin{aligned} n_c(x) &= N_d e^{-\beta e(\phi(+\infty)-\phi(x))} \\ p_v(x) &= N_a e^{-\beta e(\phi(x)-\phi(-\infty))} . \end{aligned} \tag{8.38}$$

The last equation gives the total drop in the potential across the junction but does not tell us how does the potential changes as a function of x. In order to know that we have to remember that the potential obeys the Poisson equation:

$$-\nabla^2\phi = -\frac{d^2\phi}{dx^2} = \frac{4\pi}{\epsilon}\rho(x) \tag{8.39}$$

where ϵ is the dielectric constant of the semiconductor and $\rho(x)$ is the local charge density in the system that can be written as $\rho = e\delta n$ where δn is given in (8.24):

$$\rho(x) = e(N_d(x) - N_a(x) - n_c(x) + p_v(x)) \tag{8.40}$$

where $N_d(x) = N_d\Theta(x)$ and $N_a(x) = N_a\Theta(-x)$ with $\Theta(x) = 1$ (-1) if $x > 0$ $(x < 0)$. If we use (8.40) and (8.38) into (8.39) it is clear that we will find a highly non-linear problem to solve. Instead we are going to simplify the problem and assume the that $\phi(x)$ varies only considerably in a region of size $-d_p < x < d_n$ across the junction (d_p and d_n have to be calculated), that is, for $x < -d_p$ we have

$$\phi(x) = \phi(-\infty) , \tag{8.41}$$

and for $x > d_n$ we have

$$\phi(x) = \phi(+\infty) . \tag{8.42}$$

In this case, using (8.38) it is clear that for $x > d_n$ we have $n_c(x) = N_d$ and for $x < -d_p$ we have $p_v(x) = N_a$. In this case we can break the (8.39) into different parts: for $x > d_n$ or $x < -d_p$ we have

$$\frac{d^2\phi}{dx^2} = 0 \tag{8.43}$$

while for $-d_p < x < 0$ we have

$$\frac{d^2\phi}{dx^2} = \frac{4\pi e}{\epsilon} N_a \tag{8.44}$$

and for $0 < x < d_n$ we have

$$\frac{d^2\phi}{dx^2} = -\frac{4\pi e}{\epsilon} N_d \,. \tag{8.45}$$

We have to solve these equations using the boundary conditions (8.41) and (8.42) and impose that the potential and its derivative are continuous across the interfaces at $x = -d_p$, $x = 0$ and $x = d_n$. A simple calculation shows that for $-d_p < x < 0$ we have

$$\phi(x) = \phi(-\infty) + \frac{2\pi e N_a}{\epsilon}(x + d_p)^2 \tag{8.46}$$

and for $0 < x < d_n$ we have

$$\phi(x) = \phi(+\infty) - \frac{2\pi e N_d}{\epsilon}(x - d_n)^2 \tag{8.47}$$

where

$$\begin{aligned} d_n &= \sqrt{\frac{N_a/N_d}{N_a + N_d}\frac{\epsilon\delta\phi}{2\pi e}} \\ d_p &= \sqrt{\frac{N_d/N_a}{N_a + N_d}\frac{\epsilon\delta\phi}{2\pi e}} \,. \end{aligned} \tag{8.48}$$

These equations provide the full profile of the potential generated by the junction between two semiconductors.

Suppose that an external potential V is applied to the junction. It is clear that this case the difference of potential can be either increased or decreased and that in general we must have

$$\delta\phi = \delta\phi_0 - V \tag{8.49}$$

where $\delta\phi_0$ is the potential difference in the absence of the applied potential and is given in (8.37). Because of this new potential we see that the regions of variation of potential given by d_p and d_n change to:

$$d_{n,p}(V) = d_{n,p}(0)\sqrt{1 - \frac{V}{\delta\phi_0}} \tag{8.50}$$

where $\delta_{n,p}$ is given in (8.48). Thus, by applying an external potential one can change the region where the electronic density varies because of the junction. This effect can be used to make a device called a rectifier.

In the absence of an external voltage V the number of electrons (or holes) crossing the junction in one direction is the same as the number of electrons crossing the junction in the opposite directions since the system is in equilibrium. Thus, if a hole current flowing from the p-type to the n-type is called $I_{h,0}$, there is an equal but opposite current from the n-type to the p-type. The same is true for the equilibrium electron current $I_{e,0}$. When a voltage V is applied to the junction we see that the total potential across the junction is modified according to (8.49). Since $e\delta\phi_0$ is the barrier height between the two sides of the junction when $V = 0$, it becomes clear that when a potential $-V < 0$ is applied to the n-type side of the barrier, the barrier height for holes is decreased relative to the other side. In this case, holes coming from p-type side of the junction see a smaller potential barrier while the holes on n-type side of the junction see essentially the same potential as before. In a tunneling junction the current increases exponentially with the barrier height since it depends on the tail of the wave-function below the barrier. Thus, while the current for holes going from the n-type to the p-type is I_0, the current for holes going from p-type to n-type is $I_0 e^{\beta eV}$ and thus, the net hole current in the system is:

$$I_f = I_{h,0}(e^{\beta eV} - 1)\,. \tag{8.51}$$

This is called the forward current. For electrons the situation is the same. When a potential $V > 0$ is applied to the n-type side of the junction the situation is reversed: holes moving from the p-type to the n-type side of the junction see a larger potential and its current is decrease do $I_{h,0}e^{-\beta eV}$ while holes moving from the n-type toward the p-type side of the junction have essentially the same current $I_{h,0}$. In this case the net current is simply

$$I_r = I_{h,0}(1 - e^{-\beta eV})\,. \tag{8.52}$$

This is called the reverse current. Thus, at zero temperature ($\beta \to \infty$) one sees $I_f \to \infty$ while $I_r = I_{h,0}$. This implies, that for positive voltages the current through the junction is very high while for negative voltages the current is essentially the equilibrium current. Because of this highly non-linear behavior of the current in regards to the sign of the voltage this device is called a rectifier.

8.4 Problems

1. Calculate $N_c(T)$ in (8.9) explicitly.
2. Show (8.29), (8.30) and (8.31).
3. Solve (8.39) explicitly and show that (8.46), (8.47) and (8.48) are indeed correct.
4. Consider a potential barrier between two metals 1 and 2. The potential profile of the barrier can be written as

   $$V(x) = \Theta(x)\Theta(a-x)\left[V_1 + (V_2 - V_1)\frac{x}{a}\right] \tag{8.53}$$

   where a is the thickness of the barrier and $V_1 > V_2$. In the absence of any applied external potential the electric current flowing from left to right, $I_{1\to 2} = I_0$, is equal but opposite to the current flowing from right to left ($I_{2\to 1} = -I_0$) because the two sides of the junction are in equilibrium, that is, $I_{1\to 2} + I_{2\to 1} = 0$.

   (*i*) Make a plot of the potential as a function of x.

   (*ii*) If a potential $V > 0$ is applied to the left side of the junction, what is the net current flowing in the system, that is, what is the value of $I = I_{1\to 2} + I_{2\to 1}$?

   (*iii*) If a negative potential $-V < 0$ is applied to the left side of the junction what is the net current in the system?

   (*iv*) Make a schematic plot of the current versus the voltage V at a finite temperature T. Can you use this device as a rectifier?

Chapter 9

Electron-phonon interactions

So far we have studied the problem of non-interacting systems such as free phonons and free electrons. In this chapter we are going to start the study of interacting systems and its relevance for condensed matter. It is very useful, however, to introduce a new language for the problem which will allow us to explore the physics of these systems. This new language is usually called "second quantization" and allows us to work directly with operators that act on states with well defined occupation number for one-particle states. In the next two sections we are going to discuss this new representation in detail for bosons and fermions, respectively. We are going to see that this new representation makes our life much easier when one needs to calculate physical quantities of experimental relevance.

9.1 Boson operators

As you know from the harmonic oscillator and the phonon problem discussed previously, it is possible to define creation, $b_i^\dagger$, and annihilation, b_i, operators which create and destroy bosons in a quantum state $|i\rangle$ with occupation $n_i = 0, 1, 2, ..., \infty$. These operators commute among themselves

$$\begin{aligned} \left[b_i, b_j^\dagger\right] &= \delta_{i,j} \\ [b_i, b_j] &= 0 \end{aligned} \tag{9.1}$$

and when applied to a state with a well defined occupation $|n_i\rangle$ give

$$\begin{aligned} b_i|n_i\rangle &= \sqrt{n_i}|n_i-1\rangle \\ b_i^\dagger|n_i\rangle &= \sqrt{n_i+1}|n_i+1\rangle \end{aligned} \tag{9.2}$$

which implies

$$b_i^\dagger b_i|n_i\rangle = n_i|n_i\rangle \tag{9.3}$$

and for obvious reasons the $N_i = b_i^\dagger b_i$ is called the number operator. A *many-body* state of bosons can be described in terms of the occupation of each state $|i\rangle$ with $i = 0, ..., \infty$ as

$$|n_0, n_1, n_2, ...\rangle = \frac{(b_0^\dagger)^{n_0}}{\sqrt{n_0!}}\frac{(b_1^\dagger)^{n_1}}{\sqrt{n_1!}}\frac{(b_2^\dagger)^{n_2}}{\sqrt{n_2!}}...|0\rangle \tag{9.4}$$

where $|0\rangle$ is the vacuum state with no bosons. The Hilbert space of all states which can be represented in this way is called Fock space.

A simple example is a problem of free bosons inside of a box of volume L^d (you can convince yourself that this is actually the case of phonons). In this case the eigenstates of the problem are plane waves

$$\phi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{L^{d/2}}e^{i\mathbf{p}\cdot\mathbf{r}} \tag{9.5}$$

where, due to periodic boundary conditions we have,

$$p_\alpha = \frac{2\pi n_\alpha}{L} \tag{9.6}$$

with $\alpha = x, y, z$. Thus the many-body state can be constructed from operators $b_{\mathbf{p}}$ in the way described before by giving an occupation $n_{\mathbf{p}}$ to each state. We can invert this picture to real space by defining the operator

$$\psi(\mathbf{r}) = \frac{1}{L^{d/2}}\sum_{\mathbf{p}} e^{-i\mathbf{p}\cdot\mathbf{r}}b_{\mathbf{p}} \tag{9.7}$$

which annihilates bosons in a superposition of momentum states with amplitude $e^{-i\mathbf{p}\cdot\mathbf{r}}/\sqrt{L^d}$ which is just the amplitude of having a particle annihilated at position $\mathbf{r}$. Since a superposition of plane waves is an envelope function in real space $\psi(\mathbf{r})$ actually destroys a particle at position $\mathbf{r}$. Similarly we can define the creation operator of a particle at position $\mathbf{r}$ as $\psi^\dagger(\mathbf{r})$. Another way to understand the physical meaning of $\psi^\dagger(\mathbf{r})$ comes from usual space representation of a state in Dirac notation, namely, $|\mathbf{r}\rangle$. In this representation we define the operation

$$|\mathbf{r}\rangle = \psi^\dagger(\mathbf{r})|0\rangle \tag{9.8}$$

that is, the operator $\psi^\dagger(\mathbf{r})$ creates the state $|\mathbf{r}\rangle$. This allows us to change representations using closure relations. By definition the state $|i\rangle$ is created by acting with $b_i^\dagger$ on the vacuum

$$|i\rangle = b_i^\dagger|0\rangle \tag{9.9}$$

where $|i\rangle$ forms a complete set, that is,

$$\sum_i |i\rangle\langle i| = 1\,. \tag{9.10}$$

Using the closure relation above, (9.8) and (9.9) we find

$$\begin{aligned} \psi^\dagger(\mathbf{r})|0\rangle &= \sum_i |i\rangle\langle i|\mathbf{r}\rangle \\ &= \sum_i \langle i|\mathbf{r}\rangle b_i^\dagger|0\rangle \end{aligned} \tag{9.11}$$

and since the vacuum is unique we have

$$\psi^\dagger(\mathbf{r}) = \sum_i \langle i|\mathbf{r}\rangle b_i^\dagger\,. \tag{9.12}$$

Observe now that $\langle i|\mathbf{r}\rangle$ is nothing but the complex conjugate of the projection of the state $|i\rangle$ into the space representation, that is, the single-particle wavefunction $\phi_i(\mathbf{r})$. Thus,

$$\psi^\dagger(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r}) b_i^\dagger\,. \tag{9.13}$$

This result is the generalization of (9.7) to any quantum state $|i\rangle$. Thus, we can always expand an operator in a complete basis of single-particle states. Observe that the wavefunction is a coefficient of the expansion. For this reason this process is called second quantization.

The commutation rules of these new operators defined in real space can be obtained immediately from (9.1),

$$\begin{aligned}\left[\psi(\mathbf{r}),\psi^\dagger(\mathbf{r}')\right] &= \frac{1}{L^d}\sum_{\mathbf{p},\mathbf{p}'} e^{-i\mathbf{p}\cdot\mathbf{r}+i\mathbf{p}'\cdot\mathbf{r}'}\left[b_\mathbf{p},b^\dagger_{\mathbf{p}'}\right]=\delta(\mathbf{r}-\mathbf{r}')\\ \left[\psi^\dagger(\mathbf{r}),\psi^\dagger(\mathbf{r}')\right] &= 0 \qquad (9.14)\end{aligned}$$

Thus we can represent the many-body state of N bosons in real space as

$$|\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N\rangle=\frac{1}{\sqrt{N!}}\psi^\dagger(\mathbf{r}_N)...\psi^\dagger(\mathbf{r}_2)\psi^\dagger(\mathbf{r}_1)|0\rangle\,. \qquad (9.15)$$

Observe that because of the commutation rule (9.14) we have the following identity

$$|\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N\rangle=|\mathbf{r}_2,\mathbf{r}_1,...,\mathbf{r}_N\rangle \qquad (9.16)$$

which implies that if we exchange two bosons the wavefunction does not change sign. Furthermore,

$$\psi^\dagger(\mathbf{r})|\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N\rangle=\sqrt{N+1}|\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N,\mathbf{r}\rangle \qquad (9.17)$$

so that adding a particle produces the state with the correct symmetry. We further notice that for a single particle one can recover the usual one-particle picture quite easily. Since $\psi^\dagger(\mathbf{r})$ creates a particle at position $\mathbf{r}$ the wavefunction of the particle can be obtained by (look at (9.8))

$$\begin{aligned}\langle\phi|\psi^\dagger(\mathbf{r})|0\rangle &= \phi^*(\mathbf{r})\\ \langle 0|\psi(\mathbf{r})|\phi\rangle &= \phi(\mathbf{r}) \qquad (9.18)\end{aligned}$$

where $\phi(\mathbf{r})$ is the usual wavefunction of the particle.

9.2 Fermion operators

Let us now go back to the problem of isolated atoms and ask if we can define creation and annihilation operators for fermions and what properties these operators should have. For the moment being we are going to consider the problem without spin. Consider a single state of an atom which by the Pauli principle can only be unoccupied $|0\rangle$ or occupied by a single electron $|1\rangle$ (which is the case we studied for the formation of the H_2^+ molecule). We define the creation and annihilation operators for fermions in the most intuitive way,

$$\begin{aligned} c|0\rangle &= 0 \\ c|1\rangle &= |0\rangle \\ c^\dagger|0\rangle &= |1\rangle \\ c^\dagger|1\rangle &= 0\,. \end{aligned} \tag{9.19}$$

The condition $c^\dagger|1\rangle = 0$ is the Pauli principle, that is, we cannot put two electrons in the same quantum state. Moreover, from (9.19) we can prove that

$$\begin{aligned} (cc^\dagger + c^\dagger c)|0\rangle &= |0\rangle \\ (cc^\dagger + c^\dagger c)|1\rangle &= |1\rangle \\ c^2|1\rangle = c|0\rangle &= 0 \\ (c^\dagger)^2|0\rangle = c^\dagger|1\rangle &= 0\,. \end{aligned} \tag{9.20}$$

Since the states $|0\rangle$ and $|1\rangle$ generate the whole Hilbert space of the problem we can immediately write

$$\begin{aligned} cc^\dagger + c^\dagger c = \{c, c^\dagger\} &= 1 \\ \{c, c\} = \{c^\dagger, c^\dagger\} &= 0 \end{aligned} \tag{9.21}$$

which are valid for all states of the problem. Observe that instead of commuting with each other we say that the electrons *anti-commute.* As for the case of the bosons we can define a number operator

$$N = c^\dagger c \tag{9.22}$$

which has the required properties

$$\begin{aligned} N|0\rangle &= c^\dagger c|0\rangle = 0 \\ N|1\rangle &= c^\dagger c|1\rangle = c^\dagger|0\rangle = |1\rangle\,. \end{aligned} \tag{9.23}$$

Thus we can define the state by its occupation, $|N\rangle$, as in the case of bosons.

Let us now consider the situation where we have two states with occupation N_0 and N_1 and the states can be labeled by their occupation, that is, $|N_0, N_1\rangle$. In this case we have four different states in the Hilbert space, namely, $|0,0\rangle$, $|1,0\rangle$, $|0,1\rangle$ and $|1,1\rangle$. We now define the creation and annihilation operators exactly as before, say c_0 and c_1. We define in analogy with the single level case,

$$\begin{aligned}
c_0|0,0\rangle &= 0 \\
c_0|1,0\rangle &= |0,0\rangle \\
c_0^\dagger|0,0\rangle &= |1,0\rangle \\
c_0^\dagger|1,0\rangle &= 0 \\
c_1|0,0\rangle &= 0 \\
c_1|0,1\rangle &= |0,0\rangle \\
c_1^\dagger|0,0\rangle &= |0,1\rangle \\
c_1^\dagger|0,1\rangle &= 0\,.
\end{aligned} \tag{9.24}$$

Observe that we have not defined how the operators behave when we apply them to a state which is already occupied, say, $c_0|1,1\rangle$. The reason is that we need to build into the operator language the correct symmetry of the problem, that is, the Pauli principle: the wavefunction has to be anti-symmetric when we exchange two electrons. Suppose we want to exchange two particles in the state $|1,1\rangle$. We have to perform the following operations: (*i*) we destroy, say, the particle in the state 1,

$$c_1|1,1\rangle = |1,0\rangle \tag{9.25}$$

which defines the way c_1 acts on this state; (*ii*) we destroy a particle in the state 0 following (9.24): $c_0|1,0\rangle = |0,0\rangle$; (*iii*) we create a particle in state 1 again using (9.24): $c_1^\dagger|0,0\rangle = |0,1\rangle$; (*iv*) and finally put a particle on state 0, that is, $c_0^\dagger|0,1\rangle$. This series of operations can be written as

$$c_0^\dagger c_1^\dagger c_0 c_1|1,1\rangle = c_0^\dagger|0,1\rangle \tag{9.26}$$

which by Pauli's principle must have the opposite sign of the state $|1,1\rangle$. Observe that this is possible if we impose the condition

$$c_1^\dagger c_0 = -c_0 c_1^\dagger \tag{9.27}$$

and use the number operators $N_0 = c_0^\dagger c_0$ and $N_1 = c_1^\dagger c_1$ as

$$N_0 N_1 |1,1\rangle = |1,1\rangle \,. \tag{9.28}$$

Thus we have,

$$c_0^\dagger |0,1\rangle = -|1,1\rangle \,. \tag{9.29}$$

By the same token we can show that

$$\begin{aligned} c_0^\dagger |1,1\rangle &= c_0 |0,1\rangle = 0 \\ c_1^\dagger |1,0\rangle &= |1,1\rangle \\ c_1^\dagger |1,1\rangle &= c_1 |1,0\rangle = 0 \\ c_0 |1,1\rangle &= -|0,1\rangle \,. \end{aligned} \tag{9.30}$$

The last equation requires that

$$c_1 c_0 = -c_0 c_1 \,. \tag{9.31}$$

From these considerations we see that the correct way to express the Pauli principle with creation and annihilation operators for different states is by imposing anti-commutation relations

$$\begin{aligned} \{c_i, c_j^\dagger\} &= \delta_{i,j} \\ \{c_i, c_j\} &= \{c_i^\dagger, c_j^\dagger\} = 0 \,. \end{aligned} \tag{9.32}$$

It is clear from the argument given above that the procedure can be extended to as many states as we wish. In this case the many-body state represented by electron occupation $n_0, n_1, n_2, ...$ with $n_i = 0, 1$ can be written as

$$|n_0, n_1, n_2, ...\rangle = (c_0^\dagger)^{n_0} (c_1^\dagger)^{n_1} (c_2^\dagger)^{n_2} ... |0\rangle \tag{9.33}$$

with the anti-commutation rules given in (9.32). Observe that the total number of particles in this state is well defined and it is an eigenstate of the operator

$$N = \sum_{i=0}^{\infty} c_i^\dagger c_i \,. \tag{9.34}$$

9.2.1 Free electrons in a box

Consider now, as in the case of bosons, the problem of free electrons in a box of volume L^d. Again the *one-body* eigenstates are plane waves and the momentum $\mathbf{p}$ and the spin $\sigma = \uparrow, \downarrow$ which are the quantum numbers of the problem. The operator that annihilates an electron in real space at position $\mathbf{r}$ and spin σ are written as

$$\psi_\sigma(\mathbf{r}) = \frac{1}{L^{d/2}} \sum_{\mathbf{p}} e^{-i\mathbf{p}\cdot\mathbf{r}} c_{\mathbf{p},\sigma} \,. \tag{9.35}$$

Using (9.32) it is simple to show that

$$\begin{aligned} \left\{\psi_\sigma(\mathbf{r}), \psi^\dagger_{\sigma'}(\mathbf{r}')\right\} &= \delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma,\sigma'} \\ \{\psi(\mathbf{r}), \psi_{\sigma'}(\mathbf{r}')\} &= 0 \end{aligned} \tag{9.36}$$

and the many-body state of N electrons is written as

$$|\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; ...; \mathbf{r}_N, \sigma_N\rangle = \frac{1}{\sqrt{N!}} \psi^\dagger_{\sigma_N}(\mathbf{r}_N)...\psi^\dagger_{\sigma_2}(\mathbf{r}_2)\psi^\dagger_{\sigma_1}(\mathbf{r}_1)|0\rangle \tag{9.37}$$

in complete analogy with the boson many-body state. Moreover, from the anti-commutation rules we obtain immediately

$$|\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; ...; \mathbf{r}_N, \sigma_N\rangle = -|\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1, ..., \mathbf{r}_N, \sigma_N\rangle \tag{9.38}$$

in accordance with Pauli's principle.

We can represent any operator in terms of creation and annihilation operators. Consider, for instance, number operator given in (9.34). Using (9.35) we can write

$$c_{\mathbf{p},\sigma} = \frac{1}{L^{d/2}} \int d^d r e^{i\mathbf{p}\cdot\mathbf{r}} \psi_\sigma(\mathbf{r}) \tag{9.39}$$

and from (9.34) one gets,

$$\begin{aligned} N &= \sum_{\mathbf{p},\sigma} c^\dagger_{\mathbf{p},\sigma} c_{\mathbf{p},\sigma} \\ &= \sum_{\sigma} \int d^d r \psi^\dagger_\sigma(\mathbf{r}) \psi_\sigma(\mathbf{r}) \end{aligned} \tag{9.40}$$

which allows us to define the *density* operator

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) = \sum_{\sigma} \psi^{\dagger}_{\sigma}(\mathbf{r})\psi_{\sigma}(\mathbf{r}) \tag{9.41}$$

since $N = \int d^d r \rho(r)$. The kinetic energy, K, of the electrons can also be obtained in the new operator language if we recall for each momentum $\mathbf{p}$ the kinetic energy is simply $\hbar^2 \mathbf{p}^2/(2m)$ and therefore one just has to count how many electrons with momentum $\mathbf{p}$ there are, that is,

$$K = \sum_{\mathbf{p},\sigma} \frac{\hbar^2 \mathbf{p}^2}{2m} c^{\dagger}_{\mathbf{p},\sigma} c_{\mathbf{p},\sigma} \,. \tag{9.42}$$

Using the identity (9.39) one can rewrite the kinetic energy as

$$K = \sum_{\sigma} \int d^d r \psi^{\dagger}_{\sigma}(\mathbf{r}) \left(-\frac{\hbar^2 \nabla^2}{2m}\right) \psi_{\sigma}(\mathbf{r}) \,. \tag{9.43}$$

Other operators like the current operator,

$$\mathbf{J}(\mathbf{r}) = -\frac{i\hbar}{2m} \left(\psi^{\dagger}_{\sigma}(\mathbf{r}) \nabla \psi_{\sigma}(\mathbf{r}) - (\nabla \psi^{\dagger}_{\sigma}(\mathbf{r}))\psi_{\sigma}(\mathbf{r})\right) \tag{9.44}$$

and the spin operator at position $\mathbf{r}$

$$\mathbf{S}(\mathbf{r}) = \sum_{\sigma,\sigma'} \psi^{\dagger}_{\sigma}(\mathbf{r}) \mathbf{S}_{\sigma,\sigma'} \psi_{\sigma'}(\mathbf{r}) \tag{9.45}$$

where $S_\alpha = \hbar\sigma_\alpha/2$ with $\alpha = x, y, z$ are written in terms of Pauli matrices σ_α, can be easily written in this new language.

9.2.2 Free electrons in a lattice

So far we have discussed the problem of free electrons in a box. We could, however, use any other basis of functions which is useful. For instance, in systems where the electrons are confined to be very close to the atoms (such as in the tight-binding approximation) we could use the atomic orbitals instead of the plane waves since the atomic quantum numbers describe better the physical situation. For simplicity let us go back to the H_2^+ molecule problem discussed in Chapter 1. In the second quantized language we have the states $|1\rangle$ and $|2\rangle$ which correspond to a state of the electron localized on atom 1 or atom 2, respectively. In terms of our new language the state of the whole system is given by $|n_1, n_2\rangle$ where n_i with $i = 1, 2$ gives the occupation of each atom. Acting on these states we have creation, $c_i^\dagger$, and annihilation, c_i, operators that obey the anti-commutation rules (9.32). The Hamiltonian of the system is given by (1.44) and (1.46). Observe that the states of the electron can be described in terms of the creation and annihilation operators as in (9.24). Thus, in our new language, the Hamiltonian is easily seen to be

$$H = E_0 \left(c_1^\dagger c_1 + c_2^\dagger c_2\right) - t\left(c_1^\dagger c_2 + c_2^\dagger c_1\right) . \tag{9.46}$$

Observe that the tunneling term makes the Hamiltonian non-diagonal. In order to diagonalize this Hamiltonian we define, in analogy with (1.56), the anti-bonding and bonding operators,

$$\begin{aligned} c_A &= \frac{1}{\sqrt{2}}(c_1 - c_2) \\ c_B &= \frac{1}{\sqrt{2}}(c_1 + c_2) \end{aligned} \tag{9.47}$$

which obey the anti-commutation rules. In terms of this new operators the Hamiltonian (9.46) becomes

$$H = (E_0 + t)c_A^\dagger c_A + (E_0 - t)c_B^\dagger c_B \tag{9.48}$$

as expected. Observe that the state of the system is now given by $|n_A, n_B\rangle$ and the ground state is simply $|0, 1\rangle$ in this new basis.

The molecule problem just described can be easily generalized to the case of the solid. Here we assume that the electrons to be in the tight binding approximation and only one atomic orbital A is involved. In complete analogy to the physics discussed at the end of Chapter 5 we only allow the electrons to hop between its nearest neighbor atoms. Let $\mathbf{R}_i$ be the atom site in a static lattice and $c_{i,\sigma}$ the electron operator that destroys an electron in a certain orbital at site i with spin σ. The Hamiltonian of the system as

$$H = E_A \sum_{i,\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} - t_A \sum_{<i,j>,\sigma} \left(c_{i,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{i,\sigma}\right) \tag{9.49}$$

where $< i, j >$ means that sites i and j must be nearest neighbor sites. The problem imposed by (9.49) can be easily solved by Fourier transforming the electron operator

$$c_{\mathbf{p},\sigma} = \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{p}\cdot\mathbf{R}_j} c_{j,\sigma} \tag{9.50}$$

observe that by the translation symmetry the momentum $\mathbf{p}$ is defined only in the first Brillouin zone. For simplicity we will assume a cubic lattice. You can easily show that in this case the Hamiltonian (9.49) can be written in terms of the operators in (9.50) as

$$H = \sum_{\mathbf{p},\sigma} E_{\mathbf{k}} c^{\dagger}_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} \tag{9.51}$$

with $E_{\mathbf{k}}$ given in (5.76).

9.3 Electron-phonon interaction

After all this math let us go back to the physical problem on how to treat the problem of lattice vibrations coupled to the electrons. Again we are using the Born-Oppenheimer approximation. The basic Hamiltonian can be split into, $H = H_e + H_p + H_{e-p}$ where H_e involves electrons only; H_p is given by (4.44) and H_{e-p} is the Coulomb interaction between electrons and the ions

$$H_{e-p} = \sum_{n,m} V_{e-i}(\mathbf{r}_{e,n} - \mathbf{r}_{i,m}) \tag{9.52}$$

where $\mathbf{r}_{e,n}$ is the position of the n^{th} electrons and $\mathbf{r}_{i,m}$ the position of the m^{th} ion. As previously we are going to assume that the departures of the ions from their equilibrium positions are very small so, as in Chapter 4, we write $\mathbf{r}_{i,m} = \mathbf{R}_m + \mathbf{u}_m$, and expand the interaction (9.52) to leading order in the deviations $\mathbf{u}$. Observe that to zeroth order in $\mathbf{u}$ we have only $\sum_{n,m} V_{e-i}(\mathbf{r}_{e,n} - \mathbf{R}_{i,m})$ which is the potential of the static periodic lattice which can be readily incorporated into the electron part H_e which in this case is given by (9.51). The fluctuation part of interest is,

$$\delta H_{e-p} \approx -\sum_{n,m} \mathbf{u}_m \cdot \nabla V_{e-i}(\mathbf{r}_{e,n} - \mathbf{R}_{i,m})\,. \tag{9.53}$$

If we Fourier transform the potential V_{e-i} to momentum space

$$V_{e-i}(\mathbf{r}) = \frac{1}{N}\sum_{\mathbf{p}} e^{-i\mathbf{p}\cdot\mathbf{r}} V_{e-i}(\mathbf{p}) \tag{9.54}$$

equation (9.53) becomes

$$\delta H_{e-p} \approx \frac{i}{N}\sum_{n,m,\mathbf{p}} e^{-i\mathbf{p}\cdot\mathbf{r}_{e,n}} e^{i\mathbf{p}\cdot\mathbf{R}_m} V_{e-i}(\mathbf{p})\mathbf{p}\cdot\mathbf{u}_m\,. \tag{9.55}$$

Observe, however, that,

$$\sum_n e^{-i\mathbf{p}\cdot\mathbf{r}_{e,n}} = \rho(\mathbf{p}) \tag{9.56}$$

where

$$\rho(\mathbf{p}) = \int d^d r \sum_{n=1}^{N} \delta(\mathbf{r}-\mathbf{r}_{\mathbf{e},\mathbf{n}}) e^{-i\mathbf{p}\cdot\mathbf{r}} = \int d^d r \rho(\mathbf{r}) e^{-i\mathbf{p}\cdot\mathbf{r}} \tag{9.57}$$

is the Fourier transform of the electronic density operator. Moreover, from (4.43), one has

$$\begin{aligned}\sum_m e^{i\mathbf{p}\cdot\mathbf{R}_m}\mathbf{u}_m &= \sum_{\mathbf{k}} \mathbf{e}_{\mathbf{k}} \sum_m e^{-i(\mathbf{k}-\mathbf{p})\cdot\mathbf{R}_m}\sqrt{\frac{\hbar}{2MN\omega_{\mathbf{k}}}}\left(a_{\mathbf{k}}+a^\dagger_{-\mathbf{k}}\right)\\ &= \sum_{\mathbf{G}} \mathbf{e}_{\mathbf{p}+\mathbf{G}}\sqrt{\frac{N\hbar}{2M\omega_{\mathbf{p}+\mathbf{G}}}}\left(a_{\mathbf{p}+\mathbf{G}}+a^\dagger_{-\mathbf{p}-\mathbf{G}}\right)\,. \end{aligned} \tag{9.58}$$

Using (9.56) and shifting the sum over the momentum we rewrite the electron-phonon interaction as

$$\delta H_{e-p} \approx \frac{1}{L^{d/2}}\sum_{\mathbf{p},\mathbf{G}} \tilde{V}(\mathbf{p}+\mathbf{G})\rho(\mathbf{p}+\mathbf{G})\left(a_{\mathbf{p}}+a^\dagger_{-\mathbf{p}}\right) \tag{9.59}$$

where

$$\tilde{V}(\mathbf{p}) = i\sqrt{\frac{\hbar}{2\rho_s\omega(\mathbf{p})}} V_{e-i}(\mathbf{p})\mathbf{p}\cdot\mathbf{e}_{\mathbf{p}} \tag{9.60}$$

and $\rho_s = NM/L^d$ is the *mass density* of the lattice. Now you could be asking why we have to go through all this math in order to get (9.59).

The answer is very simple if we go one step further and consider to rewrite the density operator in momentum eigenstates: using (9.41) and (9.35) we have

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_{\sigma} \psi^{\dagger}_{\sigma}(\mathbf{r})\psi_{\sigma}(\mathbf{r}) = \frac{1}{L^d}\sum_{\mathbf{p},\mathbf{k}} e^{i(\mathbf{k}-\mathbf{p})\cdot\mathbf{r}} c^{\dagger}_{\mathbf{k},\sigma}c_{\mathbf{p},\sigma} \\ &= \frac{1}{L^d}\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{p}} c^{\dagger}_{\mathbf{p}+\mathbf{q},\sigma}c_{\mathbf{p},\sigma} \qquad (9.61)\end{aligned}$$

where in the last line we have change variables to $\mathbf{q} = \mathbf{k}-\mathbf{p}$. Comparing (9.61) with (9.57) one has

$$\rho(\mathbf{q}) = \sum_{\mathbf{p},\sigma} c^{\dagger}_{\mathbf{p}+\mathbf{q},\sigma}c_{\mathbf{p},\sigma} \, . \qquad (9.62)$$

Thus the Hamiltonian, written in terms of creation and annihilation operators for electrons and phonons, becomes

$$\delta H_{e-p} \approx \frac{1}{L^{d/2}} \sum_{\mathbf{p},\mathbf{G},\mathbf{k},\sigma} \tilde{V}(\mathbf{p}+\mathbf{G}) c^{\dagger}_{\mathbf{k}+\mathbf{p}+\mathbf{G},\sigma}c_{\mathbf{k},\sigma}\left(a_{\mathbf{p}} + a^{\dagger}_{-\mathbf{p}}\right) . \qquad (9.63)$$

Let us consider first the case when $V_{e-i} = 0$ which is well-known to us: the ground state of the problem has the electrons form a Fermi sea with ground state energy, E_0 and Fermi momentum k_F which depends on the density as discussed in Chapter 5 and there are no phonons (since we are talking about zero temperature). Let us label this state by $|FS\rangle$. Observe that the perturbation has actually two different types of operators (consider only the case where $\mathbf{G} = 0$), namely, $c^{\dagger}_{\mathbf{k}+\mathbf{p},\sigma}c_{\mathbf{k},\sigma}a_{\mathbf{p}}$ and $c^{\dagger}_{\mathbf{k}+\mathbf{p},\sigma}c_{\mathbf{k},\sigma}a^{\dagger}_{-\mathbf{p}}$. In the first case a phonon with momentum $\mathbf{p}$ is destroyed, an electron state with momentum $\mathbf{k}$ is destroyed and an electron state with momentum $\mathbf{k}+\mathbf{p}$ is created. There is a simple way to represent this process graphically as in Fig.9.1 (a). Let us represent the momentum of the electron by a continuous line and the momentum of the phonon by a dashed line. Physically the process is one in which an electron *absorbs* a phonon and it is scattered to a new momentum state. In the second process an electron of momentum $\mathbf{k}$ emits a phonon of momentum $-\mathbf{p}$ and is scattered to a new momentum state $\mathbf{k}+\mathbf{p}$ as shown in Fig.9.1 (b). The diagrams which are shown in Fig.9.1 are

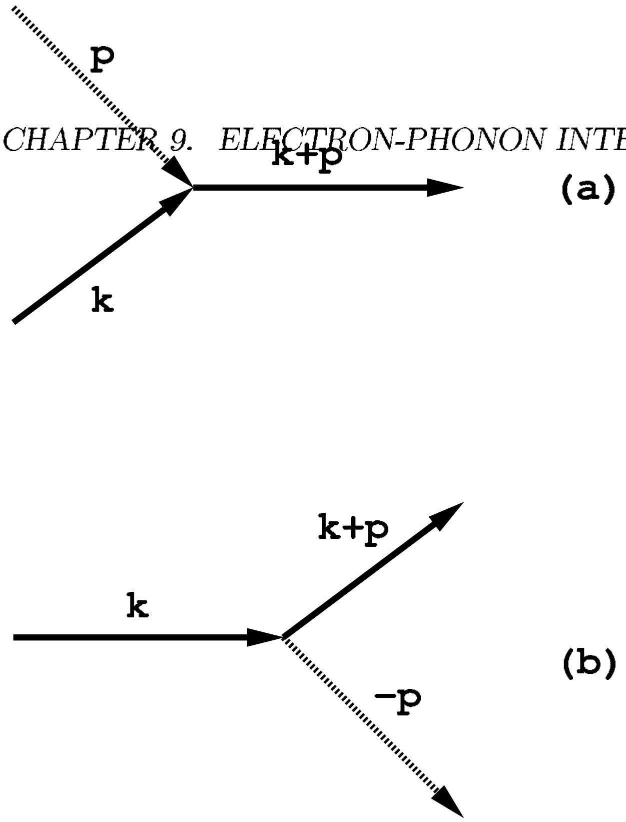

Figure 9.1: *Scattering process: (a) phonon absorption; (b) phonon creation.*

known as *Feynman diagrams* and they are very useful since they allow a clear representation of the physical process of scattering. Furthermore, they allow us to rewrite perturbation theory in very simple terms.

9.3.1 The optical case

An important type of coupling is the one between optical phonons with electrons. In the case of ionic crystals or polar semi-conductors the optical phonons produce a dipolar field when it oscillates. This dipolar field polarizes the electrons and leads to the coupling discussed here. To be more specific consider the displacement vector, **D**, which is written in terms of the electric field, **E**, and polarization vector, **P**, as

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}\,. \tag{9.64}$$

In the absence of free charges Maxwell's equations tell us that

$$\nabla \cdot \mathbf{D} = 0 \tag{9.65}$$

which, when Fourier transformed together with (9.64), leads to

$$\sum_{\mathbf{p}} \mathbf{p} \cdot (\mathbf{E}_{\mathbf{p}} + 4\pi \mathbf{P}_{\mathbf{p}}) = 0\,. \tag{9.66}$$

At long wavelengths ($G = 0$) and for longitudinal phonons both the electric field and the polarization field are parallel to $\mathbf{p}$ and we must have from (9.66) that

$$\mathbf{E}_{\mathbf{p}} = -4\pi \mathbf{P}_{\mathbf{p}}\,. \tag{9.67}$$

Observe now that the electric field will create a potential due to the electric dipole term which is simply given by

$$\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r}) = -i\sum_{\mathbf{p}} \mathbf{p} e^{i\mathbf{p}\cdot\mathbf{r}} \phi_{\mathbf{p}}\,. \tag{9.68}$$

$\phi(\mathbf{r})$ is the potential felt by the electrons due to the phonons. Comparing (9.67) with (9.68) we obtain

$$i\mathbf{p}\phi_{\mathbf{p}} = 4\pi \mathbf{P}_{\mathbf{p}} \tag{9.69}$$

which allows us to compute the potential once the polarization is known.

Since the displacement of the ions create a dipole field one must also have

$$\mathbf{P}_{\mathbf{p}} = \kappa e \mathbf{u}_{\mathbf{p}} = \kappa e \mathbf{e}_{\mathbf{p}} q_{\mathbf{p}}\,. \tag{9.70}$$

where κ is a real constant and $q_{\mathbf{p}}$ is the phonon displacement given in (4.24). Using $\mathbf{e}_{\mathbf{p}} = i\mathbf{p}/|\mathbf{p}|$ (since $\mathbf{e}^*_{\mathbf{p}} = \mathbf{e}_{-\mathbf{p}}$), together with (9.69) and (9.70) we find

$$\phi_{\mathbf{p}} = \frac{4\pi e\kappa}{|\mathbf{p}|} q_{\mathbf{p}} \tag{9.71}$$

or, in terms of the boson creation and annihilation operators, we find

$$\phi(\mathbf{r}) = \sum_{\mathbf{p}} \frac{4\pi e\kappa}{|\mathbf{p}|} e^{i\mathbf{p}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2\rho_s L^d \omega_0}} \left(a_{\mathbf{p}} + a^\dagger_{-\mathbf{p}}\right)\,. \tag{9.72}$$

Thus, the energy associated with this term is simply

$$\begin{aligned} H_{e-p} &= \sum_n e\phi(\mathbf{r}_{e,n}) = \int d^d r \rho(\mathbf{r}) e\phi(\mathbf{r}) \\ &= \frac{\alpha}{L^{d/2}} \sum_{\mathbf{p}} \frac{1}{|\mathbf{p}|} \rho(\mathbf{p}) \left(a_{\mathbf{p}} + a^{\dagger}_{-\mathbf{p}} \right) \end{aligned} \tag{9.73}$$

where

$$\alpha = 4\pi e^2 \kappa \sqrt{\frac{\hbar}{2\rho_s \omega_0}} \tag{9.74}$$

is the electron-phonon coupling constant. Observe that this result could be obtained from (9.60) with $V_{e-p}(p) \propto 1/p^2$ which is the case of the Coulomb potential in three dimensions. Substituting (9.62) into (9.73) and rewriting the whole Hamiltonian of the electron phonon problem we have

$$\begin{aligned} H &= \sum_{\mathbf{k},\sigma} E_{\mathbf{k}} c^{\dagger}_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \sum_{\mathbf{p}} \hbar\omega_0 a^{\dagger}_{\mathbf{p}} a_{\mathbf{p}} \\ &+ \frac{\alpha}{L^{d/2}} \sum_{\mathbf{p},\mathbf{k},\sigma} \frac{1}{|\mathbf{p}|} c^{\dagger}_{\mathbf{k}+\mathbf{p},\sigma} c_{\mathbf{k},\sigma} \left(a_{\mathbf{p}} + a^{\dagger}_{-\mathbf{p}} \right) \end{aligned} \tag{9.75}$$

which has the form described in (9.63).

Let us consider the effect of the phonons on the electron ground state in perturbation theory, that is, we write $H = H_0 + H_{e-p}$ where H_0 is the free electron-phonon problem and treat H_{e-p} as a perturbation. The ground state of H_0, as we said before, is a filled Fermi sea and no phonons are present. In first order we have $\langle FS|H_{e-p}|FS\rangle$ which vanishes since the perturbation does not conserve the number of phonons and therefore cannot have a finite expectation value. We have to rely on second order perturbation theory. For each value of **k** the shift in the energy is given by

$$\delta E = \sum_{n \neq 0} \frac{|\langle n|H_{e-p}|0\rangle|^2}{E^0_0 - E^0_n} \tag{9.76}$$

where $H_0|n\rangle = E^0_n|n\rangle$. Since H_{e-p} has one creation and one annihilation operator the excited states that participate in the sum (9.76) must have at least one excited phonon. Moreover, since $a_{\mathbf{p}}|0\rangle = 0$ because the ground state has no phonons we are left with $a^{\dagger}_{-\mathbf{p}}|0\rangle = |-\mathbf{p}\rangle$. Moreover, by applying the operator $c^{\dagger}_{\mathbf{k}+\mathbf{p},\sigma}c_{\mathbf{k},\sigma}$ to the ground state of the electron system we create a particle-hole pair exactly as in Fig.6.3. Thus we have to ensure that $|\mathbf{k}| < k_F$ and $|\mathbf{p}+\mathbf{k}| > k_F$ in order to get a finite result. Observe that the energy of such excited state is $E_n = E_0^0 - E_{\mathbf{k}} + E_{\mathbf{k}+\mathbf{p}} + \hbar\omega_0$. Thus, for each value of $\mathbf{k}$ one can write,

$$\delta E_{\mathbf{k}} = -2\frac{\alpha^2}{L^d}\sum_{\mathbf{p}}\frac{1}{\mathbf{p}^2}\frac{\Theta(k_F - |\mathbf{k}|)\,\Theta(|\mathbf{p}+\mathbf{k}| - k_F)}{E_{\mathbf{k}+\mathbf{p}} - E_{\mathbf{k}} + \hbar\omega_0} \tag{9.77}$$

and the total energy is, of course, given by $\delta E_0 = \sum_{\mathbf{k}} \delta E_{\mathbf{k}}$ (the factor of 2 comes from the two spin projections).

9.3.2 The polaron problem

Instead of evaluating the change in the energy for any value of k_F we are going to look at the case where there is just only one electron in the system. This is the so-called *polaron problem.* Of course this is only possible is the electron density is very low and $k_F \to 0$. In this case one does not have to worry about the step functions in (9.77). The ground state, of course, has one electron at the bottom of the band with energy $E_k = \hbar^2 k^2/(2m)$. We will consider the three dimensional case ($d = 3$). Transforming the sums into integrals we have

$$\begin{aligned}
\delta E_{\mathbf{k}} &= -\frac{4m\alpha^2}{\hbar^2}\int\frac{d^3p}{(2\pi)^3}\frac{1}{\mathbf{p}^2}\frac{1}{(\mathbf{p}+\mathbf{k})^2 - k^2 + P_0^2} \\
&= -\frac{4m\alpha^2}{(2\pi)^2\hbar^2}\int_0^{\pi} d\theta\sin\theta\int_0^{+\infty} dp\frac{1}{p^2 + 2pk\cos\theta + P_0^2} \\
&= -\frac{4m\alpha^2}{(2\pi)^2\hbar^2}\int_{-1}^{1} du\int_0^{+\infty} dp\frac{1}{p^2 + 2pku + P_0^2} \\
&= -\frac{4m\alpha^2}{(2\pi)^2\hbar^2 P_0}\int_{-1}^{1} du\int_0^{+\infty} dx\frac{1}{x^2 + 1 + 2(k/P_0)xu}
\end{aligned} \tag{9.78}$$

where $P_0 = \sqrt{2m\omega_0/\hbar}$. Since at low energies the momentum of the electron is small we perform an expansion in terms of k/P_0. We rewrite

$$\begin{aligned}\delta E_{\mathbf{k}} &\approx -\frac{4m\alpha^2}{(2\pi)^2\hbar^2 P_0}\int_0^{+\infty} dx \int_{-1}^{1} du \left(\frac{1}{x^2+1} + \frac{8}{3}(k/P_0)^2 u^2 \frac{x^2}{(1+x^2)^3}\right) \\ &= -\frac{4m\alpha^2}{(2\pi)^2\hbar^2 P_0}\left(\pi + \frac{\pi}{6}(k/P_0)^2\right) . \end{aligned} \tag{9.79}$$

Observe, therefore, that the total electron energy to second order in perturbation theory can be written as

$$E_{\mathbf{k}} \approx -E_0 + \frac{\hbar^2 k^2}{2m^*} \tag{9.80}$$

where

$$\begin{aligned} E_0 &= \frac{m\alpha^2}{2\pi\hbar^2 P_0} \\ m^* &= m\left(1 + \frac{2mE_0}{3\hbar^2 P_0^2}\right) . \end{aligned} \tag{9.81}$$

So we see that up to second order in perturbation theory the electron-phonon interaction only changes the mass of the electron and replaces it by an effective mass m^*. This is a result of the dragging of the lattice due to the electron motion.

9.3.3 The acoustic case

In many cases of interest we neglect all the reciprocal lattice vectors in (9.59) except $G = 0$. This is the long wavelength limit of the theory since the $G \neq 0$ represent short wavelengths. For *acoustic phonons* the polarization vector at long wavelengths is in the direction of the propagation of the wave, that is, $\mathbf{e}_{\mathbf{p}} = i\mathbf{p}/|\mathbf{p}|$. Moreover, in most solids the interactions between the ions and the electrons is very short ranged (since the electrons essentially feel only the atomic interaction). In this case we can replace $V_{e-i}(\mathbf{p}) = D$ by a constant. The electron-acoustic phonon interaction reduces to

$$\delta H_{e-p} \approx D \sum_{\mathbf{p}} \sqrt{\frac{\hbar}{2\rho_s L^d \omega_{\mathbf{p}}}} |\mathbf{p}| \rho(\mathbf{p}) \left(a(\mathbf{p}) + a^\dagger(-\mathbf{p})\right) . \tag{9.82}$$

Another elegant way to re-express this part of the Hamiltonian is to use (9.41), (4.85) and (4.43) and write

$$\delta H_{e-p} \approx \frac{D}{\sqrt{\bar{n}_s}} \sum_\sigma \int d^d r \int d^d r' K(\mathbf{r}-\mathbf{r}') \psi_\sigma^\dagger(\mathbf{r}) \psi_\sigma(\mathbf{r}) \phi(\mathbf{r}') \tag{9.83}$$

where $\bar{n}_s = N/V$ is the lattice density. From now on we fix $\bar{n}_s = 1$ for simplicity of notation. The kernel is given by

$$K(\mathbf{r}) = \frac{1}{L^d} \sum_{\mathbf{p}} |\mathbf{p}| e^{i\mathbf{p}\cdot\mathbf{r}} \tag{9.84}$$

The form of the kernel depends strongly on the dimensionality.

9.3.4 Solitons in one dimension

Consider the one-dimensional system, for instance. In this case the polarization vector is just 1 and from (9.60) we have

$$\begin{aligned} K(x) &= i \int_{-\infty}^{\infty} \frac{dp}{2\pi} p e^{ipx} = \frac{\partial}{\partial x} \int_{-\infty}^{\infty} \frac{dp}{2\pi} e^{ipx} \\ &= \frac{\partial \delta(x)}{\partial x}. \end{aligned} \tag{9.85}$$

Substituting the kernel into (9.83) and doing integration by parts one finds

$$\delta H_{e-p} \approx \frac{D}{\sqrt{\bar{n}_s}} \sum_\sigma \int dx \psi_\sigma^\dagger(x) \psi_\sigma(x) \frac{\partial \phi(x)}{\partial x}. \tag{9.86}$$

Observe that in this new formulation the electron-phonon problem is described by the Hamiltonian

$$\begin{aligned} H &= \sum_\sigma \int dx \psi_\sigma^\dagger(x) \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right) \psi_\sigma(x) + \int dx \left[\frac{\Pi^2}{2\rho_s} + \frac{c_s^2 \rho_s}{2}\left(\frac{\partial \phi}{\partial x}\right)^2\right] \\ &+ D \sum_\sigma \int dx \psi_\sigma^\dagger(x) \psi_\sigma(x) \frac{\partial \phi(x)}{\partial x}. \end{aligned} \tag{9.87}$$

Let us study the equations of motion for this Hamiltonian in the Heisenberg representation. You can easily show that the equations of motion are

$$\begin{aligned} i\hbar\frac{\partial\psi_\sigma(x,t)}{\partial t}+\frac{\hbar^2}{2m}\frac{\partial^2\psi_\sigma(x,t)}{\partial x^2} &= D\psi_\sigma(x)\frac{\partial\phi(x)}{\partial x} \\ \frac{\partial^2\phi(x,t)}{\partial t^2}-c_s^2\frac{\partial^2\phi(x,t)}{\partial x^2} &= \frac{D}{\rho_s}\sum_\sigma\frac{\partial}{\partial x}\left(\psi^\dagger_\sigma(x,t)\psi_\sigma(x,t)\right) \end{aligned} \tag{9.88}$$

Now observe that although we are dealing with equations of motion for operators we can *project* these equations into single particle states (since we are dealing with the problem of a single electron) as in (9.18). In this case instead of the adjoint of operators we are going to have the complex conjugate of the functions. Observe that the equation of motion for the phonon field has the form of a relativistic wave equation with a *light* velocity c_s. As we know from classical mechanics this equation has a traveling wave solution, that is, can be written as

$$\phi(x,t)=\phi(x\mp c_st)\,. \tag{9.89}$$

In order to explore this type of solution we change variables to $\chi = x - c_st$. Moreover, we are interested in the stationary states of the electron and therefore we look for a solution of the type

$$\psi(x,t)=\psi_0(x-c_st)e^{\frac{i}{\hbar}(mvx-E_0t)} \tag{9.90}$$

where ψ_0 is assumed to be real and v and E_0 are the velocity and energy of the electron. In terms of the new variables (9.88) becomes

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\psi_0}{d\chi^2}+D\frac{d\phi}{d\chi}\psi_0(\chi) &= \left(E_0-\frac{mv^2}{2}\right)\psi_0(\chi) \\ \frac{d\phi}{d\chi} &= -\frac{D}{\rho_s(c_s^2-v^2)}\psi_0^2(\chi) \end{aligned} \tag{9.91}$$

where we have integrated the second equation in (9.88) once. Observe that the first of these equations is very similar to the Schrödinger equation for a particle moving under the influence of a potential given by

$$V=D\frac{d\phi}{d\chi} \tag{9.92}$$

but the second equation allows to rewrite this potential as

$$V = -\frac{D^2}{\rho_s(c_s^2 - v^2)}\psi_0^2 \tag{9.93}$$

which shows that the potential itself depends on the wave-function. We say that the potential is determined in a *self-consistent* way. Observe that this potential is attractive if $v < c_s$ and repulsive if $v > c_s$. A very unusual situation since in non-interacting systems a situation like this one never occurs. Substituting the second equation of (9.91) into the first one finds

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_0}{d\chi^2} - \frac{D^2}{\rho_s(c_s^2 - v^2)}\psi_0^3(\chi) = \left(E_0 - \frac{mv^2}{2}\right)\psi_0(\chi) \tag{9.94}$$

which is the so-called *non-linear Schrödinger equation* which appears in many different fields of physics. You can show that the solution for this equation reads

$$\psi_0(\chi) = \frac{\sqrt{g}}{2} sech\left(\frac{g\chi}{2}\right) \tag{9.95}$$

where

$$g = \frac{m}{\rho_s(c_s^2 - v^2)}\left(\frac{D}{\hbar c_s/a}\right)^2 \tag{9.96}$$

and

$$E_0 = \frac{mv^2}{2} - \frac{\hbar^2 g^2}{8m}\,. \tag{9.97}$$

Observe that this solution exists only for $v < c_s$ and is unstable otherwise. In this case the potential felt by the electron is given by (9.93) and (9.95) as

$$V = -\frac{\hbar^2 g^2}{4m} sech^2\left(\frac{g\chi}{2}\right)\,. \tag{9.98}$$

Physically what is happening is that the electron is deforming the lattice around it creating a phonon cloud. This phonon cloud responds to the electron by creating a trapping potential which is given by (9.98). In this way, electron and phonon-distortion move together as a single object called a *soliton*. This situation is depicted on Fig.9.2.

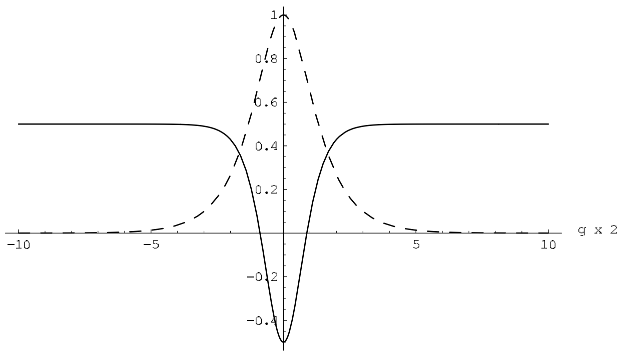

Figure 9.2: Polaron formation: electron is trapped in the self-consistent potential created by the phonons.

9.3.5 Retarded Interactions

We have seen that in the limit of empty band the main effect of the phonons on the electrons is a change in the electron mass. In a system with finite density this is no longer true. The reason being that phonons, like photons (which produce the Coulomb interaction), can induce interactions among the electrons. Phonons, however, are scalar fields while photons are vector fields. But besides this difference, from the point of view of the electrons, they have very similar effect. Here we are going to consider the dynamical problem of electrons interacting with phonons. So let us go back to the original electron-phonon Hamiltonian (9.63) in the long wavelength limit ($\mathbf{G} = 0$) together with the free theory,

$$\begin{aligned} H &= \sum_{\mathbf{k},\sigma} E_{\mathbf{k}} c^{\dagger}_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \sum_{\mathbf{p}} \hbar\omega_{\mathbf{p}} a^{\dagger}_{\mathbf{p}} a_{\mathbf{p}} \\ &+ \frac{1}{L^{d/2}} \sum_{\mathbf{p}} \tilde{V}(\mathbf{p}) \left(a_{\mathbf{p}} + a^{\dagger}_{-\mathbf{p}} \right) \rho(\mathbf{p}) \end{aligned} \tag{9.99}$$

In the Heisenberg representation the equation of motion for the phonon operators can be easily obtained

$$\begin{aligned} i\hbar \frac{da_{\mathbf{p}}}{dt} &= [a_{\mathbf{p}}, H] \\ &= \hbar\omega_{\mathbf{p}} a_{\mathbf{p}} + \frac{1}{L^{d/2}} \tilde{V}^*(\mathbf{p}) \rho^{\dagger}(\mathbf{p}) \end{aligned} \tag{9.100}$$

where we have used that $\tilde{V}(-\mathbf{p}) = \tilde{V}^*(\mathbf{p})$ and

$$\rho(-\mathbf{p}) = \sum_{\mathbf{k},\sigma} c^{\dagger}_{\mathbf{k}-\mathbf{p}} c_{\mathbf{k}} = \sum_{\mathbf{k},\sigma} c^{\dagger}_{\mathbf{k}} c_{\mathbf{k}+\mathbf{p}} = \rho^{\dagger}(\mathbf{p}) \tag{9.101}$$

a similar equation can be obtained for $a^{\dagger}_{\mathbf{p}}$ Equation (9.100) has the form of the equation for a forced harmonic oscillator and the solution is trivial

$$a_{\mathbf{p}}(t) = a_{\mathbf{p}}(t_0) e^{-i\omega_{\mathbf{p}}(t-t_0)} - \frac{i}{\hbar L^{d/2}} \tilde{V}^*(\mathbf{p}) \int_{t_0}^{t} dt' \rho^{\dagger}(\mathbf{p}, t') e^{-i\omega_{\mathbf{p}}(t-t')} \tag{9.102}$$

where t_0 is some arbitrary time. We are going to assume that the interaction between the electrons and phonons is switched on very slowly (that is, adiabaticly) so that in the infinitely distant past the interaction is off and one has the non-interaction problem. In this case one can pick $t_0 = -\infty$. Observe that in this case the first term in left hand side of (9.102) is strongly oscillating and can be neglected. The second term, however, has the electronic density on it and can produce some new effect.

If we substitute (9.102) into (9.99) we see that the Hamiltonian of the problem gets an extra piece which reads

$$H_{extra} = -\frac{1}{\hbar L^d} \sum_{\mathbf{p}} |\tilde{V}(\mathbf{p})|^2 \int_{-\infty}^{t} dt' \rho^\dagger(\mathbf{p}, t') \rho(\mathbf{p}, t) \sin\left[\omega_{\mathbf{p}}(t - t')\right] \tag{9.103}$$

Observe that this extra term only carries *electronic* degrees of freedom and moreover, it is *retarded.* The physical meaning should be clear by now: the phonons generate a retarded *density-density* interaction between the electrons. This is exactly what photons do indeed. The only difference is that for photons we can choose the Coulomb gauge where the interaction is instantaneous. But if instead one decides to use the Lorentz gauge one would generate an interaction which very much looks like (9.103). Moreover, the Hamiltonian is a conserved quantity and therefore can be defined at any time t from now on we pick $t = 0$. It is convenient to rewrite the problem in terms of Fourier components, that is, we define

$$\rho(\mathbf{p}, t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \rho(\mathbf{p}, \omega) \tag{9.104}$$

and use the identity

$$\int_{-\infty}^{t} dt' e^{i\Omega t'} = -i \frac{e^{i\Omega t}}{\Omega - i\epsilon} \tag{9.105}$$

where $\epsilon \to 0$. In this case (9.103) can be written as

$$H_{extra} = \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} \sum_{\mathbf{p}} \frac{|\tilde{V}(\mathbf{p})|^2 \omega_{\mathbf{p}} / (\hbar L^d)}{(\omega' - i\epsilon)^2 - \omega_p^2} \rho^\dagger(\mathbf{p}, \omega') \rho(\mathbf{p}, \omega) \tag{9.106}$$

The problem is not solved yet because we do not know what the electrons are doing. It could be very well that in (9.103) averages to zero.

In order to understand what is going on one needs to look at the electronic problem as well. In order to do that we are going to assume that the Fermi energy E_F of the electrons is much larger than any phonon energy (like the Debye energy, for instance) in this case the electron operator obeys the equation

$$i\hbar \frac{dc_{\mathbf{k},\sigma}}{dt} = [c_{\mathbf{k},\sigma}, H] \approx E_{\mathbf{k}} c_{\mathbf{k},\sigma} \tag{9.107}$$

since the corrections to this equation are of order $\tilde{V}/E_F$. Thus we write

$$c_{\mathbf{k},\sigma}(t) \approx c_{\mathbf{k},\sigma}(0) e^{-iE_{\mathbf{k}}t} \tag{9.108}$$

and therefore

$$\rho(\mathbf{p}, t) \approx \sum_{\mathbf{k},\sigma} c^{\dagger}_{\mathbf{k}+\mathbf{p},\sigma}(0) c_{\mathbf{k},\sigma}(0) e^{i(E_{\mathbf{k}+\mathbf{p}}-E_{\mathbf{k}})t} . \tag{9.109}$$

Thus we get from (9.104),

$$\rho(\mathbf{p}, \omega) \approx \sum_{\mathbf{k},\sigma} c^{\dagger}_{\mathbf{k}+\mathbf{p},\sigma}(0) c_{\mathbf{k},\sigma}(0)\ 2\pi\delta(E_{\mathbf{k}+\mathbf{p}} - E_{\mathbf{k}} - \omega) \tag{9.110}$$

and finally in (9.106)

$$H_{extra} = \sum_{\mathbf{p},\mathbf{k},\mathbf{k}',\sigma,\sigma'} \frac{|\tilde{V}(\mathbf{p})|^2 \omega_{\mathbf{p}}/(\hbar L^d)}{(E_{\mathbf{k}+\mathbf{p}} - E_{\mathbf{k}})^2 - \omega^2_{\mathbf{p}}} c^{\dagger}_{\mathbf{k},\sigma} c_{\mathbf{k}+\mathbf{p},\sigma} c^{\dagger}_{\mathbf{k}'+\mathbf{p},\sigma'} c_{\mathbf{k}',\sigma'} \tag{9.111}$$

which is the final result. Observe that the interaction appears in terms of four fermion operators. The reason for that is simple to understand in terms of the Feynman diagrams we used before. The process described in (9.111) is one in which two electrons, one with momentum $\mathbf{k}'$ and another with momentum $\mathbf{k} + \mathbf{p}$, are destroyed and two other electrons with momentum $\mathbf{k}' + \mathbf{p}$ and $\mathbf{k}$ are created. This is a scattering process where a momentum $\mathbf{p}$ is transferred between electrons. It is depicted on Fig.9.3.

The important point about the process described by Hamiltonian (9.111) is the fact that if $|E_{\mathbf{k}+\mathbf{p}} - E_{\mathbf{k}}| < \omega_{\mathbf{p}}$ it has a negative sign which implies *attraction*. Consider the case of optical phonons, for instance, where $\omega_{\mathbf{p}} = \omega_0$. In this case electrons states sufficiently close to the

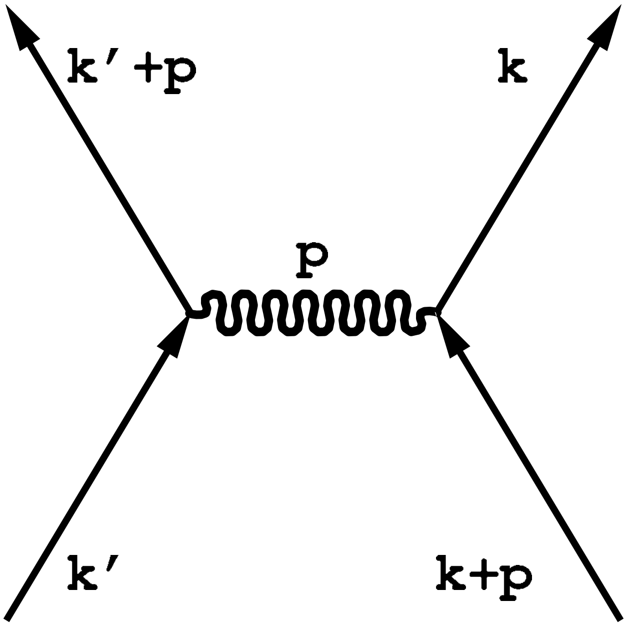

Figure 9.3: Scattering process mediated by phonons.

Fermi surface can feel an attraction between them. The constraint is that $E_F - \hbar\omega_0 < E_{\mathbf{k}+\mathbf{p}}, E_{\mathbf{k}} < E_F + \hbar\omega_0$ which implies that there is a region of thickness of size $2\hbar\omega_0$ around the Fermi surface where the electrons attract each other due to the interaction with phonons (see Fig.9.4). For acoustic phonons we just replace ω_0 by the Debye frequency ω_D but the result is essentially the same.

The physical reason for which the attraction appear can be traced back to the basic physics of the problem: as the electron moves it attracts the ions in the lattice. The lattice is an elastic medium which can propagate this information and therefore other electrons, which will also attracted by the lattice, will feel this information as if the electrons were attracting each other as depicted on Fig.9.5. The net effect is the attraction between electrons.

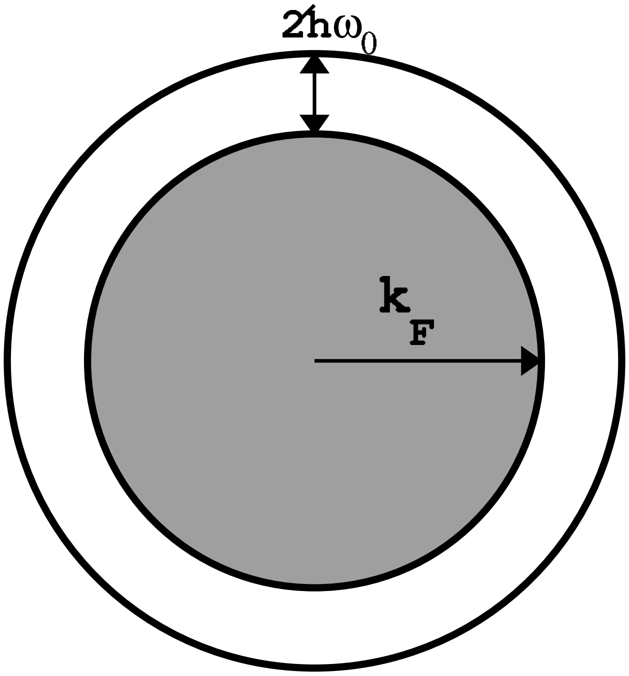

Figure 9.4: Region of attraction around the Fermi surface due to the electron-phonon coupling.

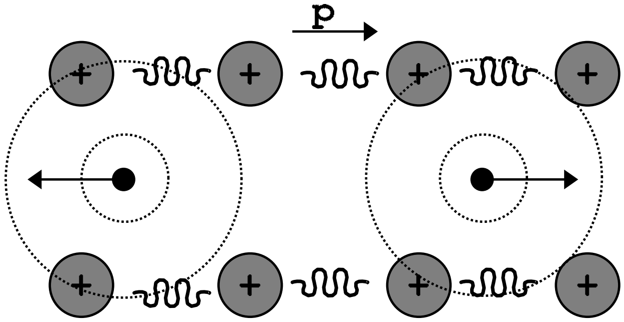

Figure 9.5: Physical coupling between phonons due to the lattice.

9.3.6 Cooper pairs

Although phonons can indeed induce attractive interactions among the electrons one has to remember that the electrons interact directly via the Coulomb repulsion. Thus the total interaction can be either attractive or repulsive, depending on the net interaction between the electrons. The possibility of having electrons attracting each other is quite "attractive" and we are going to explore this situation here. Suppose we have two electrons close enough to the Fermi surface such as they attract each other (as in Fig.9.4). The only role played by the other electrons in the system will be via the exclusion principle. In this case we are back to the problem of two particles with central attractive forces (exactly like in a H atom). We can therefore just do the simplest calculation which is to solve the problem in the center of mass of the system which we suppose to be at rest (so that the two electrons have *opposite* momentum). In this frame the problem reduces to the solution of the Schrödinger equation for the wavefunction of the pair, which we, call $\psi(\mathbf{r})$ where $\mathbf{r}$ is the relative coordinate between the electrons. The

Hamiltonian of the problem is simply

$$H = \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2m} + V(\mathbf{r}) = \frac{\mathbf{p}^2}{m} + V(\mathbf{r}) \tag{9.112}$$

where $\mathbf{p}$ is the relative momentum of the pair and $V(\mathbf{r})$ is the attractive interaction given in (9.111). In momentum space the Schrödinger equation becomes

$$\left(\frac{k^2}{m} - E_0\right)\psi(\mathbf{k}) + \frac{1}{L^d}\sum_{\mathbf{k}'} V(\mathbf{k}-\mathbf{k}')\psi(\mathbf{k}') = 0\,. \tag{9.113}$$

We will assume that the interaction is attractive and exists only when the electron is inside of the shell in Fig.9.4. Since $\mathbf{k}$ and $\mathbf{k}'$ are very close to k_F we will assume that the matrix element is essentially constant close to the Fermi surface, that is,

$$V(\mathbf{k}-\mathbf{k}') = -V_0\Theta(\omega_0 - |E_{k'}|)\,. \tag{9.114}$$

In this case the solution of (9.113) reads

$$\psi(\mathbf{k}) = \frac{\kappa}{\frac{k^2}{m} - E_0} \tag{9.115}$$

where

$$\kappa = \frac{V_0}{L^d}\sum_{\mathbf{k}'}\Theta(\omega_0 - |E_{k'}|)\psi(\mathbf{k}')\,. \tag{9.116}$$

Substituting (9.115) into (9.115) we find

$$1 = \frac{V_0}{L^d}\sum_{\mathbf{k}'}\frac{\Theta(\omega_0 - |E_{k'}|)}{\frac{(k')^2}{m} - E_0} \tag{9.117}$$

which is the equation for E_0. Using the density of states $\rho(\epsilon) = \sum_k \delta(\epsilon - k^2/m)/L^d$ the (9.117) becomes

$$1 = V_0\int_{2E_F}^{2(E_F+\hbar\omega_0)} d\epsilon \frac{\rho(\epsilon)}{\epsilon - E_0} \tag{9.118}$$

We will also assume that the density of states is constant over the interval of integration we have

$$1 = V_0\rho(E_F)\ln\left(\frac{2(E_F+\hbar\omega_0)-E_0}{2E_F-E_0}\right) \tag{9.119}$$

which can be easily solved

$$E_0 = 2E_F + \frac{2\hbar\omega_0}{1-e^{\frac{1}{\rho(E_F)V_0}}} \tag{9.120}$$

and this is the binding energy of the two electrons. Observe that when the attraction is turned off $V_0 \to 0$ one obtains the expected result, that is $2E_F$, which is energy of two electrons at the Fermi surface. Observe however that when $V_0 \neq 0$ we have $E_0 < E_F$, that is, the energy of the system is lowered by the formation of a **bound state.** What this implies is that the Fermi surface is *unstable* with attractive interactions since the electrons will lower the energy of the system by forming pairs. The binding energy of these pairs is simply

$$\Delta = 2E_F - E_0 = \frac{2\hbar\omega_0}{e^{\frac{1}{\rho(E_F)V_0}}-1} \tag{9.121}$$

which is a non-analytic expression in terms of the interaction and therefore cannot be obtained in perturbation theory (which always gives a power series expansion). These pairs are called *Cooper pairs.* Cooper pairs are the heart of a phenomena called *superconductivity* where pairs condense to form a macroscopic quantum state in clear violation of Pauli's principle. The reason for that is that Cooper pairs, being formed of two fermions, behave very much like free bosons and therefore can Bose-Einstein condense. This is a completely new state of matter. Observe, moreover, that the formation of Cooper pairs only requires an net attractive interaction between electrons and therefore does not care very much about the mechanism for the attraction. The electron-phonon interaction is only one of many mechanisms that can make the electron-electron interaction attractive. More on this in the future...

9.4 Problems

1. Using the orthogonality and closure of the states $|i\rangle$ and the creation operator in real space defined in (9.12) show that the operators $\Psi(\mathbf{r})$ and $\Psi^\dagger(\mathbf{r})$ obey bosonic commutation relations.

2. Show that for fermion operators we have

$$\begin{aligned} c_s|n_0, n_1, n_2, ...\rangle &= (-1)^{S_s}\sqrt{n_s}|n_0, n_1, ...n_s - 1, ...\rangle \\ c_s^\dagger|n_0, n_1, n_2, ...\rangle &= (-1)^{S_s}\sqrt{n_s + 1}|n_0, n_1, ...n_s + 1, ...\rangle \end{aligned}$$

   where

$$S_s = n_1 + n_2 + ... + n_{s-1} .$$

3. Show that for fermion operators

$$\begin{aligned} S_z(\mathbf{r}) &= \frac{\hbar}{2}\left(\psi_\uparrow^\dagger(\mathbf{r})\psi_\uparrow(\mathbf{r}) - \psi_\downarrow^\dagger(\mathbf{r})\psi_\downarrow(\mathbf{r})\right) \\ S_x(\mathbf{r}) &= \frac{\hbar}{2}\left(\psi_\uparrow^\dagger(\mathbf{r})\psi_\downarrow(\mathbf{r}) + \psi_\downarrow^\dagger(\mathbf{r})\psi_\uparrow(\mathbf{r})\right) \end{aligned}$$

   and using the anti-commutation rules between electrons show that

$$[S_x(\mathbf{r}), S_y(\mathbf{r}')] = i\hbar\delta(\mathbf{r} - \mathbf{r}')S_z(\mathbf{r}) . \qquad (9.122)$$

4. Show that (9.47) obeys the anti-commutation relations and prove that (9.48) is indeed correct. Write down all the states of the system from the new basis in terms of the old basis.

5. Using (9.50) prove that (9.51) is indeed correct.

6. Prove (9.79).

7. Expand (9.78) to all orders in k/P_0 and calculate the exactly value of the integral. What happens when k becomes large? What is the physical meaning of your result?

8. Prove (9.88).

9. Show that (9.95) is a solution of (9.94) by direct substitution.

10. (*i*) Find the displacement field profile, $\phi(x)$, for the static polaron ($v = 0$) by solving (9.91). What do you conclude about the lattice distortion around the electron?

    (*ii*) Show that due to translational invariance of the problem the polaron mass is given by

    $$M_0 = \rho_s \int_{-\infty}^{+\infty} dx \left(\frac{\partial \phi}{\partial x}\right)^2 \tag{9.123}$$

    and calculate the ratio between the bare electron mass m and M_0.

11. (*i*) In the polaron problem the potential felt by the electron is given in eq. (9.98). Consider the case where the polaron is at rest ($v = 0$) and solve the Schrödinger equation in this case (9.91). Show that one of the eigenstates is given by (9.95) with eigenenergy given in (9.97). (Hint: The solution can be found in the book by P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953)).

    (*ii*) Find all the other eigenstates of the problem and their respective eigenenergies. Show that these states are scattering states with finite phase shift $\delta(k)$. Give an expression for $\delta(k)$.

12. Obtain the time evolution of $a^\dagger_{\mathbf{p}}$ for the electron-phonon problem described by Hamiltonian (9.99).

13. Prove equation (9.102).

14. Prove that the Heavyside Theta function can be written as

    $$\Theta(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i} \frac{e^{i\omega t}}{\omega - i\epsilon}$$

    and from this result prove (9.105).

Chapter 10

Magnetism

One of the most important problems in condensed matter physics is the problem of magnetism. Magnetism is a pure quantum mechanical phenomenon since it has its origins on the spin of the electron, its orbital motion and the Coulomb interaction. Naturally magnetism is associated with the response of the electrons to a magnetic field. We have seen a free electron gas we have two main types of response, paramagnetic when the effect of the magnetic field is only the magnetic polarization of the medium and diamagnetic when the response of the medium is against the magnetic field. In isolated atoms in molecules a similar type of response appears, as we have seen in Chapter 1. It is however the interaction between different atoms in a solid that leads to the phenomenon of magnetic ordering that is observed in natural magnets like iron.

As we have seen in Chapter 1 the magnetic response of isolated atoms can be summarized in the three Hund's rules which are phenomenological rules which are based on energetic arguments. In short, the Hund's rules make statements about the magnetic ground state of many electron atoms when the Coulomb energy is minimized. In a solid, however, the atoms are localized in well defined positions which are given by the symmetry of the lattice. Because of that the atoms are subject to electromagnetic fields of other atoms. These are called crystal fields. We are going to discuss the effect of crystal fields and the Coulomb interaction among electrons in different atoms lead to the phenomena of magnetism in solids.

10.0.1 Crystal fields

As we have seen in Chapter 1 the degeneracy of a magnetic atom is lifted by the internal electron-electron interaction in an isolated atom. Moreover, spin-orbit effects lift the degeneracy even closer. The third Hund's rule state that the final degeneracy of an isolated atom with total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is $2J + 1$ due to the different projections of the J_z component of J. The spin-orbit interaction is very important in 4f-electron systems where the partially filled 4f shells lie deep inside of the ion and therefore are screened from the outside charges. In other systems with 3d- or p-shells the effect of the interaction between the electrons and other nuclei is very important because these orbitals are exposed to the electrostatic potential of other atoms in the lattice. Thus, in the case of transition metals with d shells the lattice potentials are more important than the than the spin-orbit effects and should be studied first (that is, Hund's third rule is not applicable). In this case the degeneracy of the $2l + 1$ states can be lifted by the Coulomb interaction as we show in Fig.10.1. In some systems the *crystal field* interaction is more important than the third Hund's rule and one has to take the effect into account first. Observe that in this case the two first Hund's rules still apply and therefore we will have a degeneracy of $(2S + 1)(2L + 1)$. Since the electrostatic field of the lattice couples only to the charge degrees of freedom only the angular momentum degrees of freedom will change. If the crystal field is very asymmetric then the degeneracy of the angular momentum is lifted and as a result the expectation value of the angular momentum has to vanish, that is, $\langle \mathbf{L} \rangle = 0$, even though we still have $\langle \mathbf{L}^2 \rangle = L(L + 1)$. Consider, for instance the case of p-orbitals in a free atom. These orbitals can be written as $xf(r)$, $yf(r)$ and $zf(r)$ where x, y, z refers to the first Legendre polynomial ($l = 1$) and $f(r)$ is the solution of the radial equation. In a free atom these orbitals are degenerate. It is easy to show that these orbitals do not carry well defined angular momentum projection which are obtained as linear combinations of them: $(x + iy)f(r)$ with $m_z = +1$, $zf(r)$ with $m_z = 0$ and $(x - iy)f(r)$ with $m_z = -1$. But since the orbitals are degenerate it really does not matter how we represent them. In the presence of an external electric field the energy of the orbitals is split as in Fig. 10.1. If the electric field is very asymmetric one can split the energy of all the states. Consider the case where the orbital $yf(r)$ has the lower energy. In this case the angular momentum of this state can be computer immediately

$$\langle L^z \rangle = \int d\mathbf{r} y f(r) \frac{1}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) y f(r) \tag{10.1}$$

but observe that

$$\begin{aligned} (\langle L^z \rangle)^* &= -\langle L^z \rangle \\ \langle (L^z)^\dagger \rangle &= -\langle L^z \rangle \\ \langle L^z \rangle &= -\langle L^z \rangle \end{aligned} \tag{10.2}$$

and therefore $\langle L^z \rangle = 0$. Where in the first line above we have integrated by parts and in the second line we used the fact that L^z is a hermitian. From the classical point of view this can be understood as the precession of the angular momentum in the crystal field such that its magnitude is fixed but it has zero average. In this case we have $\langle \mathbf{J} \rangle = \langle \mathbf{S} \rangle$ which is known as *quenching* of the orbital angular momentum and is observed in transition metals.

Thus, in 3d electron systems the spin orbit interaction is a perturbation on the crystal field effects. Let us consider this problem more closely. The spin orbit effect is described by a Hamiltonian (1.26). Let us consider the case in which an external magnetic field is applied where we add (1.19) and get

$$H_P = \lambda \mathbf{L} \cdot \mathbf{S} + \mu_B \mathbf{B} \cdot (\mathbf{L} + 2\mathbf{S}) \tag{10.3}$$

which we will consider as a perturbation of the problem in the presence of a crystal field.Moreover, we are only interested in the spin degrees of freedom since $\langle \mathbf{J} \rangle = \langle \mathbf{S} \rangle$. Therefore we will do perturbation theory on the orbital degrees of freedom alone. Let $|0\rangle$ be the ground state of the problem in a crystal field. Observe that first order perturbation theory gives

$$\delta E_1 = 2\mu_B \mathbf{B} \cdot \mathbf{S} \tag{10.4}$$

due to the quenching of the orbital angular momentum. Let us consider now the second order perturbation theory in the absence of the field.

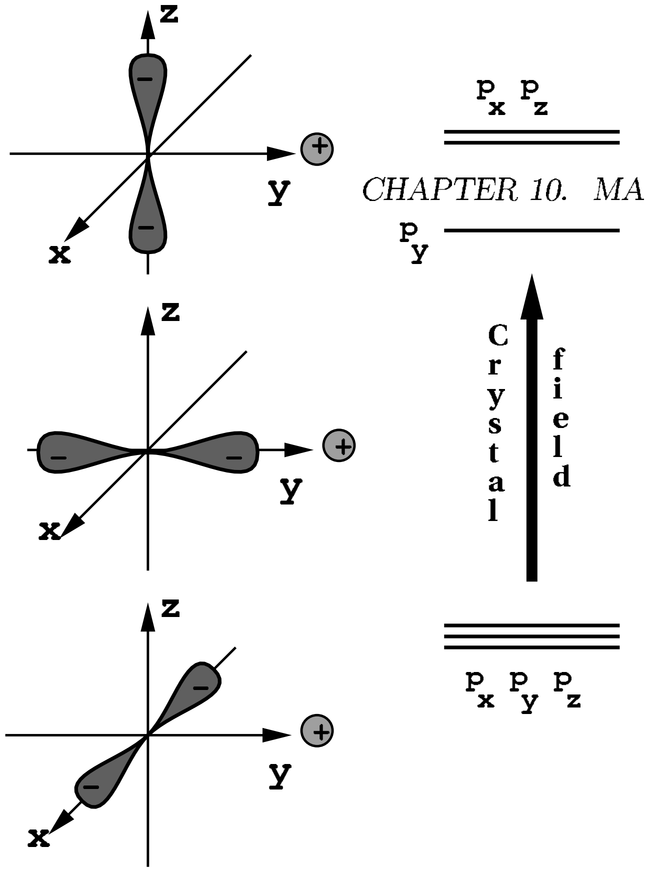

Figure 10.1: *Crystal field effects for a p-orbital.*

If $|n\rangle$ is an orbital eigenstate of the system in the presence of crystal field effects then second order perturbation theory leads to a change in energy given by

$$\begin{aligned}
\delta E_2 &= \lambda^2 \sum_{n\neq 0} \frac{|\langle n| \sum_a S_a L_a |0\rangle|^2}{E_0 - E_n} \\
&= \lambda^2 \sum_{n\neq 0} \sum_{a,b} \frac{\langle n|L_a|0\rangle\langle n|L_b|0\rangle}{E_0 - E_n} S_a S_b \\
&= -\sum_{a,b} \Gamma_{a,b} S_a S_b \qquad (10.5)
\end{aligned}$$

where

$$\Gamma_{a,b} = \lambda^2 \sum_{n\neq 0} \frac{\langle n|L_a|0\rangle\langle n|L_b|0\rangle}{E_n - E_0} \,. \qquad (10.6)$$

Observe that in this case the spin-orbit effect induces an interaction between different components of the spin. This is called *single ion* *anisotropy.* If you take the principal axis of the crystal as x, y and z and express the components of $\Gamma_{a,b}$ as Γ_x, Γ_y and Γ_z, you can show that (10.5) can be written as

$$\begin{aligned} \delta E_{so} &= -\frac{S(S+1)}{3}(\Gamma_x + \Gamma_y) + \frac{(\Gamma_x + \Gamma_y - 2\Gamma_z)}{2} S_z^2 \\ &+ \frac{(\Gamma_y - \Gamma_x)}{2}\left(S_x^2 - S_y^2\right) . \end{aligned} \tag{10.7}$$

The first term in (10.7) is just an overall shift of the energy of the problem. The second term, because it appears as a sum of two Γ is usually more important than the last term which appears with the difference. For integer S the term with S_z^2 splits the energy levels into doubly degenerate levels with $S_z = \pm S, \pm(S-1), ..., \pm 1$ and a non-degenerate level with $S_z = 0$. For half-odd integer S we will still have doubly degenerate levels with $S_z = \pm S, \pm(S-1), ..., \pm 1/2$. The term proportional to $S_x^2 - S_y^2 \propto S_+^2 + S_-^2$ induces transitions between states that have $\delta S_z = \pm 2$. Thus, for integer S this term will lift the degeneracy of the degenerate states which can be linked by ± 2. For instance, for $S = 1$ the $S_z = 0$ state is non-degenerate but the $S_z = \pm 1$ will have its degeneracy lifted by the spin-orbit. For a half-odd integer S the degeneracy persists because δS_z is always an odd integer, thus, the degenerate ground state has always $\delta S_z = \pm 1$ and therefore are not linked by the perturbation. Thus the degeneracy persists even with spin-orbit coupling. The case with integer S corresponds to an even number of electrons in the atom while a half-odd integer S corresponds to an odd number of electrons. So for atoms with an odd number of electrons even in the presence of crystal fields and spin-orbit interactions the ground state is a doublet. This degeneracy has its origin on the time reversal symmetry.

Observe that although spin-orbit and crystal fields reduce considerably the symmetry of the atom there is one symmetry that persists in the absence of external magnetic fields: *time reversal symmetry.* Time reversal symmetry changes $t \to -t$ and therefore changes $\mathbf{p} \to -\mathbf{p}$ but keeps the position invariant, that is, $\mathbf{r} \to \mathbf{r}$. It implies that by inversion of the time direction the angular momentum is reversed, that is, $\mathbf{L} \to -\mathbf{L}$. Classically it just means that we reverse the direction of rotation. Time reversal also inverts the spin, $\mathbf{S} \to -\mathbf{S}$, because spin and angular momentum are indistinguishable in quantum mechanics. In the absence of magnetic fields the Hamiltonian is invariant under time reversal. Indeed, consider the general problem of an electron moving under the influence of an external potential and the spin-orbit effect,

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + \lambda \mathbf{S} \cdot \mathbf{L} \tag{10.8}$$

and it is clear that under time reversal the Hamiltonian is invariant. Observe that the addition of a magnetic field leads to a new term of the form $\mathbf{B} \cdot (\mathbf{L} + 2\mathbf{S})$ which is not invariant under time reversal since this term changes sign. We can obviously define a quantum mechanical operator K such that

$$\begin{aligned} K|\mathbf{r}\rangle &= |\mathbf{r}\rangle \\ K|\mathbf{p}\rangle &= |-\mathbf{p}\rangle \\ K|\mathbf{S}\rangle &= |-\mathbf{S}\rangle \end{aligned} \tag{10.9}$$

and it is clear that

$$[H, K] = 0 \tag{10.10}$$

which means that if $|\psi\rangle$ is an eigenstate of the Hamiltonian with energy E ($H|\psi\rangle = E|\psi\rangle$) then $K|\psi\rangle$ is also an eigenstate of the system with the same energy. This simple exercise in group theory proves that even if all the symmetries in a quantum mechanical systems are broken and no magnetic fields are present the ground state of the system has to be doubly degenerate, that is, it must be a doublet. This is called *Kramers theorem.*

In the presence of an external magnetic field the energy shift of the ground state is given by

$$\delta E = \delta E_{so} + \sum_{a,b} \left[\mu_B g_{a,b} B_a S_b - \left(\frac{\mu_B}{\lambda}\right)^2 B_a \Gamma_{a,b} B_b \right] \tag{10.11}$$

where

$$g_{a,b} = g_0 \left(\delta_{a,b} - \frac{1}{\lambda} \Gamma_{a,b} \right) \tag{10.12}$$

is the so-called g-tensor. Observe that (10.11) has a deep physical meaning: when a magnetic field is applied to an atom the spin does not necessarily responds in the direction of the field because of the spin-orbit coupling. The magnetization of the atom is

$$\begin{aligned} M_a &= -\frac{\partial E}{\partial B_a} \\ &= -\sum_b \left(\mu_B g_{a,b} \langle S_b \rangle - 2 \left(\frac{\mu_B}{\lambda} \right)^2 \Gamma_{a,b} B_b \right) \end{aligned} \tag{10.13}$$

and it depends on the matrix $\Gamma_{a,b}$. Moreover, the susceptibility is now a tensor and it is defined as

$$\chi_{a,b} = \frac{\partial M_a}{\partial B_b} = 2 \left(\frac{\mu_B}{\lambda} \right)^2 \Gamma_{a,b} \tag{10.14}$$

is the induced orbital momentum which arises from the spin-orbit coupling. Observe that in this case an applied field in one direction can have a response in another different directions. This is a direct consequence of the crystal fields. Observe that in this case the magnetic moment of the atom can be written as

$$m_a = \mu_B \sum_b g_{a,b} \langle S_b \rangle \tag{10.15}$$

as a consequence of spatial anisotropy. Thus, in this case the application of the magnetic field in one direction can lead to a magnetization in another direction.

10.1 The molecule problem

The next step after the isolated atom problem is to study the case of a few atoms, that is, the molecule. This kind of study will help us to understand more complicated cases of the crystal later on.

10.1.1 Heitler-London theory

We have seen in Chapter 1 that in a H_2 atom the electrons that form the bonding orbital need to have their spin anti-parallel to each other due to the Pauli principle. Therefore the system does not have any net magnetic moment. As we have seen in Chapter 7 this can be described by the Hamiltonian (9.46)

$$H_0 = -t \sum_{\sigma=\uparrow,\downarrow} \left(c^\dagger_{1,\sigma} c_{2,\sigma} + c^\dagger_{2,\sigma} c_{1,\sigma}\right) . \tag{10.16}$$

where $c_{i,\sigma}$ ($c^\dagger_{i,\sigma}$) destroys (creates) an electron in a localized state at atom i ($i = 1, 2$) with spin σ ($\sigma =\uparrow, \downarrow$). As before we can diagonalize the problem by a simple linear combination of electron operators

$$\begin{aligned} c_{A,\sigma} &= \frac{1}{\sqrt{2}}(c_{1,\sigma} - c_{2,\sigma}) \\ c_{B,\sigma} &= \frac{1}{\sqrt{2}}(c_{1,\sigma} + c_{2,\sigma}) . \end{aligned} \tag{10.17}$$

In terms of this new operators the Hamiltonian (10.16) becomes

$$H = t \sum_{\sigma=\uparrow,\downarrow} \left[c^\dagger_{A,\sigma} c_{A,\sigma} - c^\dagger_{B,\sigma} c_{B,\sigma}\right] \tag{10.18}$$

Observe that in this case the ground state of the problem depends on the sign of the tunneling energy t. If the tunneling decreases the energy of the system, that is, $t > 0$, the state of lower energy is indeed the bonding state. The ground state for the case where two electrons are present is

$$\begin{aligned} |\Psi_B\rangle &= c^\dagger_{B,\uparrow} c^\dagger_{B,\downarrow} |0\rangle \\ &= \frac{1}{2}\left(c^\dagger_{1,\uparrow} c^\dagger_{1,\downarrow} + c^\dagger_{1,\uparrow} c^\dagger_{2,\downarrow} + c^\dagger_{2,\uparrow} c^\dagger_{1,\downarrow} + c^\dagger_{2,\uparrow} c^\dagger_{2,\downarrow}\right) |0\rangle \\ &= \frac{1}{2}\left(c^\dagger_{1,\uparrow} c^\dagger_{1,\downarrow} + c^\dagger_{1,\uparrow} c^\dagger_{2,\downarrow} - c^\dagger_{1,\downarrow} c^\dagger_{2,\uparrow} + c^\dagger_{2,\uparrow} c^\dagger_{2,\downarrow}\right) |0\rangle \end{aligned} \tag{10.19}$$

where $|0\rangle$ is the empty state. Notice that in the last line of (10.19) we used the anti-commutation rules between the electrons. Observe that the state represented in (10.19) is anti-symmetric as required by the Pauli principle. Another way to represent this state is to use the occupation of each atom (say $|n_{1,\sigma}, n_{2,\sigma'}\rangle$) where

$$|\Psi_B\rangle = \frac{1}{2}\left(|\downarrow\uparrow, 0\rangle + |\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle + |0, \uparrow\downarrow\rangle\right) . \tag{10.20}$$

In this new notation one has to be very careful about the order of the spins because of Fermi statistics.

Observe, however, that the Hamiltonian (10.16) cannot be a good approximation for the real problem of the molecule since it completely neglects the Coulomb repulsion between the electrons. In particular it neglects the large Coulomb repulsion for electrons in the same atom. If this Coulomb energy is very large then the double occupancy of the atom (that is, putting two electrons at the same time in the atom) costs a lot of energy. But we see from (10.19) that for the non-interacting problem this states are present. In the Heitler-London theory it is assumed that the Coulomb energy is very large and that double occupancy is avoided. In this case we see that a good approximation for the wave-function for the problem can be obtained from (10.19) by suppressing the operators that create two electrons in the same atom. In this case we see that the approximate ground state can be written as

$$|\Psi_s\rangle = \frac{1}{\sqrt{2}}\left(c^\dagger_{1,\uparrow}c^\dagger_{2,\downarrow} - c^\dagger_{1,\downarrow}c^\dagger_{2,\uparrow}\right)|0\rangle \tag{10.21}$$

which in the other notation is simply

$$|\Psi_s\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\right) \tag{10.22}$$

which is the so-called *singlet* state we discussed before. Thus the singlet state has the best of two worlds: it minimizes the Coulomb repulsion and maximizes the kinetic energy and therefore is a good starting point for the calculation of the true ground state of the problem.

10.1.2 The Coulomb interaction

Let us be more quantitative and study the Coulomb repulsion of two electrons in the H_2 molecule in more detail. The Coulomb energy of interaction between electrons is simply

$$H_C = \frac{e^2}{2}\int d^dr \int d^dr' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{10.23}$$

where $\rho(\mathbf{r})$ is the electronic density. If we now use the density in terms of the electron operators as in Chapter 7, (9.41), we have

$$H_C = \int d^d r \int d^d r' \sum_{\sigma,\sigma'} \frac{e^2}{2|\mathbf{r}-\mathbf{r}'|} \Psi^\dagger_\sigma(\mathbf{r})\Psi_\sigma(\mathbf{r})\Psi^\dagger_{\sigma'}(\mathbf{r}')\Psi_{\sigma'}(\mathbf{r}') \,. \tag{10.24}$$

Since the electron operators create or destroy electrons at the position of the atoms we can rewrite them as

$$\Psi_\sigma(\mathbf{r}) = \sum_{i=1}^{2} \phi_i(\mathbf{r}) c_{i,\sigma} \tag{10.25}$$

where $\phi_i(\mathbf{r})$ is the wavefunction of the electron localized at the atom i.

We will consider the case where the number of electrons on each atom is constant. If the number of electrons do not change it means that true motion of the electrons is completely disregarded. This approximation is only possible when we are dealing with a very large Coulomb repulsion in the atom. Actually this Coulomb repulsion has to be much larger than the kinetic energy gain for an electron to jump from one atom to another so that in first approximation one can neglect the kinetic energy. This is the case of insulating systems and therefore can only describe what is called *localized magnetism* which should be contrasted with the case of *itinerant magnetism* as we will see later. For the H_2 molecule the condition of single occupancy implies $n_{i,\uparrow}+n_{i,\downarrow}=1$. Direct substitution of (10.25) directly into (10.24) lead to 16 different terms. We will consider only the ones which do not lead to hopping of the electron from one atom to another. There are, therefore three different types of terms that interest us. The first one is

$$\begin{aligned} H_U &= \frac{U}{2}\sum_{\sigma,\sigma'}\sum_{i=1}^{2} n_{i,\sigma}n_{i,\sigma'} \\ &= U\sum_{i=1}^{2} n_{i,\uparrow}n_{i,\downarrow} + \frac{U}{2}\sum_{\sigma}\sum_{i=1}^{2} n_{i,\sigma} \end{aligned} \tag{10.26}$$

where in the last line we used that $n^2_{i,\sigma}=n_{i,\sigma}$ for a fermion and

$$U = e^2 \int d^d r \int d^d r' \frac{|\phi_i(\mathbf{r})|^2|\phi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \tag{10.27}$$

represents the Coulomb interaction in the same atom and it is the type of interaction we talked about when discussing the Hund's rules. Observe that the last term in the right hand side of (10.26) only shifts the local energy of the electrons and can be included in the non-interacting part of the Hamiltonian and does not concern us. The second type of term is the one that involves interaction between electrons in different atoms. Although this term is not important if we constraint the atoms to single occupation we will see later that this term is very important for virtual processes. This term is written as

$$H_V = V \sum_{\sigma,\sigma'} n_{1,\sigma} n_{2,\sigma'} \tag{10.28}$$

where

$$V = e^2 \int d^d r \int d^d r' \frac{|\phi_1(\mathbf{r})|^2 |\phi_2(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \,. \tag{10.29}$$

And finally the third term is called the *exchange term* and is given by

$$H_J = -J_C \sum_{\sigma,\sigma'} c^\dagger_{1,\sigma} c_{1,\sigma'} c^\dagger_{2,\sigma'} c_{2,\sigma} \tag{10.30}$$

where

$$J_C = e^2 \int d^d r \int d^d r' \frac{\phi_1^*(\mathbf{r}) \phi_1(\mathbf{r}') \phi_2^*(\mathbf{r}') \phi_2(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \,. \tag{10.31}$$

The exchange term can be written in a more illuminating way if we use the representation of the spin operators in terms of electron operators (9.45) that we define $\mathbf{S}_i = \hbar \mathbf{s}_i/2$ where

$$s_i^a = \sum_{\alpha,\gamma} c^\dagger_{i,\alpha} \sigma^a_{\alpha,\gamma} c_{i,\gamma} \tag{10.32}$$

where σ^a is a Pauli matrix ($a = x, y, z$). We need to calculate

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \sum_a \sum_{\alpha,\beta,\gamma,\delta} \sigma^a_{\alpha,\beta} \sigma^a_{\gamma,\delta} \;\; c^\dagger_{1,\alpha} c_{1,\beta} c^\dagger_{2,\gamma} c_{2,\delta} \tag{10.33}$$

and for that we can show that

$$\sum_a \sigma^a_{\alpha,\beta} \sigma^a_{\gamma,\delta} = 2\delta_{\alpha,\delta} \delta_{\beta,\gamma} - \delta_{\alpha,\beta} \delta_{\gamma,\delta} \,. \tag{10.34}$$

Using the above relation we find

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \sum_{\alpha,\beta} \left(2c^\dagger_{1,\alpha} c_{1,\beta} c^\dagger_{2,\beta} c_{2,\alpha} - c^\dagger_{1,\alpha} c_{1,\alpha} c^\dagger_{2,\beta} c_{2,\beta} \right) \tag{10.35}$$

And therefore we have from (10.30) we have

$$H_J = -\frac{J_C}{2} \sum_{\sigma,\sigma'} n_{1,\sigma} n_{2,\sigma'} - 2J_C \mathbf{s}_1 \cdot \mathbf{s}_2 \tag{10.36}$$

where the first term can be absorbed into (10.28). We are more interested in the last term which represents a spin-spin interaction between spins at the two atoms. Moreover, since $J_C > 0$ the energy will minimized if the spin is such that they are aligned pointing in the same direction. This is called a *ferromagnetic coupling.*

It is very tempting now to conclude that if the electrons are localized in the atoms, that is, the tunneling is very small then the electrons should be with their spins aligned in a *triplet* configuration. This of course contradicts our previous conclusion that in a bonding states the electrons should have their spins pointing in the opposite direction in a *singlet* state. What is wrong here?

What is wrong is that even if the electrons cannot actually hope from one atom to another they can still *virtually* hop! This is a pure quantum mechanical effect since second order perturbation allows a quantum systems to undergo transitions over excited states. Indeed let us consider the case where only interaction in the same ion are taking into account. In the limit where the ions are far apart these are the terms that dominate the physics and they are giving by (10.26)and forget about (10.28). Let us treat now the tunneling Hamiltonian (10.16) as a perturbation. The ground state of (10.26) is of course one electron in each atom since the Coulomb repulsion is minimized, that is, in the ground state one has $n_{i,\uparrow} + n_{i,\downarrow} = 1$. The energy of this state is zero. First order perturbation theory in the hopping gives a null result because the occupation of the atoms changes. In second order perturbation theory one electron can hop from one atom and come back. When it does that it goes through an excited state with double occupancy and energy U. By the Pauli principle this can only occur if the spins in different atoms are pointing in opposite direction. Indeed, in second order perturbation theory this process can be written as

$$H_E = -\frac{t^2}{U} \sum_{\sigma,\sigma'} c^{\dagger}_{1,\sigma} c_{2,\sigma} c^{\dagger}_{2,\sigma'} c_{1,\sigma'} \tag{10.37}$$

and using again (10.35) we can rewrite the above interaction as

$$H_A = \frac{2t^2}{U} \mathbf{s}_1 \cdot \mathbf{s}_2 \tag{10.38}$$

which has the same form of (10.36) but with the opposite sign implying that the spins will tend to become aligned in opposite directions. This is called an *antiferromagnetic* interaction and is called a *kinetic exchange* coupling.

If we now put put together (10.36) and (10.38) together we get the total exchange interaction between the electrons in the atoms is given by

$$H_E = J \mathbf{s}_1 \cdot \mathbf{s}_2 \tag{10.39}$$

where

$$J = \frac{2t^2}{U} - 2J_C \tag{10.40}$$

which can be ferromagnetic or antiferromagnetic depending on the relative values of t^2/U and J_C. For the H_2 molecule it turns out that the antiferromagnetic coupling is larger and therefore the ground state is a singlet.

10.1.3 Magnetic anisotropy

Observe that the Hamiltonian in (10.39) is symmetric under rotations of the spins since is the direct product of two vectors. It turns out however that in real systems we have magnetic anisotropies which appear due to spin-orbit and crystal fields as we discussed in the previous section. These anisotropies also affect the interaction between spins in a solid. Consider, for instance, the classical dipolar interaction between two magnetic moments $\mathbf{m}_1$ and $\mathbf{m}_2$ separated by a distance $\mathbf{R}$. The dipolar interaction can be written as

$$H_{dip} = \frac{\mathbf{m}_1 \cdot \mathbf{m}_2}{|\mathbf{R}|^3} - 3\frac{(\mathbf{m}_1 \cdot \mathbf{R})(\mathbf{m}_2 \cdot \mathbf{R})}{|\mathbf{R}|^5} . \tag{10.41}$$

Consider now the case of a 3d electron atom which has a quenched orbital momentum. The magnetic moment of the atom is only given by the spin degrees of freedom and the magnetic moment, due to crystal field effects, is given in (10.15). Direct substitution of (10.15) into (10.41) leads to

$$H_{dip} = \sum_{a,b} S_{1,a} C_{a,b}(\mathbf{R}) S_{2,b} \tag{10.42}$$

where

$$C_{a,b}(\mathbf{R}) = \mu_B^2 \left(\frac{\sum_c g_{c,a} g_{c,b}}{|\mathbf{R}|^3} - 3\frac{\sum_{c,d} g_{c,a} g_{d,b} R_c R_d}{|\mathbf{R}|^5} \right) . \tag{10.43}$$

Thus the total interaction between two atoms can be written as the sum of (10.39) and (10.42)

$$H = \sum_{a,b} S_{1,a} J_{a,b}(\mathbf{R}) S_{2,b} \tag{10.44}$$

where

$$J_{a,b} = J\delta_{a,b} + C_{a,b} . \tag{10.45}$$

We can diagonalize $J_{a,b}$ and find the principal magnetic axis of the system. Since $J_{a,b}$ is a 3×3 matrix we can have 3 different eigenvalues. It the problem has symmetry around an axis then two of this eigenvalues must be degenerate and so on. These kinds of anisotropies will lead to a Hamiltonian which is more general than (10.39) and it reads

$$H = J_z S_{1,z} S_{2,z} + J_y S_{1,y} S_{2,y} + J_x S_{1,x} S_{2,x} \tag{10.46}$$

where J_z, J_y and J_x can be different from each other.

10.2 Localized Magnetism

All the discussion here can be generalized for a crystal. If the system is insulating and the interaction only affects nearest neighbor atoms the generalization of the Hamiltonian (10.46) is simply

$$H = \sum_{\langle i,j \rangle} \left(J_z S_{i,z} S_{j,z} + J_y S_{i,y} S_{j,y} + J_x S_{i,x} S_{j,x} \right) . \tag{10.47}$$

The extreme limits of this Hamiltonian can be obtained by varying the parameters in (10.47). For instance, when $J_z >> J_y, J_x$ we have

$$H_I = J_z \sum_{\langle i,j \rangle} S_{i,z} S_{j,z} \tag{10.48}$$

which is the so-called *Ising model.* When $J_y = J_x = J_{xy} >> J_z$ we have

$$H_{xy} = J_{xy} \sum_{\langle i,j \rangle} \left(S_{i,y} S_{j,y} + S_{i,x} S_{j,x} \right) \tag{10.49}$$

is the so-called *XY model.* And finally when $J_x = J_y = J_z = J$ we are back to (10.39)

$$H_H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \tag{10.50}$$

is the *Heisenberg model.* Each one of these models have different symmetries. While the Heisenberg model has full rotation symmetry in spin space, the XY model only has rotation on a plane (we say that it has an *easy plane*) and finally the Ising model is the one with lowest symmetry since the spins are constrained to be on a fixed axis (we say that the system has an *easy axis*). The interesting thing about these systems is that because they have different symmetries whey will *order* magnetically in a different way leading to what is called *universality classes.* But actually in nature it is very hard to find a magnetic system that can be classified as a *pure* Ising, XY or Heisenberg. Most of the systems will be in a mixture of all of them.

10.3 Problems

1. Prove (10.7).

2. Prove (10.11).

3. Consider the H^2 molecule and obtain the expression for the anti-bonding state in terms of the localized states of the electrons.

4. Using the representation of (10.20) show that

$$\begin{aligned}
H_0|\uparrow\downarrow,0\rangle &= -t\left(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\right) \\
H_0|\uparrow,\downarrow\rangle &= -t\left(|0,\uparrow\downarrow\rangle + |0,\uparrow\downarrow\rangle\right) \\
H_0|\downarrow,\uparrow\rangle &= +t\left(|\uparrow\downarrow,0\rangle + |0,\uparrow\downarrow\rangle\right) \\
H_0|0,\uparrow\downarrow\rangle &= -t\left(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\right) \\
H_0|\sigma,\sigma\rangle &= 0\,. \qquad (10.51)
\end{aligned}$$

5. Use (10.25) and write down all the 16 terms that appear in (10.24).

6. Using the Fourier transform of the Coulomb potential show that $J_C > 0$.

7. Prove (10.34).

8. Prove (10.38).

9. Prove (10.42).

10.4 Magnetic interactions in metallic alloys

In the last section we considered the problem of magnetic interactions in insulators, that is, systems where due to the strong Coulomb interactions the electrons are localized in the atoms. This is not always the case. There are a large number of atoms that show metallic behavior, that is, they can be well described by band theory discussed in Chapter 4. Metals are usually paramagnetic (a counter example of this assertion is Fe which can be metallic and ferromagnetic) and show no particular magnetism. In many compounds atoms with magnetic moments can be introduced into a metallic host. This is the case for instance of alloys with f- or d- electron atoms. Magnetic atoms can interact with the conduction electrons that can propagate the magnetic interaction between the magnetic moments. This effect happens because the spin of the magnetic moment can interact with the spin of the conduction electron via a dipolar interaction.

Consider an atom with magnetic moment $\mathbf{m}_S$ interacting with an electron with magnetic moment $\mathbf{m}_e$ via (10.41). Eq. (10.41) is valid whenever $R \neq 0$ otherwise it becomes singular. Let us consider what happens when $R = 0$. The magnetic moment of the atom, $\mathbf{m}_S$, creates a magnetic field, $\mathbf{B}_S$, that couples with the electron via the Zeeman term, $\mathbf{B}_S \cdot \mathbf{s}$, where $\mathbf{s}$ is the spin of the electron. The magnetic field can be calculated from electrodynamics starting from the vector potential $\mathbf{A}$ as:

$$\mathbf{B}_S = \nabla \times \mathbf{A} \tag{10.52}$$

where $\mathbf{A}$ is the vector potential for a magnetic dipole which we know is given by

$$\mathbf{A} = \frac{1}{|\mathbf{R}|^3}\mathbf{m}_S \times \mathbf{R} = -\mathbf{m}_S \times \nabla\left(\frac{1}{|\mathbf{R}|}\right) . \tag{10.53}$$

Direct substitution of (10.53) into (10.52) leads to

$$\mathbf{B}_S = \nabla \times \nabla \times \left(\frac{\mathbf{m}_S}{|\mathbf{R}|}\right) . \tag{10.54}$$

Using the identities $\nabla \times \nabla \times = \nabla(\nabla \cdot) - \nabla^2$ and $\nabla^2(1/r) = -4\pi\delta(\mathbf{r})$ we find

$$\begin{aligned} \mathbf{B}_S &= \nabla\left[\nabla \cdot \left(\frac{\mathbf{m}_S}{|\mathbf{R}|}\right)\right] + 4\pi \mathbf{m}_S \delta(\mathbf{R}) \\ &= \left[\nabla\nabla - \frac{\nabla^2}{3}\right]\frac{\mathbf{m}_N}{|\mathbf{R}|} + \frac{8\pi}{3}\mathbf{m}_N \delta(\mathbf{R})\,. \end{aligned} \tag{10.55}$$

It is easy to show the first term in (10.55) is (10.41) and the second term is a contact interaction at the atom. Thus, the Zeeman energy for the electron interacting with the magnetic moment of the atom is

$$H_Z = -\frac{8\pi}{3}\mathbf{m}_e \cdot \mathbf{m}_S \delta(\mathbf{R}) \tag{10.56}$$

which is known as the *Fermi contact interaction.*

In a lattice with N magnetic atoms we can generalize (10.56) to

$$H_Z = \sum_{j,n,a,b} \mathcal{J}_{a,b}(\mathbf{r}_j - \mathbf{R}_n) s_a(\mathbf{r}_j) S_b(\mathbf{R}_n) \tag{10.57}$$

where $\mathbf{R}_n$ is the position of the n^{th} atom, $\mathbf{r}_j$ the position of the j^{th} electron, and $\mathbf{m}_S = \mu_S \mathbf{S}$ where μ_S is the atom magnetic moment. From (10.15) we have,

$$\mathcal{J}_{a,b}(\mathbf{r}_j - \mathbf{R}_n) = \frac{8\pi}{3}\mu_B \mu_S g_{a,b} \delta(\mathbf{r}_j - \mathbf{R}_n) \tag{10.58}$$

is the exchange between the spin of the electron and the magnetic moment of the nucleus in the presence of crystal fields and spin-orbit effect.

For simplicity we will assume that the metal that surrounds the magnetic nucleus is described by plane waves (although the same can be done with Bloch states) which have a Hamiltonian

$$H_e = \sum_{\mathbf{k},\sigma} E_k c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} \tag{10.59}$$

where $E_k = \hbar^2 k^2/(2m)$. We want to represent the new term in (10.57) in terms of plane waves as well. For that we need the representation of the electron spin in terms of field operators as in (9.45). It is easy to show that the Hamiltonian can be written as

$$\begin{aligned} H_J &= \sum_{\mathbf{k},\mathbf{k}',n} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n} \left\{ J_z S_z(\mathbf{R}_n) \left[c^\dagger_{\mathbf{k}',\uparrow} c_{\mathbf{k},\uparrow} - c^\dagger_{\mathbf{k}',\downarrow} c_{\mathbf{k},\downarrow} \right] \right. \\ &+ \left. \frac{J_\perp}{2} \left[S_-(\mathbf{R}_n) c^\dagger_{\mathbf{k}',\uparrow} c_{\mathbf{k},\downarrow} + S_+(\mathbf{R}_n) c^\dagger_{\mathbf{k}',\downarrow} c_{\mathbf{k},\uparrow} \right] \right\} \end{aligned} \tag{10.60}$$

where we have used $S_\pm = S_x \pm i S_y$. Observe that the effect of the interaction between the conduction electrons and the nucleus is a scattering process where a plane wave with wavevector $\mathbf{k}$ scatters to $\mathbf{k}'$. In this process the electron can flip its spin.

In order to simplify our problem let us consider first the highly anisotropic limit of (10.60) in which $J_\perp = 0$. Moreover, we are going to assume that there is just one impurity at the origin ($\mathbf{R}_n = 0$). In this case (10.57) is rewritten as

$$\begin{aligned} H_Z &= \sum_j J_z \delta(\mathbf{r}_j) s_z(\mathbf{r}_j) S_z \\ &= \sum_j J_z \delta(\mathbf{r}_j) S_z (n_\uparrow(\mathbf{r}_j) - n_\downarrow(\mathbf{r}_j)) \end{aligned} \tag{10.61}$$

In this limits it is easier to write the Hamiltonian of the problem in real space in terms of the field operators defined in (9.45):

$$H = \int d^d r \sum_{\sigma,\sigma'} \Psi_\sigma(\mathbf{r}) \left[-\frac{\hbar^2 \nabla^2}{2m} \delta_{\sigma,\sigma'} + V(\mathbf{r}) \sigma^z_{\sigma,\sigma'} \right] \Psi_{\sigma'}(\mathbf{r}) \tag{10.62}$$

where

$$V(\mathbf{r}) = J_z S_z \delta(\mathbf{r}) \tag{10.63}$$

and σ^z is a Pauli matrix and S_z is the eigenstate of the operator $\hat{S}_z$ (that is, $\hat{S}_z|S_z\rangle = S_z|S_z\rangle$ where $S_z = -S, .., S$).

Observe that we can diagonalize the problem entirely if we expand the electron field operator as

$$\Psi_\sigma(\mathbf{r}) = \sum_{E,\sigma} \phi_{E,\sigma}(\mathbf{r}) a_{E,\sigma} \tag{10.64}$$

where $a_{E,\sigma}$ is a fermion operator ($\{a^\dagger_{E,\sigma}, a_{E',\sigma'}\} = \delta_{E,E'}\delta_{\sigma,\sigma'}$) and

$$-\frac{\hbar^2\nabla^2}{2m}\phi_{E,\sigma}(\mathbf{r}) + \sigma V(\mathbf{r})\phi_{E,\sigma}(\mathbf{r}) = E\phi_{E,\sigma}(\mathbf{r}) \tag{10.65}$$

is a Schrödinger equation for the magnetic scattering of a particle by an impurity since it depends on the electron spin (here we have used that $\sigma^z_{\sigma,\sigma'} = \sigma\delta_{\sigma,\sigma'}$). In this case the Hamiltonian of the problem in the new basis reads

$$H = \sum_{n,\sigma} E_n a^\dagger_{E_n,\sigma} a_{E_n,\sigma} \tag{10.66}$$

where E_n are the solutions of (10.65).

Let us consider, for simplicity, the case where the electrons interact only weakly with the magnetic impurity and we can use perturbation theory. In (10.65) define $E = \hbar^2k^2/(2m)$ and $U = 2mV/\hbar^2$ and rewrite (10.65) as

$$\nabla^2\phi_{\mathbf{k},\sigma}(\mathbf{r}) + \left[k^2 - \sigma U(\mathbf{r})\right]\phi_{\mathbf{k},\sigma}(\mathbf{r}) = 0 \tag{10.67}$$

and transform it to Fourier space

$$\phi_{\mathbf{k},\sigma}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\phi_{\mathbf{k},\sigma}(\mathbf{q}) \tag{10.68}$$

in order to get

$$(k^2 - q^2)\phi_{\mathbf{k},\sigma}(\mathbf{q}) = \sum_{\mathbf{p}} \sigma U(\mathbf{p}-\mathbf{q})\phi_{\mathbf{k},\sigma}(\mathbf{p}) \tag{10.69}$$

where $U(\mathbf{p})$ is the Fourier transform of $U(\mathbf{r})$. In order to solve (10.69) we have to impose the condition that when $U = 0$ the solution of the problem is a plane wave, that is, $\phi_{\mathbf{k},\sigma}(\mathbf{q}) = \delta_{\mathbf{q},\mathbf{k}}$. Thus, the solution of (10.69) is

$$\phi_{\mathbf{k},\sigma}(\mathbf{q}) = \delta_{\mathbf{q},\mathbf{k}} + \sigma\sum_{\mathbf{p}}\frac{U(\mathbf{p}-\mathbf{q})}{k^2 - q^2}\phi_{\mathbf{k},\sigma}(\mathbf{p}) \tag{10.70}$$

which is an integral equation for $\phi_{\mathbf{k},\sigma}(\mathbf{q})$. We first observe that because of (10.63) we have $U(\mathbf{p}) = U = 2mJ_zS_z/\hbar^2$ is independent of momentum. Moreover, in first order the solution of the problem is given by the substitution of the delta function in the first term on the l.h.s. of (10.70) into the second term on the l.h.s. which gives,

$$\phi_{\mathbf{k},\sigma}(\mathbf{q}) \approx \frac{1}{\sqrt{N}}\left(\delta_{\mathbf{q},\mathbf{k}} + \sigma \frac{U}{k^2 - q^2}\right) \tag{10.71}$$

which when substituted into (10.68) leads to

$$\phi_{\mathbf{k},\sigma}(\mathbf{r}) \approx \frac{1}{\sqrt{N}}\left(e^{i\mathbf{k}\cdot\mathbf{r}} + \sigma U \sum_{\mathbf{q}\neq\mathbf{k}} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{k^2 - q^2}\right) \tag{10.72}$$

which is correct to first order in U and it is known as *Born approximation.*

In order to evaluate (10.72) we have to avoid the point where $\mathbf{p} = \mathbf{k}$ where the sum blows up. Moreover, we are in the thermodynamic limit and we would like to replace the sum by an integral over $\mathbf{q}$. Now, we have the problem of avoiding the points where the integral diverge. The best way to do it is to add an infinitesimal imaginary part to the integral and write

$$\sum_{\mathbf{q}\neq\mathbf{k}} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{k^2 - q^2} = \Re\left[\int \frac{d^d q}{(2\pi)^2} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{k^2 - q^2 - i\epsilon}\right] \tag{10.73}$$

where $\epsilon \to 0$ at the end of the calculation. In math this is called the *principal value* of an integral. So let us evaluate this integral

$$\begin{aligned}
\int \frac{d^d q}{(2\pi)^2} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{k^2 - q^2 - i\epsilon} &= \frac{1}{(2\pi)^2} \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dq q^2 \frac{e^{iqr\cos\theta}}{k^2 - q^2 - i\epsilon} \\
&= \frac{1}{(2\pi)^2} \int_{-1}^{+1} du \int_0^{\infty} dq q^2 \frac{e^{iqru}}{k^2 - q^2 - i\epsilon} \\
&= \frac{1}{(2\pi)^2 r} \int_{-\infty}^{+\infty} dq \frac{q \sin(qr)}{k^2 - q^2 - i\epsilon} \qquad (10.74)
\end{aligned}$$

where in the last line we used that the integrand is even in q. The integrals can now be performed by contour integration. For instance,

$$\int_{-\infty}^{+\infty} dq \frac{q e^{iqr}}{q^2 - k^2 + i\epsilon} = 2\pi i \left(\frac{e^{-ikr}}{2}\right) = \pi i e^{-ikr} \tag{10.75}$$

since we have to close the contour in the upper half-plane in order for the integral to converge. The final result is

$$\sum_{\mathbf{q}\neq\mathbf{k}} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{k^2-q^2} = 2\pi^2\frac{\cos(kr)}{r} \tag{10.76}$$

and from (10.72) we have

$$\phi_{\mathbf{k},\sigma}(\mathbf{r}) \approx e^{i\mathbf{k}\cdot\mathbf{r}} + 2\pi^2\sigma U\frac{\cos(kr)}{r}\,. \tag{10.77}$$

Observe that we can now calculate various properties using (10.64) and (10.77). In the approximation used the electrons are only scattered by the magnetic impurity but their energy remains the same. Thus the ground state is obtained by filling up the momentum states as usual. Observe, however, that the presence of the impurity modified the charge density for different spins. Indeed,

$$\begin{aligned}
\langle n_\sigma(\mathbf{r})\rangle &= \langle \Psi^\dagger_\sigma(\mathbf{r})\Psi_\sigma(\mathbf{r})\rangle \\
&= \sum_{\mathbf{k},\mathbf{k}'} \phi^*_{\mathbf{k},\sigma}(\mathbf{r})\phi_{\mathbf{k}',\sigma}(\mathbf{r})\langle a^\dagger_{\mathbf{k},\sigma}a_{\mathbf{k}',\sigma}\rangle \\
&= \sum_{\mathbf{k}} |\phi_{\mathbf{k},\sigma}|^2\Theta(k_F-k)
\end{aligned} \tag{10.78}$$

where k_F is the Fermi momentum which is related to the electron density by $k_F = (3\pi^2 n)^{1/3}$. Using (10.77) to leading order in U we find

$$\begin{aligned}
\langle n_\sigma(\mathbf{r})\rangle &= \frac{n}{2} + 4\pi^2\sigma U\int\frac{d^3k}{(2\pi)^3}\frac{\cos(kr)}{r}\cos(\mathbf{k}\cdot\mathbf{r})\Theta(k_F-k) \\
&= \frac{n}{2} + \frac{\sigma U}{r^2}\int_0^{k_F} dk k\sin(2kr) \\
&= \frac{n}{2} + \sigma\frac{8k_F^4 m J_z}{\hbar^2}S_z F(2k_F r)
\end{aligned} \tag{10.79}$$

where

$$F(x) = \frac{\sin x - x\cos x}{x^4}\,. \tag{10.80}$$

Observe that the electron density far away from the impurity reaches is bulk value $n/2$ but close to the impurity it oscillates strongly. These are called *Friedel oscillations*. Moreover, the oscillations depend on the spin of the electron. This happens because the interaction between the electron and the impurity atom is magnetic.

Consider now the problem of two magnetic impurities at positions $\mathbf{R}_n$ and $\mathbf{R}_m$. The spin $\mathbf{S}_n$ at position $\mathbf{R}_n$ will polarize the electron gas in its vicinity in the way given by (10.79). Another spin $\mathbf{S}_m$ at $\mathbf{R}_m$ will feel this polarization that allows the two moments to interact. In order to get the interaction Hamiltonian between these magnetic moments we use (10.61) and (10.79) to find

$$\begin{aligned} H_{RKKY} &= -\sum_{n,m} J_z S_z(\mathbf{R}_n)\left(n_\uparrow(\mathbf{R}_m) - n_\downarrow(\mathbf{R_m})\right) \\ &\propto -\frac{J_z^2}{E_F}\sum_{n,m} F(2k_F|\mathbf{R}_n - \mathbf{R}_m|)S_z(\mathbf{R}_n)S_z(\mathbf{R}_m) \end{aligned} \tag{10.81}$$

where E_F is the Fermi energy. This interaction between magnetic moments is called *RKKY interaction* due to Ruderman, Kittel, Kasuya and Yosida. Observe that the interaction is oscillatory and decays like $1/r^3$ and it is shown in Fig.10.2.

Notice that at short distances ($r \ll 1/(2k_F)$) the interaction is ferromagnetic but at large distances it changes sign and can be antiferromagnetic. Thus, depending on the position of the spins in the lattice this interaction can be effectively ferromagnetic or antiferromagnetic. In the case of disordered alloys both ferromagnetic and antiferromagnetic couplings are possible. At zero temperature this lead to a frustrated magnetic state called *spin glass*.

In the generic case where $J_\perp$ is not null the generic form of the RKKY is

$$H_{RKKY} = -\sum_{n,m,a,b} \Gamma_{a,b} F(2k_F|\mathbf{R}_n - \mathbf{R}_m|)S_a(\mathbf{R}_n)S_b(\mathbf{R}_m) \tag{10.82}$$

where $\Gamma_{a,b}$ depends on the spin-orbit and crystal field effects.

10.4.1 The Double Exchange problem

There are some magnetic systems like Mn that when forming a solid donate one electron for the conduction band but the remaining core

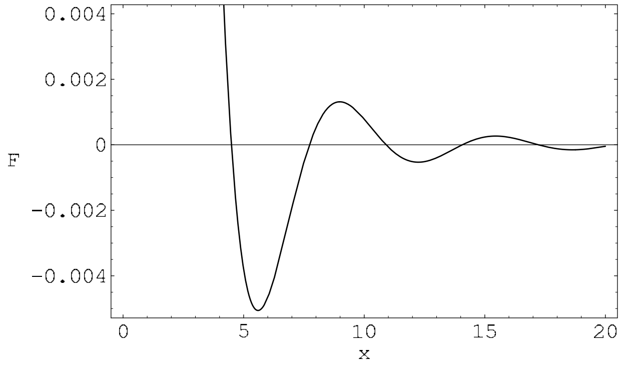

Figure 10.2: *Plot of* $F(x)$

electrons do not form a closed shell. In this case the atom in the lattice has a spin **S** that can interact with the electrons of the conduction band via an exchange interaction of the type given in (10.60). This interaction is usually ferromagnetic because of Hund's rules coupling, that is, the system wants to have *locally* the largest value of the spin. In this case the Hamiltonian of the problem can be written as:

$$H = -t \sum_{<i,j>,\sigma} \left(c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c. \right) - J \sum_i \mathbf{s}_i \cdot \mathbf{S}_i \tag{10.83}$$

where $h.c.$ means hermitian conjugate and $J > 0$ is the Hund's coupling between localized and itinerant electrons. This is a problem of great complexity since, as we have seen before, the electrons mediate the interaction between spins via the RKKY interaction.

Let us consider the case where we have a large localized spin S ($S \gg 1/2$). In this case the spin can be considered as a classical variable that can be parameterized by angles θ_i and ϕ_i relative to some fixed axis (for instance, $S^z = S\cos(\theta)$, $S^x = \sin(\theta)\cos(\phi)$, $S^y = S\sin(\theta)\sin(\phi)$). Note that the Hund's coupling forces the spin of the electron to orient

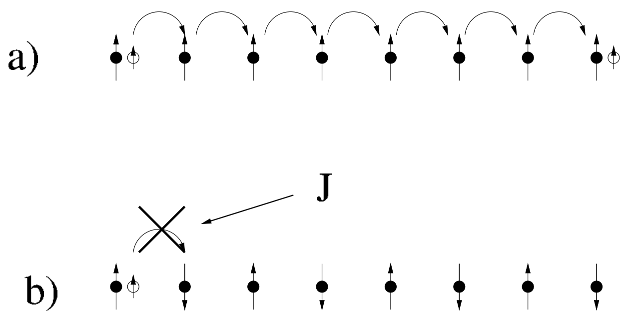

Figure 10.3: *(a) Hopping in a ferromagnetic situation; (b) Hopping in a anti-ferromagnetic situation.*

along the direction of **S**. If the local spins are all aligned with each other (ferromagnetic situation) then the second in (10.83) gives a negative energy contribution, reducing the energy of the system. If the spins are oriented π degrees from each other (anti-ferromagnetic situation) the electrons cannot hop from site to site because the hopping term in (10.83) does not flip the spin and therefore it costs an energy J to frustrate the Hund's coupling. Consider the situation on Fig.10.3(a): the electron spin (empty circle) is oriented with all the localized spins (filled circles) and can move freely over the lattice. In Fig.10.3(b) the antiferromagnetic orientation of the spins makes the hopping from one atom to the other difficult since it costs an energy J for the electron with spin up to move to an atom with spin down. When $J \gg t$ the hopping is completely suppressed.

This argument shows that in order to gain the electron kinetic energy the spins will tend to form a ferromagnetic state where all the spins are aligned to allow for the electron motion. Notice that because of the symmetry of the interaction in (10.83) the change in energy can only depend on the relative angle, $\theta_{i,j}$, between the localized neighboring spins. When $\theta_{i,j} = \pi$ the effective hopping between spins, $t_{i,j}$, is zero, when $\theta_{i,j} = 0$ the effective hopping is simply $t_{i,j} = t$.

In order to show this formally Let us consider the case of two magnetic atoms with spins $\mathbf{S}_1$ and $\mathbf{S}_2$. The Hamiltonian of the problem (in accord with (10.83) is:

$$H = -t\sum_{\sigma}(c^{\dagger}_{1,\sigma}c_{2,\sigma} + h.c) - J(\mathbf{S}_1 \cdot \mathrm{s}_1 + \mathbf{S}_2 \cdot \mathrm{s}_2) \tag{10.84}$$

In the reference frame of the local spins the energies of the states are $+JS$ or $-JS$ depending if the electron spin is anti-parallel or parallel to the local spin, respectively. Let us call these states $|i,-\rangle$ and $|i,+\rangle$, respectively ($i = 1,2$). Thus, the whole problem reduces to four states, namely, $|1,+\rangle$, $|1,-\rangle$, $|2,+\rangle$, and $|2,-\rangle$. The spins S_1 and S_2 form an angle θ between them, that is, $S_1 \cdot S_2 = S^2\cos(\theta)$. If we choose a quantization axis along S_1 (we write $S_1 = S\mathbf{z}$), for instance, we have to rotate to project the states of S_2 into this axis. This can be done by rotating the states of in atom 2 via a spin rotation operator around the Y axis:

$$\begin{aligned} U &= e^{-i\theta S_y/\hbar} = e^{-i\theta\sigma_y/2} \\ &= \cos(\theta/2) - i\sigma_y\sin(\theta/2) \end{aligned} \tag{10.85}$$

where σ_y is the Y-Pauli matrix. The states of atom 2 in the quantization axis of atom 1 can be written as:

$$|2,\alpha\rangle = \sum_{\gamma=\pm 1} U_{\alpha,\gamma}|2',\gamma\rangle \tag{10.86}$$

where $|2',\alpha\rangle$ refer to the states in the rotated frame. The rotation can be written more explicitly as:

$$\begin{aligned} |2,+\rangle &= \cos(\theta/2)|2',+\rangle + \sin(\theta/2)|2',-\rangle \\ |2,-\rangle &= -\sin(\theta/2)|2',+\rangle + \cos(\theta/2)|2',-\rangle\,. \end{aligned} \tag{10.87}$$

Moreover, from (10.84) and (10.87) we see that:

$$\begin{aligned} \langle i,\alpha|H|i,\gamma\rangle &= -\alpha JS\delta_{\alpha,\gamma} \\ \langle 1,\alpha|H|2,\gamma\rangle &= -tU_{\alpha,\gamma}\,. \end{aligned} \tag{10.88}$$

Thus, the Hamiltonian can be written as:

$$[H] = \begin{bmatrix} -JS & 0 & -t\cos(\theta/2) & -t\sin(\theta/2) \\ 0 & JS & t\sin(\theta/2) & -t\cos(\theta/2) \\ -t\cos(\theta/2) & t\sin(\theta/2) & -JS & 0 \\ t\sin(\theta/2) & -t\cos(\theta/2) & 0 & JS \end{bmatrix}$$

which can be diagonalized in the usual way. The eigenenergies are:

$$E = \frac{J}{2} \pm \sqrt{(JS)^2 + t^2 \pm 2JSt\cos(\theta/2)}\,. \qquad (10.89)$$

For $J \gg t$ the lowest energy eigenvalue is:

$$E_0 \approx -JS - t\cos(\theta/2) \qquad (10.90)$$

where the first term corresponds to the Zeeman energy of the electron in the field of the localized moment and the second term corresponds to the *effective* hopping energy for the spins between the different atoms. Notice that for $\theta = 0$ it gives $-t$ and for $\theta = \pi$ it gives zero, in agreement with the previous discussion. Notice further that while in the RKKY mechanism the first contribution to the energy is of order J^2/E_F (see (10.81)) the current mechanism produces an effect of order J and therefore should be dominant at small J. The above argument shows that, when generalized to a lattice, the effective Hamiltonian of the problem can be written, in the limit of $J \gg t$, as:

$$H_{eff} = -t \sum_{\langle i,j,\rangle,\sigma} \cos(\theta_{i,j}/2)\left(c^{\dagger}_{i,\sigma}c_{j,\sigma} + h.c.\right) \qquad (10.91)$$

where $\theta_{i,j}$ is the angle between neighboring spins. For a given lattice one has to find out the spin configuration that minimizes the energy in (10.91). The model described here was originally proposed by Zener in order to describe the physics of certain oxides with Mn and the term double exchange comes from the fact that the exchange between Mn atoms occurs via the filled p-orbitals of the O atoms.

10.5 Problems

1. Show that in two dimensions the RKKY interaction decays like $1/r^2$ at long distances.

2. Consider the problem of an electron jumping between two atoms with large spins in the limit of $J \ll t$. (*i*) What is the ground state energy in this case? (*ii*) What is the physical interpretation of the solution in this limit? (*iii*) Will the electron travel over the system for any spin configuration?

3. Consider the problem of electrons moving in a d-dimensional hyper-cubic lattice with a density n of electrons in the limit of $J \gg t$. Assume that the angle between adjacent spins is always the same, that is, $\theta_{i,j} = \theta$ independent of i, j. (*i*) What is the spin configuration in this case? (*ii*) What is the ground state energy as a function of angle? (*iii*) Assume that the angle between adjacent spins is very small and that the distance between atoms is a. Define $k = \theta/a$ and show that the energy of the system behaves like k^2. How does the electron spin behave in this case ?

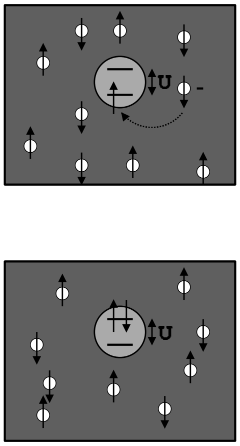

Figure 10.4: *Impurity immersed in a Fermi gas.*

10.5.1 The Anderson Hamiltonian

In the last sections we discussed Fermi contact interaction between conduction electrons and localized magnetic moments. The contact interaction is important for s-wave states where the electron has large probability of being at the atomic site. For p- or d-like orbitals which vanish at the origin the contact interaction also vanishes. In this case the interaction between a conduction electron and a localized moment has a different origin which is related with the *hybridization* between conduction electrons and localized electrons. Consider the problem of a localized impurity at a position $\mathbf{r} = 0$ in a Fermi gas as shown in Fig.10.4.

A conduction electron can hop back and forth from the electron gas into the impurity site. This hopping can be seen as a tunneling term like in (10.16). However, in order to do so, the electron has to pay an energy U if the impurity site is doubly occupied (which was studied in (10.26)). The simplest Hamiltonian that describes this situation is the *Anderson Hamiltonian*

$$\begin{aligned} H_A &= \sum_{\mathbf{k},\sigma} E_k c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + E_f \sum_\sigma f^\dagger_\sigma f_\sigma + V \sum_\sigma \left(c^\dagger_\sigma(\mathbf{r}=0) f_\sigma + f^\dagger_\sigma c_\sigma(\mathbf{r}=0) \right) \\ &+ U n_{f,\uparrow} n_{f,\downarrow} \end{aligned} \tag{10.92}$$

which in momentum space can also be written as:

$$\begin{aligned} H_A &= \sum_{\mathbf{k},\sigma} E_k c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + E_f \sum_\sigma f^\dagger_\sigma f_\sigma + \frac{V}{\sqrt{N}} \sum_{\mathbf{k},\sigma} \left(c^\dagger_{\mathbf{k},\sigma} f_\sigma + f^\dagger_\sigma c_{\mathbf{k},\sigma} \right) \\ &+ U n_{f,\uparrow} n_{f,\downarrow} \end{aligned} \tag{10.93}$$

where $c_{\mathbf{k},\sigma}$ and f_σ are electron operators for electrons on the conduction band and the localized impurity state, respectively (N is the number of sites). E_f is the atomic energy at the impurity, V is the tunneling energy between the conduction band and the impurity and U is the Coulomb energy to put two electrons on the impurity ($n_{f,\sigma} = f^\dagger_\sigma f_\sigma$).

It turns out that there is no exact solution for (10.93). That Hamiltonian describes a true many-body problem. In trying to understand the physics of this Hamiltonian we have to make approximations. Let us consider first the problem where $U = 0$, that is, the Coulomb interaction is absent. One expects from the beginning that no magnetism can be described in this case since a magnetic moment can only exist in a isolated energy level if double occupancy of the level is not allowed. We will see later how the Coulomb energy can be introduced into the problem. When $U = 0$ the problem is quadratic in the operators and therefore can be diagonalized by an unitary transformation:

$$\begin{aligned} f_\sigma &= \alpha \overline{f}_\sigma + \sum_{\mathbf{k}} \beta_{\mathbf{k}} \overline{c}_{\mathbf{k},\sigma} \\ c_{\mathbf{k},\sigma} &= \gamma_{\mathbf{k}} \overline{f}_\sigma + \sum_{\mathbf{k}} \iota_{\mathbf{k},\mathbf{k}'} \overline{c}_{\mathbf{k}',\sigma} \end{aligned} \tag{10.94}$$

where $\overline{f}_\sigma$ and $\overline{c}_{\mathbf{k},\sigma}$ are the new electron operators which diagonalize the problem, that is, after the unitary transformation the Hamiltonian (10.93) with $U = 0$ can be written as

$$H = \sum_\sigma \overline{E}_f \overline{f}^\dagger_\sigma \overline{f}_\sigma + \sum_{\mathbf{k}} \overline{E}_k \overline{c}^\dagger_{\mathbf{k},\sigma} \overline{c}_{\mathbf{k},\sigma} \tag{10.95}$$

with $\overline{E}_f$ and $\overline{E}_k$ the new eigenvalues (still to be calculated). Notice that the coefficients α, $\beta_{\mathbf{k}}$, $\gamma_{\mathbf{k}}$ and $\iota_{\mathbf{k},\mathbf{k}'}$ depend on the parameters in the Hamiltonian.

One of the ways to solve this problem is to look at the equations of motion for the operators. Using the anti-commutation relations between the fermion operators it is easy to show that

$$\begin{aligned} [f_\sigma, H] &= E_f f_\sigma + \frac{V}{\sqrt{N}} \sum_{\mathbf{k}} c_{\mathbf{k},\sigma} \\ [c_{\mathbf{k},\sigma}, H] &= E_k c_{\mathbf{k},\sigma} + \frac{V}{\sqrt{N}} f_\sigma \,. \end{aligned} \tag{10.96}$$

On the other hand, using (10.94) and (10.95) one has

$$\begin{aligned}
[f_\sigma, H] &= \alpha \overline{E}_f \overline{f}_\sigma + \sum_{\mathbf{k}} \beta_{\mathbf{k}} \overline{E}_k \overline{c}_{\mathbf{k},\sigma} \\
[c_{\mathbf{k},\sigma}, H] &= \gamma_{\mathbf{k}} \overline{E}_f \overline{f}_\sigma + \sum_{\mathbf{k}'} \iota_{\mathbf{k},\mathbf{k}'} \overline{E}_{k'} \overline{c}_{\mathbf{k}',\sigma}
\end{aligned} \tag{10.97}$$

and by direct substitution of (10.94) into (10.96) we find

$$\begin{aligned}
[f_\sigma, H] &= (\alpha E_f + \frac{V}{\sqrt{N}} \sum_{\mathbf{k}} \gamma_{\mathbf{k}}) \overline{f}_\sigma + \sum_{\mathbf{k}} (E_f \beta_{\mathbf{k}} + \frac{V}{\sqrt{N}} \sum_{\mathbf{k}'} \iota_{\mathbf{k}',\mathbf{k}}) \overline{c}_{\mathbf{k},\sigma} \\
[c_{\mathbf{k},\sigma}, H] &= (\frac{V}{\sqrt{N}} \sum_{\mathbf{k}} \beta_{\mathbf{k}} + \sum_{\mathbf{k}'} E_k \iota_{\mathbf{k}',\mathbf{k}}) \overline{c}_{\mathbf{k},\sigma} + (E_k \gamma_{\mathbf{k}} + \frac{V}{\sqrt{N}} \alpha) \overline{f}_\sigma
\end{aligned} \tag{10.98}$$

Direct comparison of (10.97) and (10.98) leads to

$$\begin{aligned}
\overline{E}_f &= E_f + \frac{V}{\sqrt{N}} \sum_{\mathbf{k}} \gamma_{\mathbf{k}} \\
(\overline{E}_f - \overline{E}_k) \gamma_k &= \frac{V}{\sqrt{N}} .
\end{aligned} \tag{10.99}$$

In solving the above equations we have to exercise some care. We are interested in the case where $\overline{E}_f$ is within the electron band which implies that the second equation in (10.99) has a singularity at $\overline{E}_f = \overline{E}_k$. This singularity can be extracted, however, if we interpret the second equation as the real part of

$$\gamma_{\mathbf{k}} = \frac{1}{\sqrt{N}} \frac{V}{\overline{E}_f - \overline{E}_{\mathbf{k}} - i\epsilon} . \tag{10.100}$$

Moreover, we are interested in the case of a single impurity in 10^{23} electrons. Thus, in this case $\overline{E}_k \approx E_k$ plus corrections of order 10^{-12}. Substitution of (10.100) into the first equation of (10.99) leads to the desired final result

$$\overline{E}_f = E_f + \frac{1}{N} \Re \left\{ \sum_{\mathbf{k}} \frac{V^2}{\overline{E}_f - E_k - i\epsilon} \right\} \tag{10.101}$$

which is an *equation* for $\overline{E}_f$. Equation (10.101) shows that the energy of the f-state is shifted by an amount proportional to V^2. One has to remember, however, that the original f-state is not an eigenstate of the Hamiltonian since it is actually coupled to the conduction band. Thus, when an f-electron is put into the many-body system it has to decay into $\overline{f}$ and $\overline{c}$ states which are the true eigenstates of the problem. Therefore, the f-electron has a finite lifetime. In order to estimate the life-time we go back to (10.101) and interpret the imaginary part of the f-electron energy as its decay rate (this, step can be formally proved with the use of Green's function method). Thus, we have:

$$\frac{\hbar}{\tau_f} = \frac{1}{N}\Im\left\{\sum_{\mathbf{k}} \frac{V^2}{\overline{E}_f - E_k - i\epsilon}\right\} = \frac{\pi V^2}{N}\sum_{\mathbf{k}} \delta(\overline{E}_f - E_k) \tag{10.102}$$

where we have used that:

$$limit_{\epsilon\to 0}\left[\frac{1}{x - i\epsilon}\right] = \mathcal{P}\left(\frac{1}{x}\right) + \pi i \delta(x) \tag{10.103}$$

where $\mathcal{P}$ means the principal value of the function. Notice that (10.102) makes a lot of sense. When $V \to 0$ the f-state is decoupled from the conduction band and therefore has infinite lifetime. But as the coupling to the conduction band increases the lifetime of the f-state becomes shorter.

It is interesting to compare the behavior of the density of states in both cases. When $V = 0$ the density of states of the problem reduces to the density of states of the f-state and the conduction band

$$\begin{aligned} N_f(E) &= \delta(E - E_f) = \frac{1}{\pi}\frac{\epsilon}{(E - E_f)^2 + \epsilon^2} = \Im\left\{\frac{1}{E - E_f - i\epsilon}\right\} \\ N_c(E) &= \frac{1}{N}\sum_{\mathbf{k}} \delta(E - E_k)\,. \end{aligned} \tag{10.104}$$

In the presence of the coupling V we replace E_f in the first equation in (10.104) by $\overline{E}_f - i\hbar/\tau_f$ in order to get

$$\begin{aligned} N_f(E) &= \Im\left\{\frac{1}{E - \overline{E}_f - i\hbar/\tau_f}\right\} \\ &= \frac{1}{\pi}\frac{\hbar/\tau_f}{(E - \overline{E}_f)^2 + \hbar^2/\tau_f^2} \end{aligned} \tag{10.105}$$

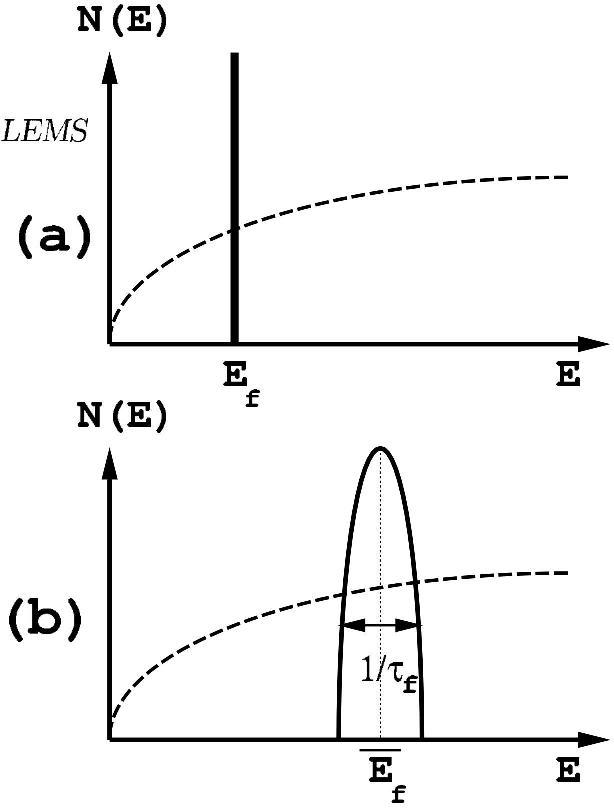

Figure 10.5: *Density of states for the* $U = 0$ *Anderson model: (a)* $V = 0$*, (b)* $V \neq 0$.

which is not a Dirac delta function any longer but a Lorentzian with width $1/\tau_f$ with is given by

$$\frac{\hbar}{\tau_f} = \pi V^2 N_c(\overline{E}_f) \tag{10.106}$$

as we can readily see from (10.102) and (10.104). Thus, as a result the f-level is not sharp any longer. This reflects the fact that when an f-level hybridizes with a conduction band it is not an exact eigenstate of the system (indeed, one sees from (10.94) that the eigenstate is a linear combination of f and conduction band states). This situation is depicted in Fig.10.5.

In order to understand what happens in the presence of U one has to treat the interaction term in (10.93). It is obvious that this term cannot be treated in the same way we treated the V term because it contain four fermion operators. The problem is highly non-linear. Instead of trying to solve the problem exactly we will search for an approximate solution. The approximation is called *mean field* or Hartree-Fock approximation. In this approximation we replace

$$Un_{f,\uparrow}n_{f,\downarrow} \to U\langle n_{f,\uparrow}\rangle n_{f,\downarrow} + Un_{f,\uparrow}\langle n_{f,\downarrow}\rangle \tag{10.107}$$

which corresponds to replace the *actual* value of the occupation at the f-level state by its average. If one make the substitution (10.107) into (10.93) one sees that the only modification is in the energy of the f-level state, that is,

$$H_f = \sum_\sigma E_f n_{f,\sigma} \to H_{f,MF} = \sum_\sigma E_{f,\sigma} n_{f,\sigma} \tag{10.108}$$

where

$$E_{f,\sigma} = E_f + U\langle n_{f,-\sigma}\rangle \tag{10.109}$$

that is, the energy of the f-level with spin, say, ↑ is increased by U times the average occupation of the state with spin ↓ and vice-versa. After this approximation is done we can proceed as earlier (in the case of $U = 0$) but taking into account that the local energy of the f-level depends also on the spin projection. In particular the density of states for each spin projection is given by:

$$N_{f,\sigma}(E) = \frac{1}{\pi}\frac{\hbar/\tau_{f,\sigma}}{(E - \overline{E}_{f,\sigma})^2 + \hbar^2/\tau_{f,\sigma}^2} \tag{10.110}$$

where

$$\begin{aligned} \overline{E}_{f,\sigma} &= E_f + U\langle n_{f,-\sigma}\rangle + \frac{1}{N}Re\left\{\sum_{\mathbf{k}} \frac{V^2}{\overline{E}_{f,\sigma} - E_k - i\epsilon}\right\} \\ \frac{1}{\tau_{f,\sigma}} &= \pi V^2 N_c(\overline{E}_{f,\sigma})\,. \end{aligned} \tag{10.111}$$

For simplicity we will assume that the electron density of states is essentially constant and therefore $\overline{E}_{f,\sigma} = \overline{E}_f + U\langle n_{f,-\sigma}\rangle$ and $\tau_{f,\sigma} = \tau_f$. In this case, the average occupation of the f-level with spin σ is given by the usual expression

$$\langle n_{f,\sigma}\rangle = \int_{-\infty}^{E_F} dE N_{f,\sigma}(E)$$

$$\begin{aligned} &= \int_{-\infty}^{E_F} \frac{dE}{\pi} \frac{\hbar/\tau_f}{(E - \overline{E}_f - U\langle n_{f,-\sigma}\rangle)^2 + \hbar^2/\tau_f^2} \\ &= \frac{1}{\pi} arccot \left(\frac{\overline{E}_f + U\langle n_{f,-\sigma}\rangle - E_F}{\hbar/\tau_f} \right) \end{aligned} \tag{10.112}$$

which is a transcendental equation for the occupations! Thus we have traded a non-linear problem in terms of operators for a non-linear problem in terms of ordinary equations. It is common to rewrite the equation above in terms of new variables defined as:

$$\begin{aligned} y &= \tau_f U/\hbar \\ x &= \frac{\overline{E}_f - E_F}{U} \end{aligned} \tag{10.113}$$

so that

$$cot(\pi\langle n_{f,\sigma}\rangle) = y(\langle n_{f,-\sigma}\rangle - x)\,. \tag{10.114}$$

Let us consider two simple limits of these equations. When $U = 0$ it is obvious that

$$\langle n_{f,\sigma}\rangle = \langle n_{f,-\sigma}\rangle = \frac{1}{2} \tag{10.115}$$

since $\langle n_{f,\sigma}\rangle + \langle n_{f,-\sigma}\rangle = 1$. This corresponds to the non-magnetic solution of the problem. Thus, as one could have guessed the Coulomb interaction is fundamental for the appearance of magnetic moments. In the limit of $U \to \infty$ the $arccot(x)$ can give π or 0 depending on the sign of the argument. It is obvious that the solution close to π corresponds to the full occupation of the level and the one close to 0 corresponds to an empty level. Thus, let us assume that $\langle n_{f,\uparrow}\rangle \approx 1$ and $\langle n_{f,\downarrow}\rangle \approx 0$ and calculate

$$\begin{aligned} \langle n_{f,\uparrow}\rangle &\approx 1 - \frac{1}{\pi y(x - \langle n_{f,\downarrow}\rangle)} \\ \langle n_{f,\downarrow}\rangle &\approx \frac{1}{\pi y(\langle n_{f,\uparrow}\rangle) - x} \end{aligned} \tag{10.116}$$

which implies that the local magnetization in the magnetic impurity is

$$m_f = \langle n_{f,\uparrow}\rangle - \langle n_{f,\downarrow}\rangle$$

$$
\begin{aligned}
&\approx 1 - \frac{1}{\pi y(1-x)} \\
&\approx 1 - \frac{V^2 N(0)}{U} \qquad (10.117)
\end{aligned}
$$

where we have used (10.106) and (10.113). Notice that the above approximation is valid for $V \ll E_F, U$. That is, in the limit in which the impurity is weakly coupled to the electron gas and the Coulomb energy is large. In this case the charge fluctuations in the impurity site will be very small and only the spin of the impurity has dynamics. This dynamics will be discussed in the next section.

Therefore, the conclusion of this calculation is that for the existence of local moments the Coulomb energy is fundamental. The physics of this problem is relatively simple: in the absence of the Coulomb interaction, $U = 0$, the singly occupied states are degenerate with energy E_f and the doubly occupied state has energy $2E_f$. In the presence of U the energy of doubly occupied state is $U + E_f > E_F$ and therefore out of the Fermi surface. Thus, this state is always empty. It is exactly because the doubly occupied state is higher in energy that moment formation is stabilized.

10.6 The Kondo problem

Although (10.93) has very interesting physics it describes a large number of effects that are not necessarily related with magnetic scattering. In this section we will be interested in processes in which the number of electrons in the impurity is constant, that is, $\sum_\sigma n_{f,\sigma} = 1$, so that the impurity has a magnetic moment. This is only possible if $V \ll E_f, U, E_F$ and $E_f < E_F$ so that the electron on the impurity does not disappear on the conduction band and $U + E_f > E_F$ so that the impurity is never doubly occupied. Instead, we are only interested in the *virtual process* in which an electron can hop from the conduction band into the impurity and back. When an electron does that it goes through and excited state of energy $E_f + U$ if the impurity is singly occupied. In perturbation theory this leads to a term which is proportional $V^2/(E_k - U - E_f)$. On the other hand an electron localized at the impurity can jump from the impurity into the conduction band

and back where the intermediate state now has energy E_k. Again in perturbation theory this leads to a term of order $V^2/(E_f - E_k)$. Observe that in both cases we have $E_k \approx E_F$. These process are not different from the ones discussed previously for the H_2 molecule. Thus, second order perturbation theory will generate an interaction between the conduction band and the electron impurity of the form

$$H_{exch}| = J\mathbf{s}(\mathbf{r}=0)\cdot\mathbf{S} \tag{10.118}$$

where

$$J \approx NV^2\left(-\frac{1}{U+E_f}+\frac{1}{E_f}\right) \tag{10.119}$$

which is always positive (we have fixed the energy so that $E_F = 0$). The Hamiltonian (10.118) is called the *Kondo Hamiltonian* and has exactly the same form as the Fermi contact interaction (10.57). Thus all our results about the RKKY interaction are valid for this model as well if we take the impurity spin to be 1/2. However, there is new physics on this model that we have not discussed yet.

As before we will consider the anisotropic Kondo problem where the exchanges in the Z and $X-Y$ directions are different from each other (something that can happen in the presence of crystal fields and spin-orbit effects). The complete Hamiltonian reads:

$$\begin{aligned} H &= \sum_{\mathbf{k},\sigma}\epsilon_k c^{\dagger}_{\mathbf{k},\sigma}c_{\mathbf{k},\sigma} + J_z S^z \sum_{\mathbf{k},\mathbf{k}',\sigma}\sigma c^{\dagger}_{\mathbf{k},\sigma}c_{\mathbf{k}',\sigma} \\ &+ J_{\perp}\left(S^+ s^-(r=0) + s^+(r=0)S^-\right) \end{aligned} \tag{10.120}$$

where J_z is the longitudinal or Ising coupling and $J_\perp$ is the transverse of XY coupling. Notice that because $J_z, J_\perp > 0$ there is an effective attraction between the impurity and the electrons when they have opposite spins. Attraction between particles implies the possibility of forming bound states. In fact, for $J_\perp = 0$ we can use the results of the previous section, in particular, we write (10.69) as:

$$(E - \frac{\hbar^2 q^2}{2m})\phi_E(\mathbf{q}) = -J_z\sum_{\mathbf{p}}\phi_E(\mathbf{p}) \tag{10.121}$$

where we reestablished the usual units. This equation can be solved as

$$\phi_E(\mathbf{q}) = \frac{C(E)}{E - \frac{\hbar^2 q^2}{2m}} \tag{10.122}$$

where

$$C(E) = -J_z \sum_{\mathbf{p}} \phi_E(\mathbf{p}) \,. \tag{10.123}$$

Substitution of (10.122) into (10.123) leads to

$$1 = -J_z \sum_{\mathbf{p}} \frac{1}{E - \frac{\hbar^2 q^2}{2m}} \tag{10.124}$$

which gives the equation for E. If we now use the definition of the density of states

$$\rho(E) \;=\; \sum_{\mathbf{p}} \delta\left(E - \frac{\hbar^2 p^2}{2m}\right) \tag{10.125}$$

we can rewrite (10.124) as

$$1 = J_z \int dE' \frac{\rho(E')}{E' - E} \,, \tag{10.126}$$

that has to be solved for $E(J_z)$, the bound state energy. Observe that (10.126) does not have any information about the occupation of the states in the system, that is, it does not carry a Fermi occupation number. However, it predicts the possibility of forming bound states that can be written as: $\mid \Uparrow, \downarrow\rangle$ or $\mid \Downarrow, \uparrow\rangle$, where $\Uparrow, \Downarrow$ represent the impurity spin and $\uparrow, \downarrow$ represent the electron spin. In the above problem the two states are degenerate in energy. In this localized picture we immediately see that the coupling $J_\perp$ in (10.120) lifts the degeneracy between these two states so that the final states of the problem are:

$$\begin{aligned} |s\rangle \;&=\; \frac{1}{\sqrt{2}}\left(\mid \Downarrow, \uparrow\rangle - \mid \Downarrow, \uparrow\rangle\right) \\ |t\rangle \;&=\; \frac{1}{\sqrt{2}}\left(\mid \Downarrow, \uparrow\rangle + \mid \Downarrow, \uparrow\rangle\right) \end{aligned} \tag{10.127}$$

which are the singlet and triplet states. Notice that due to the transverse term in the Hamiltonian the single state is lower in energy by $J_\perp$ relative to the triplet state.

For the reasons given below the approach given above has a big flaw associated with the fact that we are treating the J_z and $J_\perp$ in a very non-perturbative way and we will show that this is incorrect physically. However, we will borrow the ideas of the naive calculation above in order to simplify the problem to a treatable form. Let us first define new states by:

$$\begin{aligned} |+\rangle &= |\Uparrow,\downarrow\rangle \\ |-\rangle &= |\Downarrow,\uparrow\rangle \,. \end{aligned} \tag{10.128}$$

These states are not "pure" spin states since they involve the impurity spin and the *localized* electron spin. However, we see that the operator associated with $J_\perp$ has a very simple result when acting on those states, namely:

$$\begin{aligned} \left(S^+s^-(r=0)+s^+(r=0)S^-\right)|+\rangle &= |-\rangle \\ \left(S^+s^-(r=0)+s^+(r=0)S^-\right)|-\rangle &= |+\rangle \end{aligned} \tag{10.129}$$

that is, the $J_\perp$ operator acts as a Pauli matrix σ^x on these states. By the same token, the operator S^z has a very simple action on those states:

$$\begin{aligned} S^z|+\rangle &= |+\rangle \\ S^z|-\rangle &= -|-\rangle \end{aligned} \tag{10.130}$$

and therefore S^z acts on these states as the Pauli matrix σ^z. Thus, by changing the basis we can rewrite the Kondo Hamiltonian as:

$$H = \sum_{\mathbf{k},\sigma} \epsilon_k c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + J_z\sigma^z \sum_{\mathbf{k},\mathbf{k}',\sigma} \sigma c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k}',\sigma} + J_\perp \sigma^x \,. \tag{10.131}$$

This problem still have too many degrees of freedom. As we know from our study of metals in Chapter 6 perturbations in metals can only affect states close to the Fermi energy and unfortunately (10.131) still contains states with high energy close to the bottom of the Fermi sea.

If we consider the momenta $\mathbf{k}$ and $\mathbf{k}'$ in (10.131) close to the Fermi surface we see the effect of the impurity is to scatter and electron with momentum $\mathbf{k}$ from an occupied state inside of the Fermi sea (leaving a hole behind) and putting this electron outside the Fermi sea in a unoccupied state with momentum $\mathbf{k}'$. That is, it creates particle-hole pairs. Thus, it is more convenient to work in the language of particle-hole pairs instead of the language of the original fermions.

As we showed in Chapter 6 (see Eq.(6.104)) the low energy excitations of the Fermi gas, the particle-hole pairs, have bosonic character and at low temperatures provide a natural description of the specific heat, for instance. The energy of a particle-hole pair close to the Fermi surface is

$$\omega_q = v_F q \tag{10.132}$$

where v_F is the Fermi velocity and $q > 0$ is the module of the momentum transfer for the production of the particle-hole pair ($\mathbf{k}' = \mathbf{k} + \mathbf{q}$). Thus, particle-hole pairs behave like harmonic oscillators in momentum space (like acoustic phonons). Thus, at low energies we can replace the free electron Hamiltonian by:

$$H_0 = \sum_{\mathbf{k},\sigma}(\epsilon_k - \mu)c^\dagger_{\mathbf{k},\sigma}c_{\mathbf{k},\sigma} \rightarrow H_{ph} = \sum_{q>0}\left[\frac{P_q^2}{2M} + M\omega_q^2\frac{Q_q^2}{2}\right] \tag{10.133}$$

where μ is the chemical potential. Notice that the mass of the oscillators M is undefined. The reason is given below. Furthermore, in the scattering process the electron transfer momentum to the impurity (momentum is not conserved in the scattering problem) and this leads to the creation of particle-hole pairs with finite momentum q. Since the momentum operator associated with the pair is P_q we see that the J_z operator in (10.131) can be replaced by:

$$J_z\sigma^z \sum_{\mathbf{k},\mathbf{k}',\sigma} \sigma c^\dagger_{\mathbf{k},\sigma}c_{\mathbf{k}',\sigma} \rightarrow J_z\sigma^z \sum_{q>0} P_q\,. \tag{10.134}$$

Defining now creation and annihilation operators for the harmonic oscillators in the usual way:

$$a_q \;=\; \sqrt{\frac{M\omega_q}{2}}\left(Q_q - \frac{i}{\sqrt{M\omega_q}}P_q\right)$$

$$a_q^\dagger = \sqrt{\frac{M\omega_q}{2}}\left(Q_q + \frac{i}{\sqrt{M\omega_q}}P_q\right) \tag{10.135}$$

we find that the Hamiltonian in terms of bosons can be written as:

$$H = \sum_{q>0} \omega_q a_q^\dagger a_q + \lambda\sigma^z \sum_{q>0} \sqrt{q} i (a_q - a_q^\dagger) + J_\perp \sigma^x \,. \tag{10.136}$$

We will rewrite the Hamiltonian by redefining the creation and annihilation operators by a phase factor:

$$b_q = i a_q = e^{i\pi/2} a_q \tag{10.137}$$

so that:

$$H = \sum_{q>0} \omega_q b_q^\dagger b_q + \lambda\sigma^z \sum_{q>0} \sqrt{q}(b_q + b_q^\dagger) + J_\perp \sigma^x \,, \tag{10.138}$$

where

$$\lambda = J_z \sqrt{\frac{M v_F}{2}} \,. \tag{10.139}$$

The Hamiltonian in (10.138) is called the dissipative two-level system model since it describes a problem of a two-state system (the eigenstates of σ^z) coupled to a heat bath of harmonic oscillators. Notice that the parameter M remains undefined. The reason for that is that the oscillators are produced by the coupling of the impurity to the particle-hole excitations and therefore their mass is also determined by this coupling. The procedure presented here cannot tell how M behaves as a function of J_z and thus we can think of M (or λ) as parameters of the problem that have to be obtained by different means. What is guaranteed from our construction is that the number of degrees of freedom in the problem is correct and that the low energy physics of Hamiltonian (10.138) is the same as the original fermionic problem (10.120). One way to obtain λ is to solve the problem via Bethe ansatz or numerical methods and obtain λ as a function of J_z. From now on we will think of λ as a parameter of the problem in its own right.

The Hamiltonian in (10.138) has another free parameter that is not explicit in the Hamiltonian. Notice that the bosons are a result of the linearization of the electronic dispersion close to the Fermi surface (see Fig.6.4) and therefore our procedure is only valid if the momentum of the particle-hole pair is smaller than a cut-off, Λ. The size of this cut-off can be estimated to be of the order of the Fermi momentum, k_F, which, in most metals, is proportional to the inverse of the lattice spacing, a. That is, our approximation assumes that:

$$q \ll \Lambda \approx k_F \approx \frac{1}{a} \tag{10.140}$$

which implies that our theory only describes wavelengths much larger than a. Moreover, the sums in (10.138) are bounded from above by Λ.

Now, we have in our hands the tools to discuss the reason why perturbation theory fails for this problem. Notice that the operator $J_\perp$ flips the pseudo-spin $|+\rangle$ to $|-\rangle$ and vice-versa. In this case the sign of the interaction in the J_z term changes from $+$ to $-$, that is, there is a sudden switch on of the interaction! As long as the system is in one of the eigenstates of σ^z not much happens (there is a simple shift of the boson momentum) but once the pseudo-spin flips a potential is switched on and the ground state changes! When we study time dependent perturbation theory we learn that the perturbation potential has to be switched on very slowly so that states of the system do not change drastically. This is not the case here and this is why perturbation theory fails.

In what follows I will describe a way to treat this problem with a renormalization group (RG) method that gives results beyond perturbation theory. The main idea is to use the fact that the harmonic oscillators with energy close to $v_F\Lambda = W \approx E_F$ are very fast compared with the impurity spin. In fact, the flipping time of the spin can be estimated by the uncertainty principle to be:

$$t_{flip} \approx \frac{\hbar}{J_\perp} \gg \frac{\hbar}{W} \tag{10.141}$$

since we will assume that $J_\perp \ll W \approx E_F$. In this case, the fast (high energy) harmonic modes always "see" the impurity spin as static (in the same sense that in the Born-Oppenheimer approximation the electrons "see" a static lattice of ions). Thus, the fast oscillator oscillate many periods before the spin flips and their only effect is to "dress" the spin

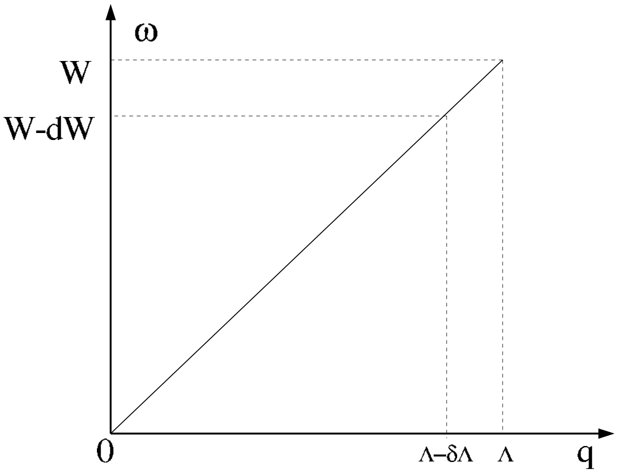

Figure 10.6: *Dispersion of the particle-hole excitations and the RG procedure of reducing the cut-off* Λ.

(in the same way that electrons "glue" the ions). In order to understand how these high energy degrees of freedom "dress", or more elegantly, renormalize the spin flips let us consider the effect of changing the cut-off Λ to $\Lambda - d\Lambda$ (see Fig.10.6). Observe that this is equivalent to change the energy scale from W to $W - dW$ ($W = v_F\Lambda$).

The state of the pseudo-spin can be now calculated in first order perturbation theory in λ as:

$$\begin{aligned}
|+,0\rangle \to |+\rangle_R &= \frac{1}{\sqrt{N}}\left\{|+,0\rangle + \lambda\sigma^z \sum_{q=\Lambda-d\Lambda}^{\Lambda} \frac{\sqrt{q}}{\omega_q} b_q^\dagger |+,0\rangle\right\} \\
&= \frac{1}{\sqrt{N}}\left\{|+,0\rangle + \frac{\lambda}{\sqrt{v_F}} \sum_{q=\Lambda-d\Lambda}^{\Lambda} \frac{1}{\sqrt{q}} |+,q\rangle\right\} \\
|-,0\rangle \to |-\rangle_R &= \frac{1}{\sqrt{N}}\left\{|-,0\rangle - \frac{\lambda}{\sqrt{v_F}} \sum_{q=\Lambda-d\Lambda}^{\Lambda} \frac{1}{\sqrt{q}} |-,q\rangle\right\} \quad (10.142)
\end{aligned}$$

where $|\pm,0\rangle$ is the state without bosons and $|\pm,q\rangle$ is the state with one boson with momentum q such that $\Lambda - d\Lambda < q < \Lambda$. The subscript R indicates that this is the renormalized state and N is the normalization factor that can be easily calculated from the condition that $\langle\pm|\pm\rangle_R = 1$, that is,

$$N \approx 1 + \left(\frac{\lambda}{v_F}\right)^2 \sum_{q=\Lambda-d\Lambda}^{\Lambda} \frac{1}{q}. \tag{10.143}$$

In order to calculate the renormalized value of the coupling constants, that is, the value of the coupling constant when we reduce the cut-off we realize that, the bare value of the coupling is given by:

$$J_\perp = \langle +, 0|H|0, +\rangle \tag{10.144}$$

as you can easily prove from (10.138). The renormalized value of the coupling, $J_\perp^R$ is then given by:

$$\begin{aligned} J_\perp^R &= \frac{1}{N}\langle +|H|+\rangle_R \\ &= \frac{1 - \left(\frac{\lambda}{v_F}\right)^2 \sum_{q=\Lambda-d\Lambda}^{\Lambda} \frac{1}{q}}{1 + \left(\frac{\lambda}{v_F}\right)^2 \sum_{q=\Lambda-d\Lambda}^{\Lambda} \frac{1}{q}} \\ &\approx 1 - 2\left(\frac{\lambda}{v_F}\right)^2 \sum_{q=\Lambda-d\Lambda}^{\Lambda} \frac{1}{q} \end{aligned} \tag{10.145}$$

where in the last line we have used the fact that we are doing perturbation theory. The sum over q can be easily performed:

$$\sum_{q=\Lambda-d\Lambda}^{\Lambda} \frac{1}{q} = \ln\left(\frac{\Lambda}{\Lambda - d\Lambda}\right) \approx \frac{d\Lambda}{\Lambda}. \tag{10.146}$$

Furthermore, the value of the renormalized cut-off is (see Fig.10.6): $W^R = W - dW = W(1 - d\Lambda/\Lambda)$ and therefore we can write

$$\begin{aligned} \frac{J_\perp^R}{W^R} &= \frac{J_\perp}{W}\frac{1 - \alpha\frac{d\Lambda}{\Lambda}}{1 - \frac{d\Lambda}{\Lambda}} \\ \frac{J_\perp^R}{W^R} &= \frac{J_\perp}{W}\left(1 + (1-\alpha)\frac{d\Lambda}{\Lambda}\right) \end{aligned} \tag{10.147}$$

where we have defined the constant α given by:

$$\alpha = 2\left(\frac{\lambda}{v_F}\right)^2 \tag{10.148}$$

which, like M and λ can be viewed as a undetermined function of J_z. Notice that (10.147) tells us how the dimensionless coupling constant

$$g_\perp = \frac{J_\perp}{W} \tag{10.149}$$

changes as we change the scale of the problem, that is, $g_\perp = g_\perp(\Lambda)$. Eq.(10.147) can be rewritten in the form:

$$\begin{aligned} g_\perp(\Lambda - d\Lambda) &= g_\perp(\Lambda)\,(1-(1-\alpha)d\ln(1/\Lambda)) \\ \frac{dg_\perp}{d\ell} &= (1-\alpha)g_\perp(\ell) \end{aligned} \tag{10.150}$$

where we have defined

$$\ell = \ln(\Lambda_0/\Lambda) = \ln(W_0/W) \tag{10.151}$$

where Λ_0 is the bare value of the cut-off. Eq.(10.150) is the RG equation for the coupling $J_\perp$. This equation can be solved as:

$$g_\perp(\ell) = g_\perp(0)e^{(1-\alpha)\ell} \tag{10.152}$$

where $g_\perp(0) = J_\perp/W$ is the coupling constant of the problem at the original scale Λ while $g_\perp(\ell)$ is the coupling at an arbitrary scale. From this result we immediately can conclude the following: if $\alpha > 1$ we have $g_\perp(\ell \to \infty) \to 0$ indicating that at longer and longer length scales (smaller Λ) the coupling vanishes and this term is irrelevant for the long wavelength physics; if $\alpha < 1$ we have $g(\ell \to \infty) \to \infty$ and the coupling constant becomes arbitrarily large as we reduce the cut-off indicating that the coupling is relevant and dominates the physics in the long wavelength limit. The case of $\alpha = 1$ is called marginal and the RG equations will only have a contribution to order $g_\perp^2$.

Thus, the conclusion of this RG calculation is that perturbation theory is only reliable in the case of $\alpha > 1$ since the perturbation becomes weaker and weaker at low energies. In this case we can effectively make $J_\perp = 0$ in the Hamiltonian and we see that the problem simply reduces to the problem discussed previously of the formation of the bound state (or scattering) out of a impurity. The state of the impurity is an eigenstate of the σ^z operator.

For $\alpha < 1$ the coupling becomes arbitrarily large and perturbation theory fails miserably and in this case we have to find a better way to solve the problem (which usually means that we have to solve the problem exactly!). We can make an educated guess of what happens in this case. Observe that the fact that $J_\perp$ becomes relevant in this limit indicates that this is the dominant term in the Hamiltonian. This implies that the state of the impurity is an eigenstate of the σ^x operator. Thus, we expect the ground state of the problem to be:

$$|s\rangle = \frac{1}{\sqrt{2}}\left(|+\rangle_R - |-\rangle_R\right) \tag{10.153}$$

which is the singlet state. This is the so-called Kondo singlet. Notice that our perturbation theory is only well defined for $J_\perp \leq W$, that is, $g_\perp \leq 1$. For $\alpha < 1$ the coupling $g_\perp$ grows under the RG until it reaches $g_\perp(\ell^*) = 1$ where, from (10.152):

$$\ell^* \approx \frac{1}{1-\alpha}\ln(1/g_\perp(0)) \tag{10.154}$$

Using (10.151) we see that this scale is associated with an energy scale $k_B T_K$ such that:

$$\begin{aligned} \ln(W_0/k_B T_K) &= \frac{1}{1-\alpha}\ln(W_0/J_\perp) \\ k_B T_K &= W_0\left(\frac{J_\perp}{W_0}\right)^{1/(1-\alpha)} . \end{aligned} \tag{10.155}$$

For energies or temperatures above T_K the coupling is small and the problem can be treated perturbatively but for temperatures smaller than T_K the system flows to strong coupling and the Kondo singlet is formed. This temperature scale is called the Kondo temperature of the problem. Observe that for $J_\perp = 0$ we have $T_K = 0$ and therefore no Kondo effect.

Thus we have found that the behavior of the problem changes dramatically when we go from $\alpha > 1$ to $\alpha < 1$. We have argued that α has to be a function of J_z and therefore there must be a critical value of J_z for which the physics of the problem changes completely. The question is: can we stare at our original Hamiltonian (10.120) and understand how J_z changes the physics of the Kondo problem? The answer is quite simple, in fact. Notice that the formation of a singlet state requires $J_z > 0$, that is, an antiferromagnetic coupling between the impurity and the electron gas. If $J_z < 0$, that is, if we had ferromagnetic coupling the state of the system would be a triplet, that is, $| \Uparrow, \uparrow\rangle$ or $| \Downarrow, \downarrow\rangle$ (degenerate). In this case notice that the $J_\perp$ term does not connect these two terms and therefore is not able to lift this degeneracy in first order perturbation theory. Thus, $J_\perp$ is irrelevant in this case. Thus, we can easily assign the case of $\alpha > 1$ with the case of $J_z < 0$ while $\alpha < 1$ for $J_z > 0$. Thus, the quantity $1 - \alpha$ is an odd function of J_z, that is, $1 - \alpha(J_z)$ can be written as a power series expansion in J_z with odd powers only. For $J_z \ll W_0$ we expect, based on this argument that:

$$\alpha(J_z) \approx 1 - C\frac{J_z}{W_0} \tag{10.156}$$

where C is a constant independent of J_z. Thus, in this limit the Kondo temperature can be written, from (10.155) as:

$$k_B T_K \approx W_0 \left(\frac{J_\perp}{W_0}\right)^{W_0/(CJ_z)} = W_0 \exp\left\{-\frac{\ln(W_0/J_\perp)}{CJ_z/W_0}\right\} \tag{10.157}$$

Notice that for $J_z = 0$ we have $\alpha = 1$ and therefore from (10.155) we have $T_K = 0$ indicating that there is no Kondo effect in this case. These results show that in the Kondo effect both the Ising, J_z, as well as the transverse, $J_\perp$, couplings are fundamental for the occurrence of the Kondo effect.

In the case of the isotropic Kondo effect ($J_\perp = J_z = J$) the RG flow can be calculated by different techniques and one can show that:

$$\frac{dg}{d\ell} = g^2 \tag{10.158}$$

where $g = J/W$. In this case the Kondo coupling is marginal (very similar to the previous case with $\alpha = 1$). We can solve this RG flow as:

$$g(\ell) = \frac{g(0)}{1 + g(0)\ell} \tag{10.159}$$

which shows that when $\ell^* = -1/g(0)$ the coupling constant diverges under the RG, indicating, as previously the failure of perturbation theory. From this result we obtain the Kondo temperature of the problem as:

$$k_B T_K = W e^{-1/g(0)} \approx W e^{-W/J} \tag{10.160}$$

and therefore the Kondo temperature is exponentially small with the Kondo coupling J.

The experimental consequences of the formation of the bound states are immediate: the magnetic susceptibility of the impurity, instead of following the Curie law, $\chi \propto 1/T$ has to saturate at $T = T_K$ so that

$$\chi_{imp}(T) \propto \frac{1}{T_K} \, ; \tag{10.161}$$

the entropy of the system, instead of being $S = k_B N \ln(2)$ as it would be for a spin $1/2$ atom has to go to zero below T_K because of the formation of the bound state, this implies that the specific heat, $C_V = TdS/dT$, has to behave like

$$C_{V,imp} \propto \frac{T}{T_K} \tag{10.162}$$

for $T < T_K$. All these effects are observed at low temperatures ($T_K \approx 1 - 5$ K) in magnetic alloys.

Moreover, the Kondo effect leads to the so-called Kondo minimum in the electric resistance of these systems. On the one hand, formation of the virtual bound states or scattering resonances implies strong scattering (with the phase shifts close to $\pi/2$ also known as the unitarity limit). The scattering increases below T_K and therefore one expects the resistivity to increase with decreasing temperatures. On the other hand, phonon scattering decreases with decreasing temperature because as the system gets cooler there are less phonons in the system. The final result is therefore a minimum in the resistivity.

Another interesting property of the Kondo effect is its non-locality. Since $E_F \gg k_B T_K$ for $T_K \sim T \ll E_F/k_B$ the only energy scale in the problem is the Kondo temperature T_K. The only information of the electron gas that is important for this problem is the Fermi velocity, v_F, since the states at the bottom of the Fermi sea are irrelevant for the physics discussed here. Using the Fermi velocity and the Kondo temperature we can construct a quantity with dimensions of length, ℓ_K, that is called the Kondo screening length:

$$\ell_K = \frac{\hbar v_F}{k_B T_K} . \tag{10.163}$$

The physical meaning of this quantity can be understood if we calculate the average value of the correlation function between the local spin $\mathbf{S}$ and the electron spin $\mathbf{s}(r)$, namely,

$$\langle \mathbf{S} \cdot \mathbf{s}(r) \rangle \sim e^{-r/\ell_K} \tag{10.164}$$

which decays exponentially with distance from the impurity. Although this result has not been demonstrated here it seems almost obvious when we realize that the only length scale in this problem is given by (10.163). This result shows that for distances larger than ℓ_K the electrons and the impurity are uncorrelated. Only electrons in a region of size ℓ_K^3 around the impurity site participate in the Kondo screening process. We can estimate the number of electrons, N_K, as:

$$N_K \sim n\ell_K^3 \sim (k_F \ell_K)^3 \propto \left(\frac{E_F}{k_B T_K}\right)^3 \tag{10.165}$$

where we used that the electronic density n is essentially proportional to k_F^3 and used (10.163) with $E_F \approx \hbar v_F k_F$. Since $E_F \approx 1$ eV and $k_B T_K \approx 10^{-4}$ eV we see that $N_K \approx 10^{12}$ electrons. That is, a huge number of electrons participate in the screening process.

10.7 Problems

1. Consider the Hamiltonian for the Kondo problem (10.118) in its isotropic form ($J_z = J_\perp$) and assume that $J \ll E_F$ and that the electrons have a spherical Fermi surface.

   (*i*) Using the first Born approximation, calculate the scattering amplitude $t^{(1)}(k, k')$ for the scattering of an electron from an state $|\mathbf{k}, \uparrow$ to a state $|\mathbf{k}', \uparrow$ as a function of J and S^z.

   (*ii*) Show that in the second Born approximation the scattering amplitude, $t^{(2)}$ is given by:

$$\begin{aligned} t^{(2)}(k, k') &= \sum_{\mathbf{k}'',\sigma} \frac{1}{E_{\mathbf{k}} - E_{\mathbf{k}'}} [(1 - n_{\mathbf{k}''})\langle \mathbf{k}, \uparrow |H_K|\mathbf{k}'', \sigma\rangle \langle \mathbf{k}'', \sigma|H_K|\mathbf{k}', \uparrow\rangle \\ &+ \; n_{\mathbf{k}}\langle \mathbf{k}'', \sigma|H_K|\mathbf{k}', \uparrow \langle \mathbf{k}, \uparrow |H_K|\mathbf{k}'', \sigma\rangle \, . \qquad (10.166) \end{aligned}$$

   Here $n_{\mathbf{k}}$ is the Fermi-Dirac occupation number. Notice that the order of the matrix elements matters! Explain why.

   (*iii*) Show that the above expression can be approximately written as:

$$t^{(2)}(k) \approx 2\,(J)^2\, S^z \sum_{\mathbf{k}''} \frac{n_{\mathbf{k}''}}{E_{\mathbf{k}} - E_{\mathbf{k}''}} \, . \qquad (10.167)$$

   Assuming a constant density of states $N(0)$ for the electrons calculate the sum above and show that it can be approximately written as:

$$t^{(2)}(k) \approx 2\,(J)^2\, S^z N(0) \ln(W/|E_F - E_k|) \qquad (10.168)$$

   where W is the bandwidth. Notice that $t^{(2)}(k_F)$ is divergent!

   (*iv*) The total scattering by the impurity, $\langle t^{(2)} \rangle$ can be obtained by integrating (10.168) around the Fermi surface in a region of energy of size $k_B T$. Show that in this case $\langle t^{(2)} \rangle$ is logarithmically divergent with the temperature.

   (*v*) The total resistance generated by the presence of the impurity is written as: $\rho(T) = \rho_0(1 - \langle t^{(2)} \rangle)$ where ρ_0 is the temperature independent part of the resistance (see Chapter 7). If the phonon contribution to the resistance is given by $\rho_P(T) = AT^5$ show that this gives rise to a resistance minimum in the behavior of the total resistivity of the material.

10.8 Itinerant Magnetism

So far we have discussed the problem of magnetism arising from impurities on a metallic host. In this type of systems there are two types of electrons: localized electrons coming from f or d shells and conduction band electrons from s or p shells. In many systems such as Fe magnetism appears due to electrons in a single atomic shell. In this case one cannot differentiate between the electron that produces the magnetism and the electron that participates in the conduction. Systems like this are called itinerant. Our starting point is going to be the Hubbard model which was discussed in the beginning of this chapter

$$H = \sum_{\mathbf{k},\sigma}(\epsilon_{\mathbf{k}} - \mu)c^{\dagger}_{\mathbf{k},\sigma}c_{\mathbf{k},\sigma} + U\sum_{i} n_{i,\uparrow}n_{i,\downarrow} . \tag{10.169}$$

Here we have introduced the chemical potential μ and will work in the canonical ensemble keeping μ fixed and allowing the number of electrons to fluctuate. The complete solution of (10.169) was only obtained in one dimension via the so-called Bethe ansatz. In higher dimensions one has to use approximate solutions. In this section we are going to treat the problem in the Hartree-Fock approximation. This is an uncontrolled approximation. Although with own limitations, this kind of approach can provide a lot of insight about the physics of the problem.

The complexity of (10.169) is associated with the treatment the interaction term. Because it involves four electron operators it is a highly non-linear problem. In mean field theory we replace the interaction term by

$$n_{i,\uparrow}n_{i,\downarrow} \to \langle n_{i,\uparrow}\rangle n_{i,\downarrow} + n_{i,\uparrow}\langle n_{i,\downarrow}\rangle - \langle n_{i,\uparrow}\rangle\langle n_{i,\downarrow}\rangle \tag{10.170}$$

where the averages are evaluated in the ground state. Notice that the factorization is done so that $\langle n_{i,\uparrow}n_{i,\downarrow}\rangle = \langle n_{i,\uparrow}\rangle\langle n_{i,\downarrow}\rangle$, that is, the fluctuations in the up and down spin channels are independent.

It is convenient to rewrite the problem in terms of the total number of electrons per site and the magnetization as

$$\begin{aligned} N_i &= \langle n_{i,\uparrow}\rangle + \langle n_{i,\downarrow}\rangle \\ M_i &= \langle n_{i,\uparrow}\rangle - \langle n_{i,\downarrow}\rangle \end{aligned} \tag{10.171}$$

or equivalently,

$$\begin{aligned} \langle n_{i,\uparrow}\rangle &= \frac{N_i + M_i}{2} \\ \langle n_{i,\downarrow}\rangle &= \frac{N_i - M_i}{2} \end{aligned} \tag{10.172}$$

in which case the mean-field Hamiltonian is given by

$$\begin{aligned} H_{MF} &= \sum_{\mathbf{k},\sigma}(\epsilon_{\mathbf{k}} - \mu)c^\dagger_{\mathbf{k},\sigma}c_{\mathbf{k},\sigma} + \frac{U}{2}\sum_i \left[N_i(n_{i,\uparrow} + n_{i,\downarrow}) - M_i(n_{i,\uparrow} - n_{i,\downarrow})\right] \\ &- \frac{U}{4}\sum_i (N_i^2 - M_i^2)\,. \end{aligned} \tag{10.173}$$

In what follows we are going to assume that state is always homogeneous and therefore

$$N_i = n = \frac{N_e}{N} \tag{10.174}$$

where N_e is the total number of electrons and N the total number of sites. In this case we can rewrite (10.173) as

$$\begin{aligned} H_{MF} &= \sum_{\mathbf{k},\sigma}\epsilon_{\mathbf{k}}c^\dagger_{\mathbf{k},\sigma}c_{\mathbf{k},\sigma} + \frac{UNn^2}{4} + \frac{Un}{2}\sum_i (n_{i,\uparrow} + n_{i,\downarrow}) \\ &+ \frac{U}{4}\sum_i M_i^2 - \frac{U}{2}\sum_i M_i(n_{i,\uparrow} - n_{i,\downarrow}) \end{aligned} \tag{10.175}$$

where the second term in the first line on the r.h.s. of (10.175) is a total energy shift, the third term is just a shift of the electron energy, the first term on the second line on the r.h.s. is the energy required to magnetize the system and the last term is the interaction between the magnetization and the electron themselves. This term has the form of

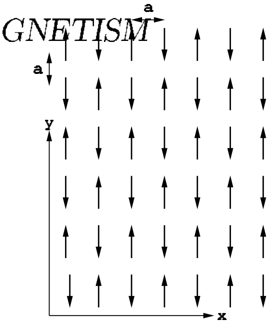

Figure 10.7: *Two-dimensional Néel state.*

a local applied magnetic field. Observe that in this problem M_i is an unknown and has to be calculated self-consistently. As usual in mean field approaches one has to guess the nature of the ground state, that is, the form of the magnetization. In a ferromagnetic system all spins point in the same direction and therefore $M_i = M_0$ for all sites. In an antiferromagnetic system the situation is more complicated because one can have different sub-lattices in which all the spins are up or all the spins are down. For instance, for a square lattice the magnetization can be given by

$$M_{i,j} = M_0(-1)^{i+j} \tag{10.176}$$

where each site is located at (ai, aj) where a is the lattice spacing. This classical state of the electron system is called the Néel state and it is shown on Fig. 10.7. Observe that although the magnetization changes from point to point in space the Fourier transform of (10.176) is quite simple

$$M(\mathbf{q}) \propto \delta(\mathbf{q} - \mathbf{Q}) \tag{10.177}$$

where $\mathbf{Q} = (\pi/a, \pi/a)$ is the so-called ordering vector. For a ferromagnet we have $\mathbf{Q} = 0$.

Here we are going to consider only the case of the ferromagnet and leave the antiferromagnet as a problem for the reader. In the ferromagnetic case we can rewrite (10.175) as

$$\begin{aligned} H_{MF} &= \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} n_{\mathbf{k},\sigma} + \frac{NUM_0^2}{4} + \frac{UM_0}{2} \sum_i (n_{i,\uparrow} - n_{i,\downarrow}) \\ &= \frac{NUM_0^2}{4} + \sum_{\mathbf{k}} \left[\left(\epsilon_{\mathbf{k}} - \mu - \frac{UM_0}{2} \right) n_{\mathbf{k},\uparrow} + \left(\epsilon_{\mathbf{k}} - \mu + \frac{UM_0}{2} \right) n_{\mathbf{k},\downarrow} \right] \end{aligned} \tag{10.178}$$

where we have used $\sum_i n_{i,\sigma} = \sum_{\mathbf{k}} n_{\mathbf{k},\sigma}$. Observe that (10.178) is already in diagonal form since it only depends on the occupation in momentum space. The total energy now only depends on the occupation of each spin state, that is, in the ground state

$$\langle n_{\mathbf{k},\sigma}\rangle = \Theta(E_{F,\sigma} - \epsilon_{\mathbf{k}}) \tag{10.179}$$

where $E_{F,\sigma}$ is the Fermi energy of each spin state and at this point it is an unknown. Moreover, M_0 in (10.178) and it is also unknown. In order to calculate this parameters one has to minimize the total energy of the system as a function of them. The energy of the system is written as:

$$\begin{aligned} E &= \frac{NUM_0^2}{4} + \sum_{\mathbf{k}} \left[\left(\epsilon_{\mathbf{k}} - \frac{UM_0}{2}\right)\Theta(E_{F,\uparrow} - \mu - \epsilon_{\mathbf{k}}) \right. \\ &+ \left.\left(\epsilon_{\mathbf{k}} - \mu + \frac{UM_0}{2}\right)\Theta(E_{F,\downarrow} - \epsilon_{\mathbf{k}})\right] \end{aligned} \tag{10.180}$$

As usual in this kind of problems it is useful to introduce the electronic density of states

$$N(\epsilon) = \frac{1}{V}\sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}}) \tag{10.181}$$

in which case the energy density $\mathcal{E} = E/V$ becomes

$$\begin{aligned} \mathcal{E} &= \frac{\rho_s UM_0^2}{4} + \int_{-\infty}^{E_{F,\uparrow}} d\epsilon \left(\epsilon - \mu - \frac{UM_0}{2}\right) N(\epsilon) \\ &+ \int_{-\infty}^{E_{F,\downarrow}} d\epsilon \left(\epsilon - \mu + \frac{UM_0}{2}\right) N(\epsilon) \end{aligned} \tag{10.182}$$

where $\rho_s = N/V$ is the solid density. In order to calculate the unknown parameters in the energy density we have to minimize it so that

$$\begin{aligned} \frac{\partial \mathcal{E}}{\partial \mu} &= -\rho \\ \frac{\partial \mathcal{E}}{\partial E_{F,\sigma}} &= 0 \\ \frac{\partial \mathcal{E}}{\partial M_0} &= 0 \end{aligned} \tag{10.183}$$

where $\rho = N_e/V$ is the electron density. Furthermore, in order to make sure that the solution is really a minimum and not a maximum one has calculate the second derivatives of the energy with respect to the variational parameters. The reader can do it as an exercise. From (10.183) one finds

$$\begin{aligned}
\int_{-\infty}^{E_{F,\uparrow}} d\epsilon N(\epsilon) + \int_{-\infty}^{E_{F,\downarrow}} d\epsilon N(\epsilon) &= \rho \\
\left(E_{F,\sigma} - \sigma\frac{UM_0}{2} - \mu\right) N(E_{F,\sigma}) &= 0 \\
\rho_s M_0 + \int_{-\infty}^{E_{F,\uparrow}} d\epsilon N(\epsilon) - \int_{-\infty}^{E_{F,\downarrow}} d\epsilon N(\epsilon) &= 0 \,.
\end{aligned} \qquad (10.184)$$

We can first solve for μ and M_0 using the two equations for the spins:

$$\begin{aligned}
\mu &= \frac{E_{F,\uparrow} + E_{F,\downarrow}}{2} \\
M_0 &= \frac{E_{F,\uparrow} - E_{F,\downarrow}}{U}
\end{aligned} \qquad (10.185)$$

which can be now substituted into the other two equations:

$$\begin{aligned}
\int_{-\infty}^{E_{F,\uparrow}} d\epsilon N(\epsilon) + \int_{-\infty}^{E_{F,\downarrow}} d\epsilon N(\epsilon) &= \rho \\
\int_{E_{F,\uparrow}}^{E_{F,\downarrow}} d\epsilon N(\epsilon) &= \rho_s \frac{E_{F,\uparrow} - E_{F,\downarrow}}{U}
\end{aligned} \qquad (10.186)$$

which is the set of equation with define $E_{F,\uparrow}$ and $E_{F,\downarrow}$. After these are calculated one can obtain the chemical potential and magnetization from (10.185). Using (10.185) we can rewrite (10.186) as

$$\begin{aligned}
\rho &= 2\int_{-\infty}^{E_{F,\uparrow}} d\epsilon N(\epsilon) + \rho_s \frac{E_{F,\uparrow} - E_{F,\downarrow}}{U} \\
\rho_s \frac{E_{F,\uparrow} - E_{F,\downarrow}}{U} &= \int_{E_{F,\uparrow}}^{E_{F,\downarrow}} d\epsilon N(\epsilon) \,.
\end{aligned} \qquad (10.187)$$

Observe that the last equation in (10.187) can be rewritten as

$$\rho_s \frac{E_{F,\uparrow} - E_{F,\downarrow}}{U} = \int_{0}^{E_{F,\uparrow}-E_{F,\downarrow}} d\epsilon N(\epsilon + E_{F,\downarrow}) \qquad (10.188)$$

which for fixed $E_{F,\downarrow}$ is a single equation for $E_{F,\uparrow} - E_{F,\downarrow}$. Since the density of states has a finite bandwidth the integral in (10.188) is a monotonic function of $x = E_{F,\uparrow} - E_{F,\downarrow}$ and saturates at large values x as shown in Fig. 10.8. The solution of (10.188) is the intercept of a straight line of slope ρ_s/U and the r.h.s. of (10.188). Observe that there is a critical value of U, say, U_C, above which one finds a solution with $x = x^* \neq 0$ and therefore from (10.185) corresponds to a system with finite magnetization, that is, a ferromagnetic state. For U smaller than U_C the only solution is $x = 0$ which is the paramagnetic state. In order to calculate U_C one has to linearize the r.h.s. of (10.188) in order to get

$$U_C = \frac{\rho_s}{N(\bar{E}_{F,\downarrow})} \tag{10.189}$$

where $\bar{E}_{F,\uparrow}$ is determined by the first equation in (10.187):

$$\rho = 2\int_{-\infty}^{\bar{E}_{F,\uparrow}} d\epsilon N(\epsilon) \tag{10.190}$$

which completes the solution of the problem at $U = U_C$. The condition for the existence of a ferromagnetic state for U larger than U_C as given in (10.189) is called Stoner criterion. This criterion, which is based on a mean field approach, is only a estimate of how large U has to be (or how large the density of states has to be) in order for the system to have a spontaneous ferromagnetic magnetization. As we are going to see in the next chapter the mean field solution is an extreme approximation that has its limitations. It provides us, however, with the information that the Coulomb interaction is fundamental for the creation of an ordered magnetic state.

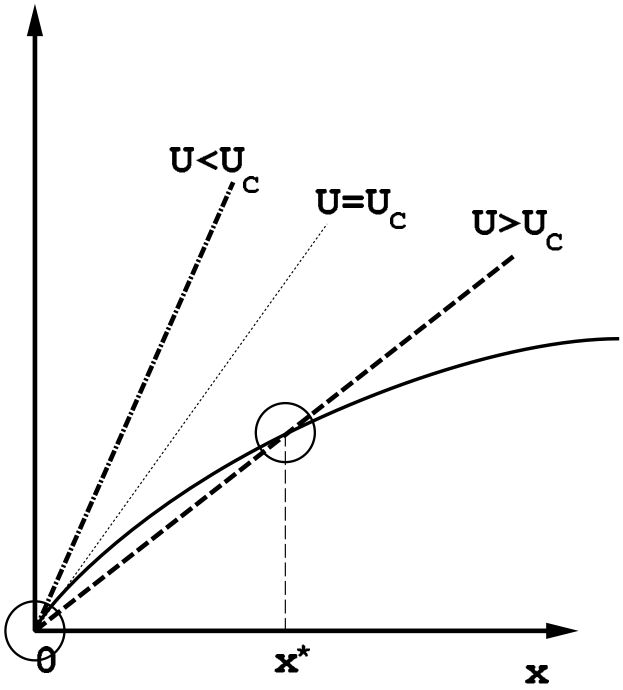

Figure 10.8: *Diagrammatic solution of (10.188): solid line is the r.h.s. of (10.188).*

10.9 Problems

1. Consider the problem of itinerant magnetism in an antiferromagnet in a square lattice in two dimensions in which the magnetization is given in (10.176). This can be rewritten as

   $$M(\mathbf{r}) = M_0 \cos(\mathbf{Q}\cdot\mathbf{r})$$

   where $\mathbf{Q} = (\pi/a, \pi/a)$.

   (*i*) Show that for a square lattice the electron dispersion relation in the tight binding approximation is given by

   $$\epsilon_{\mathbf{k}} = -2t\left(\cos(k_x a) + \cos(k_y a)\right) \,.$$

   And therefore show that $\epsilon_{\mathbf{k}} = -\epsilon_{\mathbf{k}+\mathbf{Q}}$.

   (*ii*) Make a plot of the Fermi surface in momentum space, that is, (k_x, k_y) at half filling ($\epsilon_{\mathbf{k}} = 0$). Show that the opposite sides of the Fermi surface can be linked by the vector $\mathbf{Q}$. Observe that this means that the symmetry of the problem has been broken and now states which differ by a vector $\mathbf{Q}$ are actually the same state. Explain what symmetry has been broken and show that the magnetic Brillouin zone of the problem is the Fermi surface you just plotted.

   (*iii*) Write down the mean field Hamiltonian for the problem and show that it depends on $c_{\mathbf{k},\sigma}$ and $c_{\mathbf{k}\pm\mathbf{Q},\sigma}$. Define the following spinor:

   $$[\Psi_\sigma(\mathbf{k})] = \left(\begin{array}{c} c_{\mathbf{k},\sigma} \\ c_{\mathbf{k}+\mathbf{Q},\sigma} \end{array}\right)$$

   and show that the Hamiltonian of the problem can be written as

   $$H = \frac{UM_s^2}{4} + \sum_{\mathbf{k},\sigma,\sigma'} [\Psi_\sigma(\mathbf{k})]^\dagger \, [\mathcal{H}_{\sigma,\sigma'}] \, [\Psi_{\sigma'}(\mathbf{k})]$$

   where

   $$[\mathcal{H}_{\sigma,\sigma'}] = \left[\begin{array}{cc} \epsilon_{\mathbf{k}} & \frac{UM_s}{2}\tau_z \\ \frac{UM_s}{2}\tau_z & -\epsilon_{\mathbf{k}} \end{array}\right]$$

where M_s is the staggered magnetization and τ_z is a Pauli matrix.

(*iv*) Diagonalize the above Hamiltonian and find the new electronic spectrum. Show that a gap opens in the spectrum at the Fermi surface. Interpret your result in terms of the symmetry of the problem.

(*v*) Calculate the total energy of the problem by filling up all the energy states below the gap (since the system is at half filling) and by minimizing it find the equation that determines M_s.

(*vi*) In this item we are going to use the Debye theory for phonons in the context of the antiferromagnet. Expand the spectrum around the $(\pi/a, \pi/a)$ point to second order in the momentum and perform the integral of item

(*v*). Note that you have to introduce a cut-off in the upper limit of the integral so it converges. This cut-off, say Λ, can be calculated by using Debye's theory for phonons. What is the functional form of M_s as a function of U and t.

Chapter 11

Magnetic phase transitions

In the last chapter we discussed the origins of magnetic interactions in solids and how they lead to magnetic order. At high temperatures magnetic atoms behave independently from each other leading to the paramagnetic behavior. At low temperatures the atoms can take advantage of magnetic exchange interactions and lower their energy by ordering in a some specific form that depends on the particular character of the interactions. The two main types of ordering are ferromagnetic and antiferromagnetic, depending if the system orders with its magnetic moments parallel or anti-parallel to each other.

In this chapter we focus on the problem of magnetic ordering and its consequences to the magnetic behavior of solids. When the system orders magnetically we say that long range order has been established. When a system attains long range order the internal symmetry of the system is lowered. Thus, with the decreasing of the temperature there is a spontaneous lowering of the symmetry and thus a phase transition: a transition between a highly symmetric phase at high temperatures and a low symmetry phase at low temperatures. The study of the phase transition has reached a great deal of development with the introduction of the concept of renormalization group and universality. These are one of the most important concepts in modern condensed matter physics.

11.1 Spontaneous symmetry breaking

In order to understand how a phase transition occurs in a magnetic system we consider for instance the ferromagnetic Ising model,

$$H = -\frac{1}{N}\sum_{i,j=1}^{N} J_{ij} S_i^z S_j^z \tag{11.1}$$

where $J_{ij} > 0$. Observe that the Hamiltonian (11.1) has a symmetry for the reversal of the spins, that is, we can reverse all the spins and the Hamiltonian remains the same. Mathematically the Hamiltonian is invariant under $S_j^z \to -S_j^z$. The question here is: is the ground state of the (11.1) invariant under this symmetry? Firstly let us assume that the ground state is invariant under the overturn of spins. We can specify any state of the system in the terms of the eigenstates of S^z, that is,

$$|0\rangle = |S_1^z, S_2^z, ..., S_N^z\rangle\,. \tag{11.2}$$

If this states is invariant under the overturn of spins we certainly have

$$|-S_1^z, -S_2^z, ..., -S_N^z\rangle = |S_1^z, S_2^z, ..., S_N^z\rangle\,. \tag{11.3}$$

It follows immediately that

$$\begin{aligned}\langle S_1^z, ..., S_N^z|S_j^z|S_1^z, ..., S_N^z\rangle &= \langle -S_1^z, ..., -S_N^z|S_j^z|-S_1^z, ..., -S_N^z\rangle \\ &= -\langle S_1^z, ..., S_N^z|S_j^z|S_1^z, ..., S_N^z\rangle \end{aligned}\tag{11.4}$$

from which we have to conclude

$$\langle 0|S_j^z|0\rangle = 0\,. \tag{11.5}$$

Thus, if the ground state has the symmetry of the Hamiltonian then the average magnetic moment is zero. It is possible, however, that the ground state does not have the symmetry of the Hamiltonian, that is, it is not invariant under $S_j^z \to -S_j^z$. In this case we cannot conclude (11.5) and we can have that $\langle 0|S_j^z|0\rangle \neq 0$. If this happens the symmetry of the Hamiltonian is broken and the system acquires finite magnetic moment. In a system without disorder, that is, a system with the translation symmetry of the lattice, all the spins are equivalent and therefore it does not make sense to speak of a particular spin. In this case we define an average quantity over all spins

$$M = \frac{1}{N}\sum_{j=1}^{N}\langle 0|S_j^z|0\rangle \tag{11.6}$$

where $M \neq 0$ in the phase with broken symmetry. M is the *magnetization* of the system and it can be finite because the spins interact ferromagnetically so they can align on some given direction. If the ground state of the system is such that (11.6) is true than we can that the symmetry is *spontaneously broken* since the ground state does not have the symmetry of the Hamiltonian. Observe, however, that we have two possibilities: either all the spins point in the up direction or they point in the down direction. For these two states the symmetry is broken and they are *degenerate* since they have the same energy. This degeneracy can be lifted by applying a magnetic field to the system. In the presence of an infinitesimal field the degeneracy of these two states is lifted and the system picks the state with lowest energy. We say that the external magnetic field is the *symmetry breaking field.*

At high temperatures we expect the magnetic moments to act independently, that is, paramagnetically. At these temperatures we would have $M = 0$ since the spins point randomly. If the the system, at zero temperature, has $M \neq 0$ then there is a *critical temperature* T_c such that above T_c the system is *disordered*, that, is $M(T > T_c) = 0$, and above which the system is *ordered*, that is, $M(T < T_c) \neq 0$. At $T = T_c$ we have a *phase transition.* Since the magnetization changes from zero to a finite value at the transition we say that $M(T)$ is the *order parameter* of the magnetic problem. Moreover we have two possibilities at $T = T_c$: *i)* the magnetization can jump discontinuously from $M(T = T_c + \epsilon) = 0$ to $M(T = T_c - \epsilon) \neq 0$ at $T = T_c$ ($\epsilon \to 0$) in which case we say that the transition is of *first order* as shown in Fig.11.1(a); *ii)* the magnetization can go continuously from $M(T = T_c + \epsilon) = 0$ to $M(T = T_c - \epsilon) \neq 0$ at $T = T_c$ in which case we say that the transition is of *second order* as shown Fig.11.1(b). Observe that the fact that the magnetization

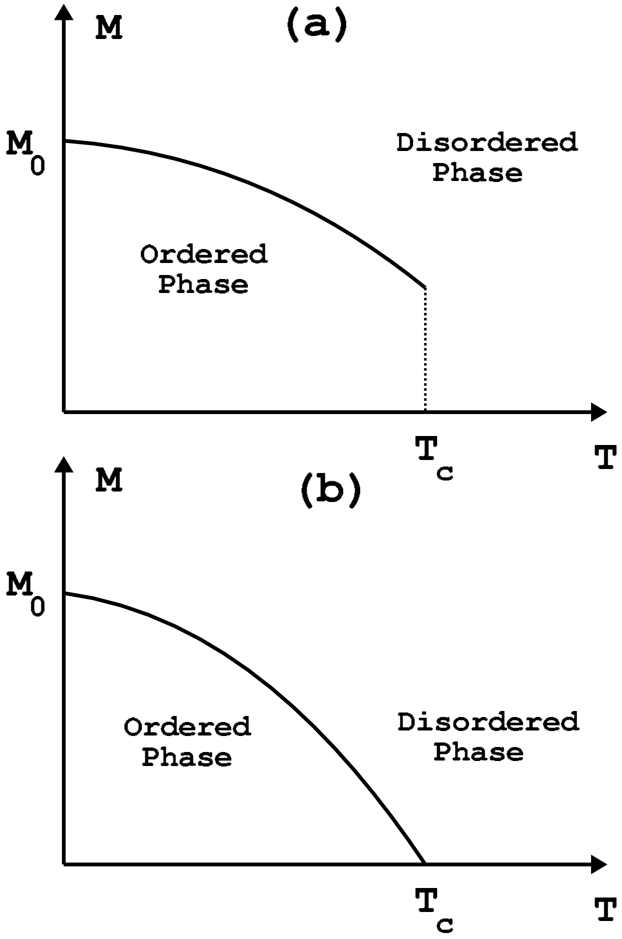

Figure 11.1: *Magnetization of a system during a phase transition: a) First order; b) Second order.*

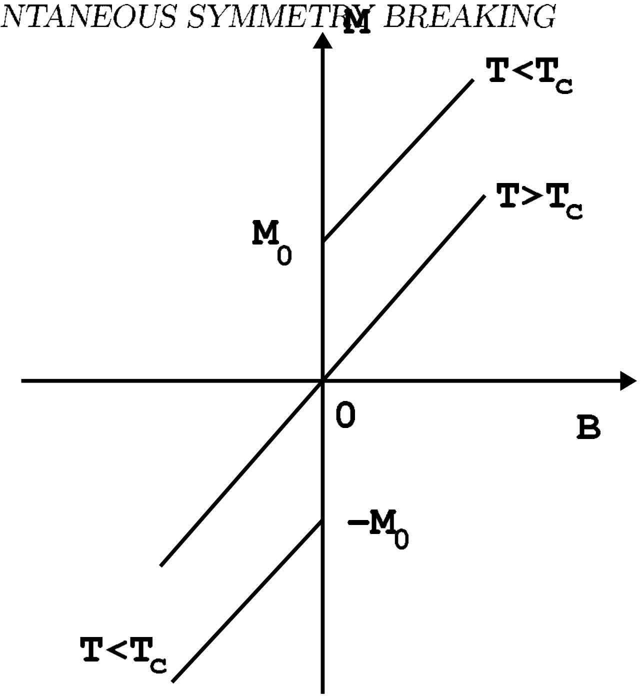

Figure 11.2: *Magnetization as a function of external field at fixed temperature.*

changes at $T = T_c$ implies that the magnetic susceptibility, that is,

$$\chi(T) = \left(\frac{\partial M}{\partial B}\right)_{B\to 0} \tag{11.7}$$

diverges at $T = T_c$. In order to understand why this is so consider the plot of the magnetization as a function of the magnetic field at fixed temperature as shown in Fig.11.2. At $T > T_c$ the magnetization is just paramagnetic and is zero at $B = 0$. If $T < T_c$ one has $M(T) \neq 0$ for $B = 0$. Thus, at $T = T_c$, the magnetization has infinite curvature implying a divergent susceptibility.

Although we have talked about ferromagnets the concept of broken symmetry, order parameter and symmetry breaking field can be generalized to any system with long range order. As an example consider the case of an antiferromagnet such as the one shown on Fig. 10.7. Observe that in this case the system indeed has $\langle S_j^z \rangle \neq 0$ at each site but the total magnetization as defined in (11.6) vanishes even in the ordered phase. This is because the homogeneous magnetization is not the order parameter of the antiferromagnet. Let us look at the magnetization of an antiferromagnet as the one in Fig. 10.7. It is easy to see that the local magnetization at position $\mathbf{r} = (n, m)a$ is

$$M(\mathbf{r}) = M_s(-1)^{n+m} \tag{11.8}$$

where M_s is a constant. Observe that the magnetization oscillates from site to site and therefore vanishes if we sum over all sites. However, it is clear from the equation above that M_s has to be finite in the ordered phase. We can obtain M_s from (11.8) if we multiply both sides by $(-1)^{n+m}$ and sum over all sites:

$$M_s = \frac{1}{N}\sum_{\mathbf{r}}(-1)^{n+m}M(\mathbf{r}) = \frac{1}{N}\sum_{j=1}^{N}(-1)^j\langle S_j^z\rangle \tag{11.9}$$

which is called the staggered magnetization of the system. Furthermore, observe that the ferromagnetic state retains the symmetry of the lattice while in the antiferromagnetic case the unit cell doubles (one needs at least one spin up and one spin down in the same unit cell) and then the translational invariance of the lattice is also broken (you explored this effect in the last problem on Chapter 8). A clear way to see that, is to Fourier transform the local magnetization in each case. For the ferromagnet the local magnetization is uniform, $M(\mathbf{r}) = M_0$, and therefore its Fourier transform has Dirac delta peaks at $\mathbf{k} = 0$ and all other reciprocal lattice vectors $\mathbf{G}$. Thus the ferromagnet has the symmetry of the lattice. In the antiferromagnetic case as given in (11.8) the Fourier transform has Dirac delta peak at $\mathbf{Q} = (\pi/a, \pi/a)$ as you can easily show. Finally, the symmetry breaking field in this case is not an homogeneous magnetic field since it cannot differentiate between the two degenerate states of the antiferromagnet (which are obtained by flipping all the spins in the system). In the antiferromagnetic case a staggered field is the symmetry breaking field!

11.1.1 Critical exponents

In the case of second order phase transitions the order parameter goes smoothly to zero at the critical temperature which implies that the magnetization has to behave like

$$M(T) \propto (T_c - T)^{\beta} \tag{11.10}$$

for T very close (and smaller) than T_c. β is known as a *critical exponent.* The magnetic susceptibility is given by

$$\chi(T) \propto (T - T_c)^{-\gamma} \tag{11.11}$$

for $T > T_c$ and

$$\chi(T) \propto (T_c - T)^{-\gamma'} \tag{11.12}$$

for $T < T_c$ since the susceptibility has to diverge on both sides of transition but not necessarily with the same exponents. Another exponents are defined for other physical quantities. For instance, the specific heat at fixed field also diverges at $T = T_c$ and one has

$$C_H(T) \propto (T - T_c)^{-\alpha} \tag{11.13}$$

for $T > T_c$ and

$$C_H(T) \propto (T_c - T)^{-\alpha'} \tag{11.14}$$

for $T < T_c$. Another interesting property is that the magnetization does not have to be linear with the magnetic field at $T = T_c$ and we define another exponent δ by

$$M \propto |B|^{1/\delta} sgn(B) \,. \tag{11.15}$$

Besides the critical exponents that define the thermodynamic functions there are exponents that define dynamical correlations. Correlation functions are important for experiments that measure spatial and temporal correlations among spins. In the phonon problem we showed that the dynamical form factor $S(\mathbf{k}, \omega)$ is given in terms of a density-density correlation function. Remember that the neutrons interact with the system of interest via the spin-spin interaction. Thus, neutron scattering is very sensitive to magnetic order. Like in the case of scattering of neutrons by phonons we would have Bragg scattering of the neutrons below T_c when the system has long range order. Observe that as in the case of atoms in a solid the Bragg peaks are directly related with the magnetic ordering in the system. In the case of the ferromagnet the magnetic ordering does not break the symmetry of the lattice and in the case where the ordering is commensurate with the lattice the Bragg peaks are at the reciprocal lattice vectors $\mathbf{G}$. Thus, in a ferromagnet magnetic peaks superimpose to lattice peaks. This is not the case of an antiferromagnet where a Bragg peak appears at $\mathbf{Q}$ which is not a reciprocal lattice vector. As in the case of phonons, perfect order implies the presence of infinitely sharp Bragg peaks. In the magnetically disordered phase we do not expect these peaks to disappear immediately but to become broader due to lack of long range order. In momentum space this broadening is given by $1/\xi$ where ξ is called the magnetic correlation length. In order to understand the meaning of the correlation length let us assume for simplicity that the shape of the peak (or intensity) in the magnetically disordered phase is given by a Lorentzian shape

$$I(\mathbf{k}) = \frac{I_0/\xi}{(\mathbf{k}-\mathbf{Q})^2 + 1/\xi^2} \tag{11.16}$$

where $\mathbf{Q}$ is the ordering vector ($\mathbf{Q} = 0$ for the ferromagnet and $\mathbf{Q} \neq 0$ for the antiferromagnet) and I_0 is a constant. Observe that when $\xi \to \infty$ the Lorentzian in (11.16) goes to a Dirac delta function at $\mathbf{k} = \mathbf{Q}$ as expected in the case of complete order. Thus ξ is a function of temperature and diverges at $T = T_c$. Moreover, it is easy to show that the intensity is proportional to the spin-spin correlation function for spins at different sites, $\langle S_i^z S_j^z \rangle$. In order to see how the correlation function behaves one has to Fourier transform (11.16) to real space. It is a simple exercise to show that

$$I(\mathbf{r}_i - \mathbf{r}_j) \propto \langle S_i^z S_j^z \rangle \propto \exp\left\{-\frac{|\mathbf{r}_i - \mathbf{r}_j|}{\xi(T)}\right\}. \tag{11.17}$$

Now the meaning of the term correlation length is clear: it tells what is the characteristic distance above which the spins are uncorrelated. At $T = T_c$ one expects the spins to be strongly correlated and $\xi(T)$ diverges. One then defines the critical exponents for $\xi(T)$ as

$$\xi(T) \propto (T - T_c)^{-\nu} \tag{11.18}$$

when $T > T_c$ and $B = 0$ and

$$\xi(T) \propto (T_c - T)^{-\nu'} \tag{11.19}$$

when $T < T_c$ and $B = 0$. In some cases the correlation function decays algebraically with the distance (in which case the neutron scattering intensity is not a Lorentzian)

$$\langle S_j^z S_j^z \rangle \propto \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|^{d-2+\eta}} \tag{11.20}$$

with a new exponent η for a system in d dimensions.

It turns out that these critical exponents are not independent of each other because of the thermodynamic relations between the various quantities. This is related with the so-called *scaling hypothesis.* Consider the free energy $F(T, B)$ which we parameterize in terms of the reduced temperature

$$t = \frac{T - T_c}{T_c}\,. \tag{11.21}$$

The *scaling hypothesis* asserts that, close to the phase transition, it is always possible to find two parameters a_t and a_B such that

$$F(\lambda^{a_t} t, \lambda^{a_B} B) = \lambda F(t, B) \tag{11.22}$$

for any value of the real number λ.

In order to understand how the exponents are relate let us differentiate (11.22) with respect to B in order to get the magnetization:

$$\begin{aligned} \lambda^{a_B} \frac{\partial F(\lambda^{a_t} t, \lambda^{a_B} B)}{\partial(\lambda^{a_B} B)} &= \lambda \frac{\partial F(t, B)}{\partial B} \\ \lambda^{a_B} M(\lambda^{a_t} t, \lambda^{a_B} B) &= \lambda M(t, B)\,. \end{aligned} \tag{11.23}$$

Consider the case where $B = 0$ and $t \to 0$. From (11.23) we have:

$$M(t, 0) = \lambda^{a_B - 1} M(\lambda^{a_t} t, 0) \tag{11.24}$$

that is valid for any λ. In particular for

$$\lambda = \left(-\frac{1}{t}\right)^{1/a_t} \tag{11.25}$$

we find

$$M(t,0) = (-t)^{\frac{1-a_B}{a_t}} M(-1,0)\,. \tag{11.26}$$

But from (11.10) we have in the limit of $t \to 0^-$

$$\beta = \frac{1-a_B}{a_t}\,. \tag{11.27}$$

Let us now take $t = 0$ and let $B \to 0$ in (11.23)

$$M(0,B) = \lambda^{a_B - 1} M(0, \lambda^{a_B} B) \tag{11.28}$$

and choose $\lambda = B^{-1/a_B}$ in order to get

$$M(0,B) = B^{\frac{1-a_B}{a_B}} M(0,1) \tag{11.29}$$

which by direct comparison with (11.15) leads to

$$\delta = \frac{a_B}{1-a_B}\,. \tag{11.30}$$

Similarly we can derive twice with respect to B in order to obtain

$$\lambda^{2a_B} \chi(\lambda^{a_t} t, \lambda^{a_B} B) \;=\; \lambda \chi(t,B)\,. \tag{11.31}$$

Taking the limit of $B = 0$ first and choosing $\lambda = (-t)^{-1/a_t}$ we can prove

$$\gamma' = \frac{2a_B - 1}{a_t} \tag{11.32}$$

and using again (11.31) with $\lambda = t^{-1/a_t}$ one finds

$$\gamma' = \gamma \tag{11.33}$$

implying that the susceptibility diverges with the same exponents on both sides of the transition. Moreover, combining (11.32) with (11.27), (11.30) and (11.33) one finds

$$\gamma = \beta(\delta - 1) \tag{11.34}$$

which relates three different exponents.

Using exactly the same arguments for derivatives with respect to the temperature we can show that

$$\alpha' + \beta(\delta + 1) = 2 \tag{11.35}$$

and

$$\alpha = \alpha' \tag{11.36}$$

and combining (11.35) with (11.34) one finds

$$\alpha + 2\beta + \gamma = 2\,. \tag{11.37}$$

Many other relations between the exponents can be obtained in this way. Although the scaling hypothesis is an assumption and cannot be proved, it makes many predictions for critical exponents that can be checked experimentally or analytically for specific models. This hypothesis has been very successful in explain critical behavior in systems with second order phase transitions.

11.2 Mean field approach

In order to calculate the exponents that define the critical behavior of a magnetic systems we have several options. One of them is to solve the problem exactly. This is a major task since the problems at hand are very complicated. The other approach is to use mean field theories. In mean field theories we look at a particular spin and try to replace all the other spins in the problem by a the average field of the other spins. We have discussed this procedure in the case of itinerant magnetic systems at the end of Chapter 8. Here we are going to discuss it in the context of localized magnetism. Let us go back to the problem of the ferromagnetic Ising problem in a magnetic field. We will assume that the interaction occurs only among next nearest neighbors. The Hamiltonian given by

$$H = -\frac{J}{N}\sum_{\langle i,j\rangle} S_i^z S_j^z - g\mu_B \sum_i S_i^z B\,. \tag{11.38}$$

In the mean field approach we replace the interaction by

$$S_i^z S_j^z \rightarrow \langle S_i^z \rangle S_j^z + \langle S_j^z \rangle S_i^z \,. \tag{11.39}$$

Moreover, we assume that the magnetization is uniform so that $\langle S_i^z \rangle = M$ in which case Hamiltonian (11.38) is replaced by

$$H_{MF} = -g\mu_B \sum_i B_{eff} S_i^z \tag{11.40}$$

where

$$B_{eff} = B + \lambda M(T,B) \tag{11.41}$$

is the *effective magnetic field*, Z is the number of nearest neighbors and $M(T,B)$ is the magnetization given in (11.6) and

$$\lambda = \frac{2ZJ}{(g\mu_B)^2} \tag{11.42}$$

is the so-called *molecular field*. Observe that (11.40) is the Hamiltonian of a set of independent spins S in a magnetic field. This problem was studied for paramagnets in Chapter 8. In particular the magnetization of this problem is given in (1.38),

$$\begin{aligned} M(T,B) &= M_0 B_S[\beta g S \mu_B B_{eff}] \\ &= M_0 B_S[\beta g S \mu_B (B + \lambda M(T,B))] \end{aligned} \tag{11.43}$$

where $M_0 = g\mu_B S$. Notice that (11.43) has to be solved self-consistently to give the magnetization. For $B = 0$ this equation reduces to

$$M = M_0 B_S[\beta g S \mu_B \lambda M] \tag{11.44}$$

which is shown graphically on Fig.11.3. Observe that this equation has the trivial solution $M = 0$ for all T. This equation has also a non-trivial solution $M \neq 0$ if the slope of the straight line is larger than the slope of Brillouin function. Thus let us consider the Brillouin function close to $M = 0$. The expansion of $B_S(x)$ for small x is

$$B_S(x) \approx \frac{S+1}{3S} x - \frac{(S+1)(1+2S+2S^2)}{90S^3} x^3 \tag{11.45}$$

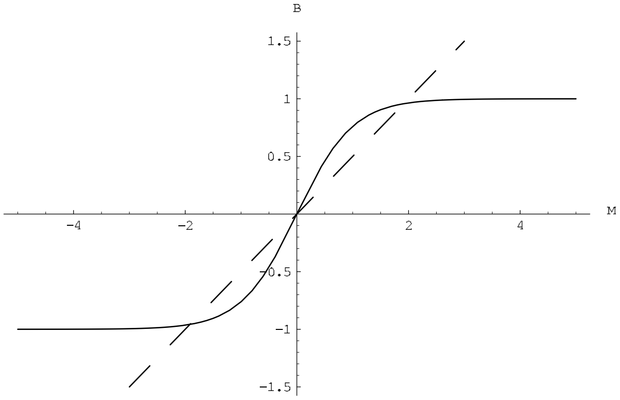

Figure 11.3: *Graphical solution of eq.* (11.44)

and therefore there is a non-trivial solution for temperatures $T < T_c$. In order to calculate T_c we use (11.44) to find where the slopes in both sides of (11.44) equal each other. That is,

$$1 = g\mu_B S \frac{S+1}{3S} \frac{g\mu_B S\lambda}{k_B T_c} \tag{11.46}$$

and therefore (11.42) we have

$$T_c = \lambda\mathcal{C} = \frac{2ZJS(S+1)}{3k_B} \tag{11.47}$$

where

$$\mathcal{C} = \frac{(g\mu_B)^2 S(S+1)}{3k_B} \tag{11.48}$$

is the Curie constant.

For simplicity let us consider the case of a $S = 1/2$ spin in which the Brillouin function reduces to $B_{1/2}(x) = \tanh(x/2)$ and (11.43) reduces to

$$M = M_0 \tanh\left(\beta g \mu_B (B + \lambda M)/2\right) . \tag{11.49}$$

In order to simplify our calculations we define

$$\begin{aligned} m &= \frac{M}{M_0} \\ \tau &= \frac{T}{T_c} \end{aligned} \tag{11.50}$$

and (11.49) becomes

$$m = \tanh\left(\frac{g\mu_B B\beta}{2} + \frac{m}{\tau}\right) \tag{11.51}$$

which can be rewritten with the help of trigonometric identities as

$$b = \frac{m - \tanh(m/\tau)}{1 - m\tanh(m/\tau)} \tag{11.52}$$

where

$$b = \tanh\left(\frac{g\mu_B B\beta}{2}\right) . \tag{11.53}$$

Let us consider the case that $T \approx T_c$ where $m \approx 0$ and expand (11.52) as

$$b \approx m\left(1 - \frac{1}{\tau}\right) + m^3\left[\frac{1}{3\tau^3} + \frac{1}{\tau}\left(1 - \frac{1}{\tau}\right)\right] . \tag{11.54}$$

In zero field, $b = 0$, (11.54) gives

$$m^2 \approx 3\tau^2\left(\frac{1}{\tau} - 1\right) \propto (T_c - T) \tag{11.55}$$

which can be immediately compared with (11.10) to give

$$\beta_{MF} = \frac{1}{2} . \tag{11.56}$$

At the critical temperature, that is, $\tau = 1$, and small fields one finds

$$\frac{g\mu_B B}{2k_B T_c} \approx \frac{m^3}{3} \tag{11.57}$$

which, by comparison with (11.15), gives

$$\delta_{MF} = 3\,. \tag{11.58}$$

In order to calculate the susceptibility we observe that

$$\begin{aligned} \chi(T) &= \frac{\partial M}{\partial B} = \frac{\partial M}{\partial m}\frac{\partial m}{\partial b}\frac{\partial b}{\partial B} \\ &= \frac{\mathcal{C}}{T}\frac{\partial m}{\partial b}\,. \end{aligned} \tag{11.59}$$

If we differentiate (11.54) with respect b we get

$$\frac{\partial m}{\partial b} \approx \left[\left(1 - \frac{1}{\tau}\right) + \frac{m^2}{\tau^3}\right]^{-1} \tag{11.60}$$

and from (11.59) one finds

$$\chi(T) \approx \frac{\mathcal{C}}{T}\left[\left(1 - \frac{1}{\tau}\right) + \frac{m^2}{\tau^3}\right]^{-1}\,. \tag{11.61}$$

In the disordered phase ($T > T_c$) we have $m = 0$ and therefore

$$\chi(T) \approx \frac{\mathcal{C}}{T - T_c} \tag{11.62}$$

which from (11.11) gives

$$\gamma_{MF} = 1 \tag{11.63}$$

while in the ordered phase ($T < T_c$) we use (11.55) and find

$$\chi(T) \approx \frac{\mathcal{C}}{2T}\frac{1}{T_c - T} \tag{11.64}$$

which from (11.12) we find

$$\gamma'_{MF} = 1\,. \tag{11.65}$$

Observe that the scaling hypothesis predicts from (11.35) and (11.36) that $\alpha_{MF} = \alpha'_{MF} = 0$ which implies that the specific heat does not diverge at the transition.

11.3 Mean field and beyond

Observe that the mean field theory has no small parameter and cannot be explained in terms of a perturbative expansion. In order to understand better the nature of the mean field let us consider the problem in the basis of S_i^z ($S_i^z|\sigma_i\rangle = \sigma_i|\sigma_i\rangle$ where $\sigma_i = \pm 1$). In this case the energy of the problem depends on the configuration $\{\sigma_i\}$ and from (11.38) we have

$$E(\{\sigma_i\}, B) = -\sum_{i,j} J_{i,j}\sigma_i\sigma_j - \sum_i \sigma_i B\,. \tag{11.66}$$

where we assume that $J_{i,j}$ only depends on the relative distance $|\mathbf{r}_i - \mathbf{r}_j|$ between the two spins. The partition function of the problem is given by

$$Z[B] = \sum_{\{\sigma_i\}} e^{-\beta E(\{\sigma_i\}, B)} \tag{11.67}$$

where the sum is over all the spin configurations. Observe that (11.67) is quite useful since the magnetization at zero field of the system is

$$\begin{aligned} M &= \frac{\sum_{\{\sigma_i\}}\sum_j \sigma_j e^{-\beta E(\{\sigma_i\}, B=0)}}{\sum_{\{\sigma_i\}} e^{-\beta E(\{\sigma_i\}, B=0)}} \\ &= \frac{1}{\beta Z[B=0]}\left(\frac{\partial Z[B]}{\partial B}\right)_{B=0}\,. \end{aligned} \tag{11.68}$$

We will rewrite (11.67) in a different way using a well known identity

$$\int_{-\infty}^{+\infty} dx e^{-x^2/(4a^2)+sx} = \sqrt{2\pi a}\; e^{a^2 s^2}\,. \tag{11.69}$$

Using (11.66) in zero field ($B = 0$) and the above identity we can write

$$\begin{aligned} Z &= \sum_{\{\sigma_i\}} e^{\sum_{i,j} K_{i,j}\sigma_i\sigma_j} \\ &\propto \sum_{\{\sigma_i\}} \int_{-\infty}^{\infty} \prod_{j=1}^{N} d\phi_j e^{-\frac{1}{4}\sum_{i,j}\phi_i J_{i,j}^{-1}\phi_j + \sum_i \phi_i\sigma_i} \\ &\propto \int_{-\infty}^{\infty} \prod_{j=1}^{N} d\phi_j e^{-\frac{1}{4}\sum_{i,j}\phi_i J_{i,j}^{-1}\phi_j} \sum_{\{\sigma_i\}} e^{\sum_i \phi_i\sigma_i} \end{aligned} \tag{11.70}$$

where $K_{i,j} = \beta J_{i,j}$. We now observe that

$$\sum_{\{\sigma_i\}} e^{\sum_i \phi_i \sigma_i} = \prod_i 2\cosh(\phi_i) = 2e^{\sum_i \ln(\cosh(\phi_i))} . \tag{11.71}$$

Moreover, we define,

$$\psi_i = \sum_j \frac{1}{2} J_{i,j}^{-1} \phi_j \tag{11.72}$$

and the partition function becomes

$$Z \propto \int_{-\infty}^{\infty} \prod_{j=1}^{N} d\psi_j e^{-\sum_{i,j} \psi_i K_{i,j} \psi_j + \sum_i \ln\left(\cosh(2\sum_j K_{i,j}\psi_j)\right)} . \tag{11.73}$$

Observe that what we have done was to trade a sum over discrete variables for an integral over a continuous variable. But in doing so we have generated a non-linear term in the partition function.

11.3.1 Interactions with infinite range

Let us now consider the "artificial" case of interactions with infinite range. In this case we have

$$\begin{aligned} J_{i,j} &= \frac{2J}{N} \\ K_{i,j} &= \frac{K}{N} = \frac{2J\beta}{N} . \end{aligned} \tag{11.74}$$

Observe that in this case the partition function in (11.73) simplifies considerably since we can change variables to a "center of mass" variable

$$\psi = \frac{1}{N} \sum_i \psi_i \tag{11.75}$$

in which case the partition function can be written as

$$Z \propto \int_{-\infty}^{+\infty} d\psi \; e^{-N\left\{K\psi^2 - \ln(\cosh(2K\psi))\right\}} \tag{11.76}$$

which is a simple integral but with a very complicated integrand. Notice that the exponent in (11.76) scales with N the number of spins in the system. But we are interested in the limit of $N \to \infty$ in which case the integral is dominated by the *saddle point* value of the integral that is, the minimum of the function

$$S(\psi) = K\psi^2 - \ln\left(\cosh(2K\psi)\right) \tag{11.77}$$

which is plotted of Fig.11.4. The minimum of this function is given by

$$\begin{aligned} \frac{\partial S}{\partial \psi} &= 0 \\ \psi &= \tanh(2K\psi) \end{aligned} \tag{11.78}$$

which gives the value of ψ. Observe that (11.78) is identical to (11.49) with $\psi \propto M$. In particular, if $K < 1/2$ ($T > T_c = 2J/k_B$) the only solution is $\psi = 0$ and for $K > 1/2$ ($T < T_c = 2J/k_B$) a solution with $\psi \neq 0$ exists. This simple calculation shows that mean field theory is equivalent to solve the problem with interactions with infinite range! Thus, we should suspect that in the real case with short range interactions fluctuations around the mean field solution are going to be very important.

In order to understand the how the phase transition occurs let us consider the *free energy* for the *order parameter* as given by (11.77). Let us expand $S(\psi)$ to fourth order in ψ ($\ln\cosh x \approx x^2/2 - x^4/12$):

$$S(\psi) \approx K(1-2K)\psi^2 + \frac{4K^4}{3}\psi^4 \,. \tag{11.79}$$

Observe that the quadratic term changes from negative to positive when $K > 1/2$ to $K < 1/2$. Therefore the curvature of the free energy at $\psi = 0$ changes at $K = 1/2$. In this case the ground state of the system for $K < 1/2$ which is given by $\psi = 0$ becomes metastable at $K = 1/2$. For $K > 1/2$ the state with $\psi = 0$ becomes unstable and the ground state is given by the two solutions of (11.78) which are degenerate reflecting the symmetry of the problem. It is clear that the full form of (11.77) is not needed. The physics of the problem is already present in (11.79). The term proportional to ψ^4 is only need to keep the free energy bounded from below in the ordered phase. Without this

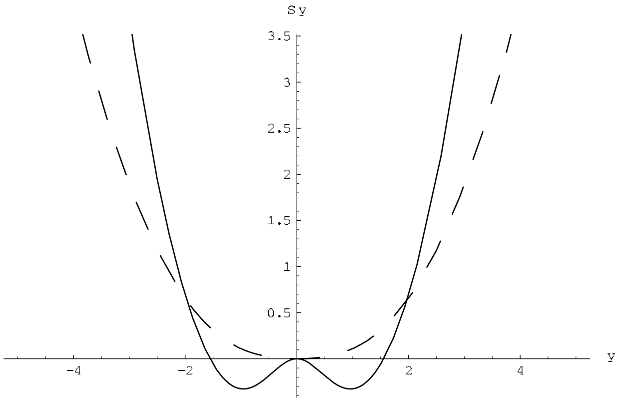

Figure 11.4: *Plot of eq.* (11.77). *Dashed line:* $K < 1/2$; *Continuous line:* $K > 1/2$.

term the system would be thermodynamic unstable since the ground state would be given by $\psi \rightarrow \pm\infty$ with infinite negative energy when $K > 1/2$ which is clearly unphysical. In the disordered phase $K < 1/2$ the free energy is naturally bounded and the term in ψ^4 is irrelevant for the physics.

11.3.2 Local interactions

Naturally the interactions between spins are short-ranged. In this case the previous approach is not appropriate. Indeed $K_{i,j}$ is really localized close to $\mathbf{r}_i = \mathbf{r}_j$ instead. The best way to realize this is to look at the Fourier transform of $K_{i,j}$,

$$K(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} K(\mathbf{k})\,. \tag{11.80}$$

On the one hand, if $K(\mathbf{r})$ has infinite range then $K(\mathbf{k})$ is a Dirac delta function at $\mathbf{k} = 0$. On the other hand, if $K(\mathbf{r})$ is localized then $K(\mathbf{k})$

is a smooth function of **k**. Therefore, if we work in momentum space we can always work with functions that can be expand in power series. So let us introduce the Fourier transform of ψ_i,

$$\psi(\mathbf{r}_i) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_i} \psi(\mathbf{k})\,. \tag{11.81}$$

Moreover, because $K(\mathbf{r})$ and $\psi(\mathbf{r}_i)$ are real functions we must have $K(-\mathbf{k}) = K^*(\mathbf{k})$ and $\psi(-\mathbf{k}) = \psi^*(\mathbf{k})$.

As we explained in the case of the interactions with infinite range interactions we do not need to work with the full free energy (11.73). Instead we are going to use a truncated form of the free energy

$$F \approx \sum_{i,j} \psi_i K_{i,j} \psi_j - 2\sum_i \left(\sum_j K_{i,j}\psi_j \right)^2 + \frac{4}{3} \sum_i \left(\sum_j K_{i,j}\psi_j \right)^4 . \tag{11.82}$$

For the moment being we are going to focus on the quadratic terms. It is very easy to show with the use of these Fourier transforms the following relations

$$\begin{aligned} \sum_{i,j} \psi_i K_{i,j} \psi_j &= \sum_{\mathbf{k}} K(\mathbf{k}) \psi(\mathbf{k}) \psi(-\mathbf{k}) \\ \sum_i \left(\sum_j K_{i,j}\psi_j \right)^2 &= \sum_{\mathbf{k}} K(\mathbf{k}) K(-\mathbf{k}) \psi(\mathbf{k}) \psi(-\mathbf{k})\,. \end{aligned} \tag{11.83}$$

Thus the quadratic part of (11.82) can be written as

$$F_0 = \sum_{\mathbf{k}} \left(K(\mathbf{k}) - 2|K(\mathbf{k})|^2 \right) |\psi(\mathbf{k})|^2\,. \tag{11.84}$$

Observe that if the interaction was a Dirac delta function in real space (local interaction) then $K\mathbf{k})$ should be a constant. Let us assume that $K(\mathbf{k})$ is a real function of its argument. Then (11.84) as

$$F_0 = \sum_{\mathbf{k}} K(\mathbf{k}) \left(1 - 2K(\mathbf{k})\right) |\psi(\mathbf{k})|^2\,. \tag{11.85}$$

This equation is very important because it tells us that if there is a wave-vector **Q** for which

$$K(\mathbf{Q}) > \frac{1}{2} \tag{11.86}$$

then the system is *unstable* at that particular wave-vector. Observe that this condition implies that the phase transition happens to the component $\psi(\mathbf{Q})$. Since ψ is essentially the magnetization of the system is implies that the order parameter of the system is given by

$$M(\mathbf{r}) = M_0 \Re\left(e^{i\mathbf{Q}\cdot\mathbf{r}}\right) . \tag{11.87}$$

This is in complete agreement with our previous discussion.

Let us now go back to the ferromagnetic problem and study what happens at the unstable wave-vector, that is, $\mathbf{k} = 0$. Close to $\mathbf{k} = 0$ we can expand $K(\mathbf{k})$ as

$$K(k) \approx K_0 \left(1 - (\ell k)^2 + \mathcal{O}(k^4)\right) \tag{11.88}$$

where ℓ is a constant with dimensions of length. From now on we are going to disregard all the terms of order k^4 and higher. Observe that K_0 is the Fourier component of $K(k)$ with zero momentum, that is,

$$K_0 = \sum_{\mathbf{r}} K(\mathbf{r}) = Z\beta J \tag{11.89}$$

where we have assumed that the interaction only couples the Z nearest neighbor atoms. Direct substitution of (11.88) into (11.84) one gets

$$F_0 = \sum_{\mathbf{k}} K_0 \left[(1 - 2K_0) + (4K_0 - 1)(\ell k)^2\right] |\psi(\mathbf{k})|^2 . \tag{11.90}$$

Observe that, exactly like in the case of the mean field theory when $k = 0$ this part of the free energy becomes negative when $K_0 > 1/2$ which defines the critical temperature

$$T_c = \frac{2ZJ}{k_B} . \tag{11.91}$$

At this level of approximation we are recovering the mean field approximation.

If we are interested only in temperatures close to T_c then we can write

$$\begin{aligned} K_0 &\approx \frac{1}{2} + \mathcal{O}(T - T_c) \\ 1 - 2K_0 &\approx \frac{T - T_c}{T_c} + \mathcal{O}(T - T_c)^2 \\ 4K_0 - 1 &\approx 1 + \mathcal{O}(T - T_c) \end{aligned} \tag{11.92}$$

and the free energy (11.90) as

$$F_0 \approx \frac{1}{2}\sum_{\mathbf{k}}\left(\frac{T-T_c}{T_c}+(\ell k)^2\right)|\psi(\mathbf{k})|^2\,. \tag{11.93}$$

It is usual to rewrite (11.93) in a slightly different way by defining

$$\begin{aligned} \phi(\mathbf{k}) &= \ell\,\psi(\mathbf{k}) \\ \mu^2 &= \frac{T-T_c}{\ell^2 T_c} \end{aligned} \tag{11.94}$$

in which case (11.93) becomes

$$F_0 \approx \frac{1}{2}\sum_{\mathbf{k}}\left(\mu^2+k^2\right)|\phi(\mathbf{k})|^2\,. \tag{11.95}$$

If one Fourier transform (11.95) back to real space we find

$$F_0 = \frac{1}{2}\int d\mathbf{r}\left\{(\nabla\phi(\mathbf{r}))^2+\mu^2\,(\phi(\mathbf{r}))^2\right\} \tag{11.96}$$

which actually has a very interesting form. Let us calculate, for instance, the correlation function for for the fields ϕ when they are separated by a distance $\mathbf{r}$,

$$\langle\phi(\mathbf{r})\phi(0)\rangle = \frac{\int\prod_{\mathbf{r}} d\phi(\mathbf{r})\phi(\mathbf{r})\phi(0)e^{-F_0}}{\int\prod_i d\phi(\mathbf{r}_i)e^{-F_0}} \tag{11.97}$$

Notice however that the integration can be done easier if we Fourier transform since

$$\langle\phi(\mathbf{r})\phi(0)\rangle = \sum_{\mathbf{k},\mathbf{k}'} e^{i\mathbf{k}\cdot\mathbf{r}}\langle\phi(\mathbf{k})\phi(\mathbf{k}')\rangle \tag{11.98}$$

and

$$\langle\phi(\mathbf{k})\phi(\mathbf{k}')\rangle = \frac{\int\prod_{\mathbf{p}} d\phi(\mathbf{p})d\phi(-\mathbf{p})\phi(\mathbf{k})\phi(\mathbf{k}')e^{-\frac{1}{2}\sum_{\mathbf{q}}(\mu^2+q^2)|\phi(\mathbf{q})|^2}}{\int\prod_{\mathbf{p}} d\phi(\mathbf{p})d\phi(-\mathbf{p})e^{-\frac{1}{2}\sum_{\mathbf{q}}(\mu^2+q^2)|\phi(\mathbf{q})|^2}} \tag{11.99}$$

and therefore, after a simple gaussian integral,

$$\langle\phi(\mathbf{k})\phi(\mathbf{k}')\rangle = \frac{\delta_{\mathbf{k},-\mathbf{k}'}}{k^2+\mu^2} \tag{11.100}$$

and therefore from (11.98) we have

$$\langle\phi(\mathbf{r})\phi(0)\rangle = \sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{k^2+\mu^2}\,. \tag{11.101}$$

Observe that the integral above has poles at $k = \pm i\mu$ which indicates that the correlation function will decay exponentially at large distances, that is,

$$\langle\phi(\mathbf{r})\phi(0)\rangle \propto e^{-r/\xi} \tag{11.102}$$

where using (11.94)

$$\xi \propto \frac{1}{\mu} \propto \frac{1}{\sqrt{T-T_c}} \tag{11.103}$$

is the magnetic correlation length. Observe that the magnetic correlation length diverges at the critical temperature when we lower the temperature from the disordered phase. Comparing with (11.18) we find a new exponent $\nu_{MF} = 1/2$.

Up to this point we have not talked about the non-linear term in (11.82). Observe that close to the phase transition the value of the magnetization, or ψ, is very small and therefore we can keep only the $\mathbf{k} = 0$ part of $K(\mathbf{k})$. In this case the whole free energy simplifies to a very simple form which is

$$F = \int d\mathbf{r}\left\{\frac{1}{2}\left(\nabla\phi(\mathbf{r})\right)^2 + \frac{\mu^2}{2}\left(\phi(\mathbf{r})\right)^2 + \frac{\lambda}{4!}\left(\phi(\mathbf{r})\right)^4\right\} \tag{11.104}$$

where $\lambda/4! = K_0^4/\ell^4$ is a positive constant. (11.104) is known as the *Ginzburg-Landau* free energy which was proposed by Ginzburg and Landau only based on the symmetry and the existence of a second order phase transition. This kind of free energy is the heart of many discussions of the problem of phase transitions in magnetic and non-magnetic systems.

11.4 Continuous symmetries and the Goldstone theorem

In the previous sections we have considered only the Ising problem which has a discrete symmetry of spin inversion. As we have seen this discrete symmetry is reflected in the free energy of the system as the existence of two minima which are separated by an energy barrier as shown in Fig. 11.4. In higher symmetric systems, like the Heisenberg model, the Hamiltonian has the symmetry of rotation in the spin space since the interaction energy, $\mathbf{S}_i \cdot \mathbf{S}_j$, only depends on the relative orientation of the spins but not on their absolute orientation like in the Ising model. The symmetry of rotation in spin space is a continuous symmetry and therefore we expect that the physics to be very different from the discrete case. However, the phenomenon of a phase transition is again the same thing: in the ordered phase the symmetry is broken. The question then is: what happens when a continuous symmetry is broken? Do we get the same type of physics as in the discrete case?

The simplest way to understand the consequences of a broken continuous symmetry is to consider the Ginzburg-Landau free energy for the so called O(N) model. In this model the order parameter has N components. The Ising case is the particular case where $N = 1$! Thus we define a N component vector $\vec{\phi} = (\phi_1, \phi_2, ..., \phi_N)$ which is governed by a free energy which is the analogue of (11.104)

$$F = \int d\mathbf{r} \left\{ \frac{1}{2} \left(\nabla\vec{\phi}(\mathbf{r})\right)^2 + \frac{\mu^2}{2} \left(\vec{\phi}(\mathbf{r})\right)^2 + \frac{\lambda}{4!} \left(\vec{\phi}(\mathbf{r})\right)^4 - \mathbf{B} \cdot \vec{\phi}(\mathbf{r}) \right\} \tag{11.105}$$

where $\mathbf{B}$ is the symmetry breaking field. Observe that by construction the free energy (11.105) is invariant under rotations of the order parameter $\vec{\phi}$. This is the so-called O(N) symmetry. The XY model which involves only the X and Y components of the spin is a particular case of $N = 2$ while the Heisenberg model has $N = 3$ since it involves all the components, namely, X,Y and Z.

The main difference between (11.105) and (11.104) for $N > 1$ is the fact that one can rotate continuously the vector in the N dimensional space. Let us consider first the case where $N = 2$ and the components of the vector $\vec{\phi}$ are constant in space (in which case we disregard the derivatives in the action). The homogeneous part of the Ginzburg-Landau free energy is simply

$$\frac{U(\phi_1, \phi_2)}{V} = \frac{\mu^2}{2}(\phi_1^2 + \phi_2^2) + \frac{\lambda}{4!}(\phi_1^2 + \phi_2^2)^2 \tag{11.106}$$

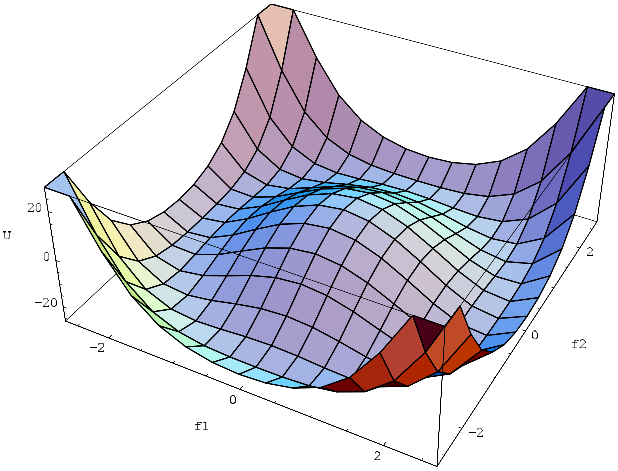

Figure 11.5: *Energy potential for a $O(2)$ model.*

where V is the volume of the system. The invariance of the system under rotations becomes obvious if we plot this free energy in the space of (ϕ_1, ϕ_2). If $\mu^2 > 0$, that is, in the disordered phase, the minimum of the energy is at $\phi_1 = \phi_2 = 0$ but if $\mu^2 < 0$ the potential energy looks as in Fig. 11.5. In this case the ground state is infinitely degenerate, that is, we can rotate continuously the vector around the origin without changing the energy of the system.

The heart of Goldstone theorem is to state that it requires no energy to move the order parameter continuously along the minima of the potential. Thus, if an infinitesimal field is applied in this particular direction we can rotate the order parameter by a finite amount. The susceptibility of the system in this particular direction is therefore infinity! That is, we get a finite response with an infinitesimal cost. It implies that there must be excitations of the system which cost no energy in the direction transverse to the ordering direction. This is Goldstone theorem: if a system has a spontaneously broken continuous symmetry there is always an excitation of the system in the ordered phase that costs no energy to excite.

We have seen already a good example of an application of this theorem: when a set of atoms forms a crystal the translational invariance (which is a continuous symmetry) is lost. This has to be contrasted with the liquid or gas phase where the translational symmetry persists! In the case of the crystal we know very well what is the order parameter: it is the Fourier transform of the density, $\langle \rho(\mathbf{q}) \rangle$ which now have Dirac delta peaks at the reciprocal lattice vectors $\mathbf{G}$. The peaks only exist if the system is crystalline and they disappear in the gas phase. Thus, Goldstone's theorem predicts the existence of modes with zero energy in this phase. But what are these modes? If you go back a few chapters you will find that there are indeed modes which are gapless in this phase: acoustic phonons! Because acoustic phonons have zero energy at zero wavevector an infinitesimal energy is required to excite them! There are many other examples of Goldstone modes which we will discuss in the next chapter and these are very important to understand the behavior of systems in ordered phases with spontaneously broken continuous symmetries.

11.5 Problems

1. Show that the Fourier transform of the local magnetization of a two dimensional antiferromagnet has Dirac delta peaks at $\mathbf{Q} = (\pi/a, \pi/a)$ and $\mathbf{Q} + \mathbf{G}$ where $\mathbf{G}$ is a reciprocal lattice vector.

2. Consider the case of an one dimensional magnet with a Lorentzian neutron scattering line shape and show that the spin-spin correlation function decays exponentially with the correlation function ξ.

3. What is the neutron line shape corresponding to the correlation function given in (11.20).

4. Prove (11.31), (11.32), (11.33) and (11.34).

5. Prove (11.35), (11.36) and (11.37).

6. Prove (11.52) and (11.54).

7. Prove that $\alpha_{MF} = \alpha'_{MF} = 0$ by calculating the specific heat of a ferromagnet in the mean field approximation.

8. Consider the O(N) model where the magnetization in the α direction is:

   $$M_\alpha = \langle \phi_\alpha \rangle = M n_\alpha$$

   where M is the magnitude of the magnetization vector $\mathbf{M}$ and $\mathbf{n}$ is an unit vector. Define susceptibility tensor

   $$\chi_{\alpha\beta} = -\frac{\partial^2 U}{\partial B_\alpha \partial B_\beta},$$

   where $\alpha, \beta = 1, ..., N$ are the components of the order parameter and B_α are components of magnetic field in the N directions. Using the chain rule

   $$\begin{aligned} \frac{\partial U}{\partial B_\alpha} &= \frac{\partial B}{\partial B_\alpha}\frac{\partial U}{\partial B} \\ &= \frac{B_\alpha}{B}\frac{\partial U}{\partial B} \end{aligned}$$

where $B = \sqrt{\sum_{\alpha=1}^{N} B_\alpha^2}$, prove that

$$\chi_{\alpha\beta} = n_\alpha n_\beta \chi_{||}(B) + (\delta_{\alpha\beta} - n_\alpha n_\beta)\,\chi_\perp(B)$$

where

$$\begin{aligned} \chi_{||}(B) &= -\frac{\partial^2 U}{\partial B^2} \\ \chi_\perp(B) &= -\frac{1}{B}\frac{\partial U}{\partial B} = \frac{M}{B}\,. \end{aligned}$$

Observe that $\chi_{||}(B)$ gives the susceptibility of the system in the direction of the order parameter **M** while $\chi_\perp(B)$ gives the susceptibility in the direction transverse to **M**. While $\chi_{||}(B)$ is finite in the ordered phase $\chi_\perp(B)$ diverges since $M \neq 0$ even when $B = 0$. This is again a result of continuous symmetry and therefore related to Goldstone theorem.

Chapter 12

Magnetic excitations

In the last chapter we have seen that systems with continuous broken symmetries exhibit gapless modes in the excitation spectrum. The clearest example of a Goldstone mode is the acoustic phonon that exist in crystals due to the breaking of the translation symmetry. However, crystals also support optical modes which have a gap. Optical modes are related to the breaking of a different symmetry that is discrete: the doubling of unit cell. Therefore, when the system of interest has a particular symmetry that is broken a new mode appears in the system. If the symmetry is continuous the mode is gapless and when the symmetry is discrete the mode has a gap. Since experimentally speaking we are always probing excited states of a given system it is important to understand the nature of these excitations. As we have seen the nature of the ground state, and the symmetries characterize it, determine the nature of the excitation spectrum.

In this chapter we are going to study the excitation spectrum of magnetic systems and distinguish between the various universality classes: the Ising model that has a discrete symmetry of spin inversion, the Heisenberg model that has the full symmetry of rotation in spin space and the XY model that has the symmetry of rotation in a plane.

12.1 The 1D Ising model

Let us consider what is perhaps the simplest magnetic system: the one-dimensional Ising model. Consider a chain with N atoms that interact via a Hamiltonian given by:

$$H = -\sum_{i=1}^{N}\left(J\sigma_i^z\sigma_{i+1}^z + h\sigma_i^z\right) \tag{12.1}$$

where $J > 0$ is the magnetic exchange and $h = \mu_B g B$ is the magnetic field energy. Since (12.1) is completely described in terms of the σ^z operator we can use the eigenstates of this operator (namely, $\sigma_i^z|\sigma_i\rangle = \sigma_i|\sigma_i\rangle$) to write the energy of the system as:

$$E[\{\sigma\}] = -\sum_{i=1}^{N}\left(J\sigma_i\sigma_{i+1} + h\sigma_i\right) \tag{12.2}$$

which is a functional of the configuration $\{\sigma_1, \sigma_2, ..., \sigma_N\}$ (we will assume periodic boundary conditions so that $\sigma_{N+1} = \sigma_1$). Observe that this problem is *classical* in the sense that the states of the system are generated by classical configurations of the spins. There are no quantum mechanical effects such as spin flips (that is, a tunneling of the spins between different configurations). The ground state of the system is obviously ferromagnetic and described by the configuration $\{+1, +1, ..., +1\}$ if $h > 0$. Although the ground state configuration is straightforward the excited states are not so obvious. Consider, for instance a spin flip in the system given by the configuration $\{+1, +1, -1, +1..., +1\}$. This spin flip costs $2J$ in energy ($h = 0$). Actually this state is highly degenerated because one can flip a spin anywhere along the chain. Now consider a two spin flip which is given by $\{+1, +1, -1, +1..., +1, -1, +1\}$ which costs $4J$ in energy and compare with another two spin flip where the flipped spins are neighbors $\{+1, +1, -1, -1, ..., +1\}$. This last state costs only $2J$ of energy. Actually the state where the flipped spins are all together only cost $2J$ of energy, no matter how long the flipped sequence is. Thus, there is an enormous amount of degenerate states in the problem. The question that comes out here is: at what temperatures does the system order magnetically?

In order to answer this question one has to calculate the partition function for the problem,

$$\begin{aligned} Z &= tr(e^{-\beta H}) \\ &= \sum_{\sigma_1,\ldots,\sigma_N=\pm 1} e^{-\beta E[\{\sigma\}]} . \end{aligned} \tag{12.3}$$

The whole problem in calculating this partition function is related with the problem of calculating the contribution of the interaction term. In order to evaluate this contribution we are going to use a trick which is valid for spin 1/2 particles. Consider the following matrix element:

$$\begin{aligned} \langle\sigma|e^{\theta\sigma^x}|\sigma'\rangle &= \langle\sigma|(\cosh(\theta)+\sigma^x\sinh(\theta))|\sigma'\rangle \\ &= \cosh(\theta)\delta_{\sigma,\sigma'}+\sinh(\theta)\delta_{\sigma,-\sigma'} \end{aligned} \tag{12.4}$$

where we used that $(\sigma^x)^2 = 1$ and that $\sigma^x|\sigma\rangle = |-\sigma\rangle$. The above identity can be written in a more interesting way as:

$$\begin{aligned} \langle\sigma|e^{\theta\sigma^x}|\sigma'\rangle &= \sqrt{\sinh(\theta)\cosh(\theta)\left(\frac{\cosh(\theta)}{\sinh(\theta)}\right)^{\sigma\sigma'}} \\ &= \sqrt{\frac{\sinh(2\theta)}{2}}\, e^{\frac{\sigma\sigma'}{2}\ln(coth(\theta))} \end{aligned} \tag{12.5}$$

as you can easily show. Thus, in (12.3) the interaction term in (12.1) can be written as

$$e^{\beta J\sigma_i\sigma_{i+1}} = \left(\frac{\sinh(2\theta)}{2}\right)^{-1/2} \langle\sigma_i|e^{\theta\sigma^x}|\sigma_{i+1}\rangle \tag{12.6}$$

if we identify $2\beta J = \ln(coth(\theta))$ or equivalently

$$\theta = \frac{1}{2}\ln(\coth(\beta J)) . \tag{12.7}$$

Observe that in this case the partition function can be written as:

$$Z = \sum_{\sigma_1,\ldots,\sigma_N}\prod_{i=1}^{N}\left(\frac{\sinh(2\theta)}{2}\right)^{-1/2} \langle\sigma_i|e^{\beta h\sigma^z}e^{\theta\sigma^x}|\sigma_{i+1}\rangle . \tag{12.8}$$

Now using the fact that the states are complete, that is, $\sum_{\sigma_i=\pm 1}|\sigma_i\rangle\langle\sigma_i| = 1$ we can rewrite the partition function as:

$$\begin{aligned} Z &= \left(\frac{\sinh(2\theta)}{2}\right)^{-N/2} \sum_{\sigma}\langle\sigma|\left(e^{\beta h\sigma^z}e^{\theta\sigma^x}\right)^N|\sigma\rangle \\ &= \left(\frac{\sinh(2\theta)}{2}\right)^{-N/2} tr\left[\left(e^{\beta h\sigma^z}e^{\theta\sigma^x}\right)^N\right]. \end{aligned} \tag{12.9}$$

Let us consider the case without the magnetic field ($h = 0$). In this case (12.9) is straightforward to calculate:

$$Z = \left(\frac{\sinh(2\theta)}{2}\right)^{-N/2} tr\left[e^{N\theta\sigma^x}\right] \tag{12.10}$$

which is the partition function of a completely different problem from the initial one, namely, one which is described by the "Hamiltonian":

$$H = -\Gamma\sigma^x \tag{12.11}$$

where

$$\Gamma = \frac{N\theta}{\beta} = \frac{N}{2\beta}\ln(coth(\beta J)). \tag{12.12}$$

Observe that we have mapped our original problem (12.1) of a chain of Ising spins (a classical one-dimensional problem) into a problem of a *single spin* in a transverse field of strength Γ (this is a *zero dimensional* problem). How this is possible?

What we have shown here is an essential feature of relationship between quantum statistical mechanics in d dimensions and the classical statistical mechanics in $d+1$ dimensions. The eigenstates of problem (12.11) are symmetric ($|s\rangle = (|+1\rangle + |-1\rangle)/\sqrt{2}$) and antisymmetric ($|a\rangle = (|+1\rangle - |-1\rangle)/\sqrt{2}$) combinations of eigenstates of σ^z with energy $-\Gamma$ and $+\Gamma$, respectively. Thus, if we prepare the state of the system at time $t = 0$, say, with spin up (that is, $|+1\rangle$) quantum mechanics tells us that for $t > 0$ the state of the system will be:

$$\begin{aligned} |\psi(t)\rangle &= \frac{1}{\sqrt{2}}\left(e^{-i\Gamma t/\hbar}|s\rangle + e^{i\Gamma t/\hbar}|a\rangle\right) = \cos(\Gamma t/\hbar)\,|+1\rangle \\ &- \; i\sin(\Gamma t/\hbar)\,|-1\rangle \end{aligned} \tag{12.13}$$

that is, the spin will oscillate from up to down with time. Thus, if we imagine the time evolution as a line with N steps we see that along the line the spins are never ordered, except when $\Gamma = 0$ in which case $|\psi(t)\rangle = |+1\rangle$ for all time t. In this case the chain is ferromagnetically ordered! Thus, with this argument one finds that the system is only ordered when $\Gamma = 0$. Going back to (12.12) we see that this is possible in the limit of $N \to \infty$ when $\beta = \infty$, that is $T = 0$. For any finite β, no matter how small, $t \to \infty$ as $N \to \infty$ and the system has to be disordered.

Furthermore, from (12.10) we can immediately compute the partition function and free energy of problem since we have a problem of a single 1/2 spin. We can diagonalize the operator that appears in the exponent of (12.10) which has the eigenvalues:

$$E_{\pm} = \pm\frac{N}{2}\ln(coth(\beta J)). \qquad (12.14)$$

Thus, we get immediately:

$$e^{-\beta F} = Z = 2\left(\frac{\sinh(2\theta)}{2}\right)^{-N/2}\cosh\left(\frac{N}{2}\ln(coth(\beta J))\right) \qquad (12.15)$$

and in the limit of $N \to \infty$ we find

$$\frac{F}{N} = -\frac{1}{\beta}\ln(2\cosh(\beta J)) \qquad (12.16)$$

which is the *exact* free energy of the 1D Ising model at any temperature. Observe that the free energy is a smooth function of the temperature: for $k_B T \ll J$ we have $F \approx -JN$ which is the energy of the fully aligned ferromagnetic state and for $k_B T \gg J$ we find $F \approx ln(\sqrt{2})k_B T$.

In order to calculate the magnetization as a function of temperature we need to re-examine (12.9) again. Observe that because we are dealing with Pauli matrices we can write:

$$e^{\beta h\sigma^z}e^{\theta\sigma^x} = \begin{bmatrix} \cosh(\theta)e^{\beta h} & \sinh(\theta)e^{\beta h} \\ \sinh(\theta)e^{-\beta h} & \cosh(\theta)e^{-\beta h} \end{bmatrix} \qquad (12.17)$$

and it is easy to show that the partition function in (12.9) becomes:

$$Z = tr\left(\begin{bmatrix} e^{\beta(h+J)} & e^{\beta(h-J)} \\ e^{-\beta(h+J)} & e^{-\beta(h-J)} \end{bmatrix}^N\right). \qquad (12.18)$$

Since the trace of a matrix is invariant to an unitary transformation (since $tr(A) = tr(U^{-1}UA) = tr(UAU^{-1})$) we rewrite (12.18) as

$$\begin{aligned} Z &= tr(A^N) = tr\left(\left(UAU^{-1}\right)^N\right) \\ &= tr(\Lambda^N) = \lambda_+^N + \lambda_-^N \end{aligned} \tag{12.19}$$

where Λ is a diagonal matrix ($UAU^{-1} = \Lambda$) and $\lambda_\pm$ its eigenvalues. Thus, in order to solve the problems we just have to diagonalize the matrix that appears in (12.18). It is a simple matter to show that the eigenvalues are:

$$\lambda_\pm = \cosh(\beta h)e^{\beta J} \pm \sqrt{\sinh^2(\beta h)e^{2\beta J} + e^{-2\beta J}} \tag{12.20}$$

which ends with the solution of the problem. Observe that $\lambda_+ > \lambda_-$ and since we are interested in the limit of $N \to \infty$ we can rewrite (12.19) as:

$$\begin{aligned} Z &= e^{-\beta F} = \lambda_+^N \\ \frac{F}{N} &= -\frac{1}{\beta}\ln\left(\cosh(\beta h)e^{\beta J} + \sqrt{\sinh^2(\beta h)e^{2\beta J} + e^{-2\beta J}}\right) \end{aligned} \tag{12.21}$$

which is the exact expression for the free energy of the problem and reduces to (12.16) when $h \to 0$. Observe that the magnetization per spin in the problem is given by:

$$\begin{aligned} M(h) &= -\frac{\partial F/N}{\partial H} \\ &= \frac{\sinh(\beta h)}{\sqrt{\sinh^2(\beta h) + e^{-4\beta J}}} . \end{aligned} \tag{12.22}$$

Notice that (12.22) is a quite interesting function. If we take the limit of $h \to 0$ with β finite we find $M(h \to 0) = 0$ that is, there is no magnetization in the system at any finite temperature. If however we take the limit of $\beta \to \infty$ **before** we take the limit of $h \to 0$ we find $M(h \to 0) = 1$! That is, the system is magnetized at zero temperature as we have argued before. Therefore, the magnetization is a singular function of the temperature since there is a discontinuous jump in the

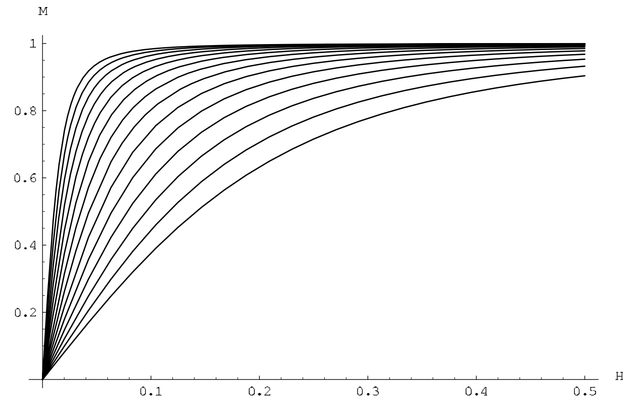

Figure 12.1: *Magnetization of the one dimensional Ising model as a function of external field for different temperatures (temperatures increases from top to bottom).*

magnetization at $T = 0$. A most amazing effect! The approach to zero temperature is shown on Fig.12.1.

The problem of phase transitions in one-dimensional systems can be understood very well by an argument due to Landau-Lifshitz. Consider a state with a finite magnetization M and free energy F. In the ordered state the free energy would be given by:

$$F = E - TS \tag{12.23}$$

where E is the energy of the ordered state and S its entropy. Consider the configurations discussed at the beginning of this section in which all the spins to the right of a point n are reversed creating a *domain wall* like $(+1, +1, +1, ..., +1, -1, -1, -1)$. The internal energy of the system will be increased by an amount $\delta E \approx 2M^2 J$ ($M = 1$ at $T = 0$). But we can choose the point n at any point of the lattice of N sites and therefore there is an entropy of the order $\delta S \approx k_B \ln(N)$ associated with the creation of the domain wall. Thus, the net change in free energy due to the creation of domain wall is

$$\delta F \approx 2M^2 J - k_B T \ln(N) \, . \tag{12.24}$$

Observe, therefore, that if we make N sufficiently large, that is,

$$N > N^* = e^{\frac{2M^2 J}{k_B T}} \tag{12.25}$$

the free energy of the problem becomes negative and the system becomes unstable. Thus, we have to conclude that $M = 0$ for any finite temperature. Observe that at $T = 0$ order is possible because $N^* \to \infty$.

12.2 The Heisenberg-Ising Hamiltonian

Let us consider a system described by the Hamiltonian

$$H = -\sum_{\langle i,j \rangle} \left[J_z S_i^z S_j^z + J_\perp \left(S_i^x S_j^x + S_i^y S_j^y \right) \right] - g\mu_B H \sum_i S_i^z \tag{12.26}$$

which describes an anisotropic magnet in a external magnetic field H. We first point out that the total spin of the system, $\mathbf{S}_T^2 = \left(\sum_i \mathbf{S}_i\right)^2$

and the z component of the total spin, $S_T^z = \sum_i S_i^z$, commute with the Hamiltonian. Thus, we can classify all the states with respect to their eigenstates, namely, $S_T(S_T+1)$ and S_T^z. Observe that $S_T = SN, S(N-1), ..., 0$ while $S_T^z = -S_T, ..., S_T$ has $2S_T + 1$ possible values. We will consider two important case of this Hamiltonian: the ferromagnetic case with $J_z > 0$ and the antiferromagnetic case with $J_z < 0$. As we are going to see these two cases have completely different excitation spectrum and physical properties.

12.2.1 The ferromagnetic case

In the *classically* ordered state of a ferromagnetic system all the spins are polarized in one direction and therefore we have $S_T = S_T^z = NS$ where N is the total number of atoms in the system. This corresponds to the mean value of the operator to be fully polarized that is $\langle S_i^z \rangle = S$. Observe that the ground state would be described in this way if $J_\perp = 0$ but because of the presence of $J_\perp$ this is not completely correct. Let us rewrite:

$$S_i^\pm = S_i^x \pm i S_i^y \tag{12.27}$$

which the raising and lowering operators for spins. In this case Hamiltonian (12.26) is rewritten as

$$H = -\sum_{\langle i,j \rangle} \left[J_z S_i^z S_j^z + \frac{J_\perp}{2} \left(S_i^+ S_j^- + S_i^- S_j^+ \right) \right] - g\mu_B H \sum_i S_i^z \tag{12.28}$$

which clearly shows that $J_\perp$ flips the spins. Classically this term is equivalent to the precession of the magnetic moment around the z axis.

Suppose the magnetic system is in the ordered phase. One expects the total magnetization of the system to be very close to NS. As in the case of phonons one expects that the fluctuations can be described by some kind of bosonic excitation with operators b_i and $b_i^\dagger$ which obey canonical commutation relations:

$$\left[b_i, b_j^\dagger \right] = \delta_{i,j} \,. \tag{12.29}$$

The problem is to find out the relationship between these bosonic operators and the original spin operators. This was done by Holstein and

Primakoff. They propose to write the spin operators as:

$$\begin{aligned} S_i^z &= S - b_i^\dagger b_i \\ S_i^+ &= \sqrt{2S}\left(1 - \frac{b_i^\dagger b_i}{2S}\right)^{1/2} b_i \\ S_i^- &= \sqrt{2S} b_i^\dagger \left(1 - \frac{b_i^\dagger b_i}{2S}\right)^{1/2} \end{aligned} \tag{12.30}$$

which are known as the *Holstein-Primakoff* transformations. These transformations have nice properties: 1) using (12.29) it can be shown that the operators defined in (12.30) obey the spin algebra; 2) it is easy to show that $\mathbf{S}_i^2 = S(S+1)$ as it should be.

Observe that at zero temperature, because the excitations are bosons, we expect $\langle b_i^\dagger b_i \rangle = 0$. Thus it is reasonable to assume that $\langle b_i^\dagger b_i \rangle / S << 1$ and we can expand the transformation in (12.30) as

$$\begin{aligned} S_i^z &= S - b_i^\dagger b_i \\ S_i^+ &\approx \sqrt{2S} b_i \\ S_i^- &\approx \sqrt{2S} b_i^\dagger \end{aligned} \tag{12.31}$$

which, of course, is not a true operator relationship but can be shown to be a good approximation *a posteriori*. Moreover, the operator S_i^z is unchanged. The physical meaning of this transformation becomes clear now. S_i^z in (12.30) measures the number of overturned spins. This flipping of spins is generated by $S_i^{\pm}$. If we imagine that the number of spins equals the number of bosons in the system then $S_i^{\pm}$ behave like creation and annihilation operators for bosons.

If we substitute (12.31) into (12.28) and keep only the leading order in the operators we obtain:

$$H = -J_z N Z S^2 - J_\perp N Z S - g\mu_B H N S + \mathcal{H} \tag{12.32}$$

where

$$\mathcal{H} = (2J_z Z + g\mu_B H) \sum_i b_i^\dagger b_i - J_\perp S \sum_{\langle i,j \rangle} \left(b_j^\dagger b_i + b_i^\dagger b_j \right) . \tag{12.33}$$

Observe that $\mathcal{H}$ has exactly the same form of the tight binding Hamiltonian for electrons moving on a lattice with the difference is that now we have bosons. Thus, like electrons, the ground state is made out of *Bloch waves*. For the problem where there is just one atom per unit cell solve this problem exactly in the same way as before, that is, by Fourier transform:

$$\begin{aligned} b_{\mathbf{k}} &= \frac{1}{\sqrt{N}}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_j} b_j \\ b_i &= \frac{1}{\sqrt{N}}\sum_{j} e^{-i\mathbf{k}\cdot\mathbf{r}_j} b_{\mathbf{k}} \end{aligned} \tag{12.34}$$

and since the system is periodic the wavevector is defined only in the first Brillouin zone (also called *magnetic* Brillouin zone). The Fourier transform changes (12.33) into

$$\mathcal{H} = \sum_{\mathbf{k}} E_{\mathbf{k}} b^{\dagger}_{\mathbf{k}} b_{\mathbf{k}} \tag{12.35}$$

where

$$E_{\mathbf{k}} = 2J_z Z + g\mu_B H - 2J_{\perp} S Z \gamma_{\mathbf{k}} \tag{12.36}$$

and

$$\gamma_{\mathbf{k}} = \frac{1}{Z}\sum_{\vec{\delta}} e^{i\mathbf{k}\cdot\vec{\delta}} \tag{12.37}$$

where $\vec{\delta}$ is the vector that links two nearest neighbor atoms. The excitations described in Hamiltonian (12.35) are called *ferromagnetic magnons*. Observe that if $J_{\perp} = 0$ the magnon spectrum is dispersionless and therefore there is no propagation! This is the case of the Ising model. If there is a finite $J_{\perp}$ (or finite XY component) the magnons can propagate since there is a finite group velocity $c_{\mathbf{k}} = \nabla E_{\mathbf{k}}$. Let us consider now the case of long wavelength magnons, that is, in the limit where $|\mathbf{k}\cdot\vec{\delta}| << 1$. In this case we can write $\gamma_{\mathbf{k}} \approx 1 - (ka)^2/2$ where a is the lattice spacing in a cubic system. Therefore from 12.36) we have

$$E_k \approx 2(J_z - J_{\perp})Z + g\mu_B H + J_{\perp} S (ka)^2 \tag{12.38}$$

which can be rewritten as

$$E_k \approx \Delta + \frac{k^2}{2m^*} \tag{12.39}$$

where

$$\begin{aligned} \Delta &= 2(J_z - J_\perp)Z + g\mu_B H \\ m^* &= \frac{1}{4J_\perp S a^2} . \end{aligned} \tag{12.40}$$

Observe that (12.39) has the form of the dispersion of a free particle with mass m^*. This particle is the magnon. Observe that in the limit of $J_\perp \to 0$ the mass of the magnon diverges indicating that it localizes in the system. One could ask how these magnons are related to Goldstone's theorem. Goldstone's theorem requires the system to have a continuous symmetry which in the case of this Hamiltonian is obtained in the Heisenberg limit ($J_\perp = J_z$) and in the absence of fields ($H = 0$) which leads to $\Delta = 0$, that is, there is no gap in the system at $k = 0$ implying that the gapless ferromagnetic magnon is the Goldstone mode.

From (12.31) we can calculate the magnetization per atom of the system immediately

$$M = S - \frac{1}{N}\sum_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle \tag{12.41}$$

where $n_{\mathbf{k}} = b^\dagger_{\mathbf{k}} b_{\mathbf{k}}$ is the occupation number operator for magnons. This number is given by the Bose-Einstein occupation as for the case of phonons. We have

$$M = S - \frac{1}{\rho}\int d^d k \frac{1}{e^{\beta E_k} - 1} \tag{12.42}$$

where $\rho = N/V$ is the density. Observe that at low temperatures ($\beta \to \infty$) the integral is dominated by the long wavelength behavior and we can use (12.39) with $d = 3$:

$$\begin{aligned} M &= S - \frac{1}{2\pi^2 \rho}\int_0^\infty dk \frac{k^2}{e^{\beta\Delta} e^{\beta k^2/(2m^*)} - 1} \\ &= S - \frac{1}{2\pi^2\rho}(2m^* k_B T)^{3/2} \int_0^\infty dx \frac{x^{1/2}}{e^{\beta\Delta} e^{x} - 1} . \end{aligned} \tag{12.43}$$

In the absence of external field and in the fully isotropic system, $J_\perp = J_z$, we have $\Delta = 0$ and the last integral is a constant and therefore the magnetization decreases with a power $T^{3/2}$ of the temperature showing that indeed the magnons tend to disorder the classically ordered state. If $\Delta \neq 0$ the magnetization decreases exponentially with temperature.

The energy per atom of the system is of course obtained directly from (12.35). Again, at low temperatures, we use (12.31):

$$
\begin{aligned}
E &= \frac{1}{N}\sum_{\mathbf{k}} E_{\mathbf{k}}\langle n_{\mathbf{k}}\rangle \\
&= \Delta + \frac{1}{4\pi^2\rho m^*}\int_0^\infty dk \frac{k^4}{e^{\beta\Delta}e^{\beta k^2/(2m^*)}-1} \\
&= \Delta + \frac{1}{4\pi^2\rho m^*}(2m^* k_B T)^{5/2}\int_0^\infty dx \frac{x^{3/2}}{e^{\beta\Delta}e^{x}-1}. \qquad (12.44)
\end{aligned}
$$

which shows that in the absence of magnetic field and anisotropy the energy of the system goes like $T^{5/2}$ and because of that the specific heat behaves like $C_V \propto T^{3/2}$.

12.2.2 Antiferromagnetic Case

Let us now consider the case when $J_z < 0$ in (12.26). In this case the spins orient anti-parallel to each other in a structure similar to the one shown in Fig.10.7 which is called the Néel state. We are going to assume a similar structure where only two sublattices, A and B, are present each one with $N/2$ sites (that is, two different ferromagnetic lattices which are immersed into each other). This is due to the fact that an antiferromagnet breaks the translational symmetry of the original lattice and doubles the unit cell. This, of course, does not happen in a ferromagnetic system. In sublattice A the magnetization is essentially $\langle S_i^z\rangle = +S$ while in sublattice B we have $\langle S_i^z\rangle = -S$. Thus, in defining the spin operators in terms of bosons one has to be careful about each sublattice. The easiest way to proceed is to follow the recipe of the ferromagnetic problem and define:

$$
\begin{aligned}
S_{A,i}^z &= S - a_i^\dagger a_i \\
S_{B,i}^z &= -S + b_i^\dagger b_i
\end{aligned}
$$

$$\begin{aligned} S^+_{A,i} &= \sqrt{2S}\left(1-\frac{a_i^\dagger a_i}{2S}\right)^{1/2} a_i \\ S^-_{B,i} &= \sqrt{2S}\left(1-\frac{b_i^\dagger b_i}{2S}\right)^{1/2} b_i \\ S^-_{A,i} &= \sqrt{2S}a_i^\dagger\left(1-\frac{a_i^\dagger a_i}{2S}\right)^{1/2} \\ S^+_{B,i} &= \sqrt{2S}a_i^\dagger\left(1-\frac{a_i^\dagger a_i}{2S}\right)^{1/2} . \end{aligned} \tag{12.45}$$

Notice that the role played by the lowering and raising spin operators are exchanged between the two sublattices because they have different orientation of the spins. Using the same approximations as in the ferromagnetic case and Fourier transforming the bosonic operators you can easily show that the Hamiltonian (12.28) with J replaced by $-J$ and in the presence of a staggered magnetic field $g\mu_B H_s \sum_j (-1)^j S^z_j$ becomes:

$$H = -NZJ_zS^2 - N\mu_B H_s S + \mathcal{H} \tag{12.46}$$

where

$$\begin{aligned} \mathcal{H} &= ZS\sum_{\mathbf{k}}\left\{J_\perp\gamma_{\mathbf{k}}\left(a^\dagger_{\mathbf{k}}b^\dagger_{\mathbf{k}} + a_{\mathbf{k}}b_{\mathbf{k}}\right) + J_z\left(a^\dagger_{\mathbf{k}}a_{\mathbf{k}} + b^\dagger_{\mathbf{k}}b_{\mathbf{k}}\right)\right\} \\ &+ \mu_B H_s\sum_{\mathbf{k}}\left(a^\dagger_{\mathbf{k}}a_{\mathbf{k}} + b^\dagger_{\mathbf{k}}b_{\mathbf{k}}\right) \end{aligned} \tag{12.47}$$

which has a structure which is very different from the ferromagnetic case since the operators from different sublattices mix with each other. The mixing of these operators becomes more obvious if one rewrites (12.47) as:

$$\mathcal{H} = -N(J_zZS + \mu_B H) + \sum_{\mathbf{k}} \Psi^\dagger_{\mathbf{k}}[H(\mathbf{k})]\Psi_{\mathbf{k}} \tag{12.48}$$

where

$$\Psi_{\mathbf{k}} = \begin{pmatrix} a_{\mathbf{k}} \\ b^\dagger_{\mathbf{k}} \end{pmatrix} \tag{12.49}$$

and

$$[H(\mathbf{k})] = \left[\begin{array}{cc} J_z ZS + \mu_B H_s & J_\perp ZS\gamma_{\mathbf{k}} \\ J_\perp ZS\gamma_{\mathbf{k}} & J_z ZS + \mu_B H_s \end{array} \right] . \tag{12.50}$$

In order to diagonalize the Hamiltonian we look for a transformation U such that

$$\begin{aligned} \Psi_{\mathbf{k}} &= U(\mathbf{k})\Phi_{\mathbf{k}} \\ U^\dagger(\mathbf{k})[H(\mathbf{k})]U(\mathbf{k}) &= \epsilon_{\mathbf{k}} I \end{aligned} \tag{12.51}$$

where ϵ is a diagonal matrix and

$$\Phi_{\mathbf{k}} = \left(\begin{array}{c} \alpha_{\mathbf{k}} \\ \beta^\dagger_{\mathbf{k}} \end{array} \right) \tag{12.52}$$

with $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$ are bosonic operators. The simplest transformation has the form

$$U(\mathbf{k}) = \left[\begin{array}{cc} u_{\mathbf{k}} & v_{\mathbf{k}} \\ v_{\mathbf{k}} & u_{\mathbf{k}} \end{array} \right] \tag{12.53}$$

where $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are real. Moreover, because the operators are bosons we must impose that $u^2_{\mathbf{k}} - v^2_{\mathbf{k}} = 1$. Thus,we can write

$$\begin{aligned} u_{\mathbf{k}} &= \cosh(\theta_k) \\ v_{\mathbf{k}} &= \sinh(\theta_k) . \end{aligned} \tag{12.54}$$

This implies that the inverse of U is

$$U^{-1}(\mathbf{k}) = \left[\begin{array}{cc} u_{\mathbf{k}} & -v_{\mathbf{k}} \\ -v_{\mathbf{k}} & u_{\mathbf{k}} \end{array} \right] \tag{12.55}$$

and therefore U is not unitary ($U^{-1} \neq U^\dagger$). Actually it is easy to see that $U^\dagger = U$ and therefore the equation for the energy in (12.51) is $UHU = \epsilon$ or $HU = \epsilon U^{-1}$ which is not our usual eigenfunction problem. Observe moreover that these matrix can be written in terms of Pauli matrices,

$$\begin{aligned} H(\mathbf{k}) &= E_0 I + E_1(\mathbf{k})\sigma^x \\ U(\mathbf{k}) &= u_{\mathbf{k}} I + v_{\mathbf{k}}\sigma^x \\ U^{-1}(\mathbf{k}) &= u_{\mathbf{k}} I - v_{\mathbf{k}}\sigma^x \end{aligned} \tag{12.56}$$

where $E_0 = J_z ZS + \mu_B H_s$ and $E_1 = J_\perp ZS\gamma_{\mathbf{k}}$. Thus, the equation $HU = \epsilon U^{-1}$ leads to the following set of equations:

$$\begin{aligned} (\epsilon - E_0)u_k - E_1 v_k &= 0 \\ E_1 u_k + (\epsilon + E_0)v_k &= 0 \end{aligned} \tag{12.57}$$

which for a non-trivial solution requires $(\epsilon - E_0)(\epsilon + E_0) + E_1^2 = 0$, that is,

$$\begin{aligned} \epsilon_{\mathbf{k}} &= \sqrt{E_0^2 - E_1^2(\mathbf{k})} \\ &= \sqrt{(J_z ZS + \mu_B H_s)^2 - (J_\perp ZS)^2\gamma_{\mathbf{k}}^2} \end{aligned} \tag{12.58}$$

and moreover we find

$$\tanh(2\theta_k) = -\frac{E_0}{E_1(\mathbf{k})}\,. \tag{12.59}$$

Thus, the Hamiltonian becomes

$$\mathcal{H} = -NE_0 + \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \left(\alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} + \beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}} + 1\right) \tag{12.60}$$

which has the appropriate diagonal form.

Let us now look for the Goldstone mode. In the absence of a staggered field and in the isotropic limit ($J_z = J_\perp$) the dispersion (12.58) becomes

$$\epsilon_{\mathbf{k}} = 2JZS\sqrt{1 - \gamma_{\mathbf{k}}^2} \tag{12.61}$$

and in the long wavelength limit we find

$$\epsilon(k) \approx c_s k \tag{12.62}$$

where $c_s = 4\sqrt{3}JSa$ is the spin wave velocity in three dimensions. Observe that as indicated by Goldstone theorem the antiferromagnetic magnon is gapless with linear dispersion relation. This has to be contrasted with the ferromagnetic case where the dispersion goes like k^2. Like the case of acoustic phonons the antiferromagnetic magnons have a characteristic velocity. Ferromagnetic magnons, on the other hand, have Galilean invariance which is characterized by an effective mass which determines the curvature of the dispersion.

Let us now consider the sublattice magnetization given by

$$\begin{aligned} M_A &= \sum_i \langle S^z_{A,i} \rangle = NS - \sum_{\mathbf{k}} a^\dagger_{\mathbf{k}} a_{\mathbf{k}} \\ &= NS - \sum_{\mathbf{k}} \left(u^2_{\mathbf{k}} \alpha^\dagger_{\mathbf{k}} \alpha_{\mathbf{k}} + v^2_{\mathbf{k}} \beta_{\mathbf{k}} \beta^\dagger_{\mathbf{k}} \right) \end{aligned} \tag{12.63}$$

which at $T = 0$ becomes

$$\begin{aligned} M_A &= NS - \sum_{\mathbf{k}} v^2_{\mathbf{k}} = NS - \sum_{\mathbf{k}} \sinh^2(\theta_k) \\ &= NS - \frac{1}{2} \sum_{\mathbf{k}} \left[(1 - \gamma^2_{\mathbf{k}})^{-1/2} - 1 \right] . \end{aligned} \tag{12.64}$$

Thus, the magnetization per unit of volume can be written as

$$\frac{M_A}{V} = nS + n/2 - \frac{1}{2} \int \frac{d^d k}{(2\pi)^d} \frac{1}{\sqrt{1 - \gamma^2_{\mathbf{k}}}} \tag{12.65}$$

which for a cubic lattice in three dimensions is given by

$$\frac{M_A}{V} = n(S - 0.078) . \tag{12.66}$$

This is the result of a numeric integration of the equation above. Observe that due to quantum fluctuations (zero point motion of the spins) the staggered magnetization is reduced relative to its classical value.

12.3 Problems

1. Using the formalism of subsection (1.1) and the operator identity

$$lim_{M\to\infty}\left(e^{\frac{A}{M}}e^{\frac{B}{M}}\right)^M = e^{A+B}$$

show that the one-dimensional Ising model in a transverse field which is described by

$$H_q = \sum_n \left(-J'\sigma_n^z\sigma_{n+1}^z - \Gamma\sigma_n^x\right)$$

where Γ is the strength of the magnetic field has the same partition function as the classical Ising model in a square lattice (with N^2 sites) which is given by

$$H_c = -J\sum_{n,m}\left(\sigma_{n,m}^z\sigma_{n+1,m}^z + \sigma_{n,m}^z\sigma_{n,m+1}^z\right) . \qquad (12.67)$$

Find the relationship between J' and Γ to J, β and M.

2. Prove equation (12.18).

3. Calculate (12.20) explicitly and show (12.22) to be correct.

4. Consider the one-dimensional Ising model with an interaction which has finite range, that is,

$$H = -\sum_{i,j} J_{i,j}\sigma_i\sigma_j$$

where

$$J_{i,j} = \frac{J}{|i-j|^n}$$

where n characterizes the power of decay of the interaction. Using the Landau-Lifshitz argument show that it is possible to have long range order at finite temperatures if $n < 2$. Show that for the system to have a well defined thermodynamic limit one has to require $n > 1$. Show that for $n = 2$ the same argument requires that the magnetization M cannot vanish continuously, in order words, either there is zero magnetization at all temperatures or the magnetization is non zero with a discontinuity at the transition.

5. Prove (12.28).

6. Using (12.29) show that $[S_i^x, S_i^y] = 2i\delta_{i,j}S_i^z$ and prove that $\mathbf{S}_i^2 = S(S+1)$.

7. Prove equations (12.36).

8. Calculate the spin wave velocity for an isotropic spin 1/2 Heisenberg model in d space dimensions for a hypercubic lattice.

9. In the Debye model for the antiferromagnet one assumes the dispersion of the spin waves to be $\epsilon(k) = c_s k$ but cuts-off the dispersion at large wavelengths, say, at Λ. (*i*) Calculate Λ by assuming that the number of states in the spherical zone is the same as in the cubic Brillouin zone. (*ii*) Calculate the sublattice magnetization for the Debye model as a function of temperature. (*iii*) Find the critical temperature T_N above which the sublattice magnetization vanishes.

10. Consider the problem of antiferromagnetic magnons in a uniform magnetic field H for the Heisenberg-Ising Hamiltonian. Using the non-unitary transformation find the magnon spectrum in this case. Show that the $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$ modes are separated in energy. Calculate the **uniform** magnetization of the system at finite temperature assuming a Debye model for the magnons.

11. Using (12.42) and (12.65) find the lower value of the dimensionality d_c above which long range order is possible (at finite and zero temperature) for a ferromagnet and antiferromagnet, respectively.

Chapter 13

The Interacting Electron Gas

In studying the electron gas in previous chapters we have assumed that the electrons do not interact with each other. This assumption is not intuitive because we know that electrons in free space interact with each other via a long range Coulomb potential that behaves like $1/r$ where r is the distance between the two electrons. From the experimental point of view we know that electrons in simple metals behave very much like non-interacting particles. In this chapter we are going to discuss the basic properties of the interacting electron problem.

Since in a electron system the electrons effectively do not interact via a long range force (as is experimentally observed) there is something else in the system that intervenes to modify or weaken the interaction among electrons. From the microscopic point of view the only way an interaction between two particles can be different from its value in vacuum is if there is a *medium*. This medium propagates the interaction and therefore can effectively change the way the particles interact.

The simplest way to understand how this occurs at the microscopic level is to study by the equations of electromagnetism. When an electric field is applied to a dielectric, the observed field is different from the applied field because it *polarizes* the dielectric. When the system is polarizable we can describe the polarization $\mathbf{P}$ as the electric dipole moment per unit of volume. In this case the electric field $\mathbf{E}$ in the system is not simply the applied field but $\mathbf{E} = \mathbf{D} - 4\pi\mathbf{P}$ where $\mathbf{D}$ is the displacement field which depends only on the external distribution of charges and obeys the Maxwell equation

$$\nabla \cdot \mathbf{D} = 4\pi e \rho_{ext} \tag{13.1}$$

where e is the electric charge, ρ_{ext} is the external (applied) electron density. In many simple systems the polarization $\mathbf{P}$ is linearly related to the electric field through $\mathbf{P} = \chi_e \mathbf{E}$ where χ_e is the electric susceptibility of the medium. Thus we immediately obtain that

$$\mathbf{D} = \epsilon \mathbf{E} \tag{13.2}$$

where $\epsilon = 1 + 4\pi\chi_e$ is the dielectric function of the medium. In systems like crystals the dielectric function is not a simple constant but a tensor that depends on the direction the field is applied. Here we are going to consider the simple case of the isotropic electron gas where the dielectric constant is just a scalar.

As an example consider a simple charge Q at the origin in the presence of the electron gas (in this case $\rho_{ext}(\mathbf{r}) = Q\delta(\mathbf{r})$). If this charge is positive it will attract electrons close to it, if it is negative it will repel. In principle one would think that this charge could attract an infinity number of electrons. This is not true not only because the electrons repel each other and therefore it would lead to an enormous increase of the electrostatic energy of the system but also because electrons are fermions and therefore cannot occupy the same position is space. Thus, intuition tells us that the positive charge will attract enough electrons so that, as seen from far away, it will look like a neutral charge. This is called *screening*. The same argument works for the case of a negative charge. Thus, in the presence of an external charge the electron gas can not be uniform! This non-uniformity can be described by $\delta\rho(\mathbf{r})$ that describes the local changes in the density of the electron gas. Observe that in the jellium model of the electron gas there is always a background of positive ions which neutralize the average density ρ_0 otherwise the whole system would be unstable. The main idea behind screening is that the electric filed in the system is created by the *total* density $\rho_{ext} + \delta\rho$ in such a way that

$$\nabla \cdot \mathbf{E} = 4\pi e \left(\rho_{ext} + \delta\rho\right) . \tag{13.3}$$

In the general case the external charge can also change in time so that we can Fourier decompose it as

$$\rho_{ext}(\mathbf{r},t) = \int d\mathbf{k} \int d\omega e^{i(\omega t - \mathbf{r}\cdot\mathbf{k})} \rho_{ext}(\mathbf{q},\omega)\,. \tag{13.4}$$

One can now Fourier transform (13.1) and (13.3) and use (13.2) to find

$$\begin{aligned} \epsilon(\mathbf{q},\omega) &= \frac{\mathbf{q}\cdot\mathbf{D}(\mathbf{q},\omega)}{\mathbf{q}\cdot\mathbf{E}(\mathbf{q},\omega)} = \frac{\rho_{ext}(\mathbf{q},\omega)}{\rho_{ext}(\mathbf{q},\omega)+\delta\rho(\mathbf{q},\omega)} \\ &= \frac{1}{1+\frac{\delta\rho(\mathbf{q},\omega)}{\rho_{ext}(\mathbf{q},\omega)}} \end{aligned} \tag{13.5}$$

which gives the dielectric function once the displaced charged can be measured (or calculated!). Another way to obtain the dielectric function is to observe that in (13.5) only the longitudinal part of the displacement and electric field vector enter in the definition of the dielectric function. This is because we assume the system to be isotropic. Associated with the longitudinal component of the field there we can always define a potential such that $\mathbf{E} = -\nabla\phi$ and $\mathbf{D} = -\nabla\phi_{ext}$ which accordingly to (13.1) and (13.3) obey the equations

$$\begin{aligned} \nabla^2\phi_{ext}(\mathbf{r},t) &= -4\pi e \rho_{ext}(\mathbf{r},t) \\ \nabla^2\phi(\mathbf{r},t) &= -4\pi e\left(\rho_{ext}(\mathbf{r},t)+\delta\rho(\mathbf{r},t)\right)\,. \end{aligned} \tag{13.6}$$

The potential energies associated with the potentials given above is simple $V = -e\phi$ and $V_{ext} = -e\phi_{ext}$. From (13.6) and (13.5) we immediately conclude that

$$\epsilon(\mathbf{q},\omega) = \frac{V_{ext}(\mathbf{q},\omega)}{V(\mathbf{q},\omega)} \tag{13.7}$$

which gives the dielectric function in terms of the external potential and the total potential generated by the external fields. Thus, in order to describe screening one has to calculate the potential function.

13.1 The Thomas-Fermi approach

When one applies an electric field to an electron gas the electrons move from the point of higher potential to the point with lower potential. In the Thomas-Fermi approach one assumes that as the electrons move they are always in thermodynamic equilibrium with its surroundings. In a three dimensional electron gas the number of electrons per unit of volume in the absence of the field can be obtained from (6.4) and is given by:

$$\rho_0 = \frac{N}{V} = \frac{(2mE_{F,0})^{3/2}}{3\hbar^3\pi^2} \,, \tag{13.8}$$

where $E_{F,0} = \hbar^2 k_F^2/(2m)$ is the Fermi energy of the system. Because of the electric field the charge density is not homogeneous and we have a displaced density $\delta\rho(\mathbf{r})$ which is given by

$$\delta\rho(\mathbf{r}) = \rho\mathbf{r}) - \rho_0 \,. \tag{13.9}$$

Associated with this charge density there is a local shift in the Fermi energy of the system which is given by

$$E_F(\mathbf{r}) = E_{F,0} - V(\mathbf{r}) \tag{13.10}$$

where $V(\mathbf{r})$ is the total potential felt by the electrons. In the Thomas-Fermi approach we assume that (13.8) gives the change in the charge density due to the shift in the local chemical potential as given by (13.10), that is,

$$\begin{aligned} \rho(\mathbf{r}) &= \frac{(2mE_F(\mathbf{r}))^{3/2}}{3\hbar^3\pi^2} \\ &= \frac{(2mE_{F,0} - V(\mathbf{r}))^{3/2}}{3\hbar^3\pi^2} \\ &= \rho_0 \left(1 - \frac{V(\mathbf{r})}{E_{F,0}}\right)^{3/2} \end{aligned} \tag{13.11}$$

which gives the relationship between the potential energy and the displaced charge. From (13.6) we see that the potential energy obeys the Poisson equation

$$\begin{aligned} \nabla^2 V(\mathbf{r}) &= 4\pi e^2 (\rho_{ext}(\mathbf{r}) + \delta\rho(\mathbf{r})) \\ &= 4\pi e^2 \left[\rho_{ext}(\mathbf{r}) + \rho_0 - \rho_0 \left(1 - \frac{V(\mathbf{r})}{E_{F,0}}\right)^{3/2}\right] \end{aligned} \tag{13.12}$$

where we have used (13.9) and (13.11). Notice that (13.12) is a non-linear equation for $V(\mathbf{r})$. It turns out, however, that for practical purposes $V \ll E_{F,0}$ and therefore we can linearize (13.12) to give

$$\left(\nabla^2 + q_{TF}^2\right) V(\mathbf{r}) = 4\pi e^2 \rho_{ext}(\mathbf{r}) \tag{13.13}$$

where

$$\begin{aligned} q_{TF}^2 &= \frac{6\pi e^2 \rho_0}{E_{F,0}} = \frac{4me^2 k_F}{\hbar^2 \pi} \\ &= \frac{4k_F}{\pi a_0} \end{aligned} \tag{13.14}$$

where $a_0 = \hbar^2/(me^2)$ the Bohr radius. q_{TF} is the so-called Thomas-Fermi screening length. To understand the physical meaning of this length scale let us solve (13.13) by Fourier transform

$$\begin{aligned} V(\mathbf{k}) &= -\frac{4\pi e^2 \rho_{ext}(\mathbf{k})}{k^2 + q_{TF}^2} \\ &= \frac{V_{ext}(\mathbf{k})}{1 + \frac{q_{TF}^2}{k^2}} \end{aligned} \tag{13.15}$$

where

$$V_{ext}(\mathbf{k}) = -\frac{4\pi e^2 \rho_{ext}(\mathbf{k})}{k^2} \tag{13.16}$$

is the external potential created by the charge distribution ρ_{ext}. Comparing (13.15) with (13.7) one immediately concludes that

$$\epsilon_{TF}(\mathbf{k}) = 1 + \frac{q_{TF}^2}{k^2} \tag{13.17}$$

which is the dielectric constant in the Thomas-Fermi approximation. Consider now the case of a single impurity of charge Q at the origin. In this case $\rho_{ext}(\mathbf{q}) = Q$ and therefore from (13.15) we find that the total potential is given by

$$V(\mathbf{r}) = \int \frac{d^3k}{(2\pi)^3} \frac{-4\pi e Q}{k^2 + q_{TF}^2}$$

$$\begin{aligned} &= -\frac{2eQ}{\pi r}\int_0^{\infty} dk \frac{k\sin(kr)}{k^2+q_{TF}^2} \\ &= -\frac{eQ}{i\pi r}\int_{-\infty}^{+\infty} dk \frac{ke^{ikr}}{k^2+q_{TF}^2} \\ &= -\frac{eQ}{r}e^{-q_{TF}r} \end{aligned} \tag{13.18}$$

where the last integral is done by choosing the contour in the upper half complex plane. Observe that in the Thomas-Fermi approach the *effective* potential produced by the charge Q at the origin is not the bare potential $v_{ext}(r) = -eQ/r$ but has a Yukawa form and decays exponentially with a characteristic length

$$\lambda_{TF} = \frac{1}{q_{TF}} = \sqrt{\frac{\pi a_0}{4k_F}} . \tag{13.19}$$

In this case we say that the electrons screen the bare potential to a distance of order λ_{TF}. The Thomas-Fermi approximation gives a simple but powerful picture of the electrostatic behavior of metals. The screening effect comes from the fact that the system has a Fermi surface and therefore it has mobile electrons that can move around in order to screen the external charge. Thus, electrons far away from the impurity indeed cannot feel the potential created by the impurity and moves freely in the system.

13.2 The Random Phase Approximation - RPA

Let us now consider a more involved picture of the screening process which is called Random Phase Approximation or simply RPA. In this approach one considers the problem of the response of the electron gas to the total potential $V(\mathbf{r}, t)$. The assumption, as before, is that the electrons do not couple only to the external applied potential but to the total potential produced by all charges in the system. The energy associated with this coupling is simply

$$H_V = \int d\mathbf{r} V(\mathbf{r}, t)(\rho(\mathbf{r}, t) - \rho_0) \tag{13.20}$$

where $\rho(\mathbf{r},t) = \sum_\sigma \Psi^\dagger_\sigma(\mathbf{r},t)\Psi_\sigma(\mathbf{r},t)$ is the particle density. Observe that we have subtracted from the energy the energy of the positive background of charge that neutralizes the electron gas. If one Fourier transforms the above equation we get

$$H_V = \sum_{\mathbf{q}\neq 0} V_{\mathbf{q}}(t)\rho_{\mathbf{q}}(t) \tag{13.21}$$

where

$$\rho_{\mathbf{q}} = \sum_{\mathbf{k},\sigma} c^\dagger_{\mathbf{k}+\mathbf{q},\sigma} c_{\mathbf{k},\sigma} \,. \tag{13.22}$$

Notice that the term with $q = 0$ is excluded from the integral in (13.21) since $\rho_{q=0} = \rho_0$ is the average particle density. The physical meaning of (13.21) is quite straightforward: the potential created by the charges in the system induces charge fluctuations which are particle-hole pairs described by (13.22) around the Fermi surface.

The total Hamiltonian of the system can be written as $H = H_0 + H_V$ where

$$H_0 = \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} \tag{13.23}$$

is the free electron Hamiltonian. In order to calculate the dielectric function one has to calculate the displaced charge. In order to do it we are going to look for the equation of motion for the density operator in the Heisenberg representation, that is,

$$i\hbar\frac{d}{dt}\left[c^\dagger_{\mathbf{k}+\mathbf{q},\sigma} c_{\mathbf{k},\sigma}\right] = \left[H, c^\dagger_{\mathbf{k}+\mathbf{q},\sigma} c_{\mathbf{k},\sigma}\right] \tag{13.24}$$

It is a very simple exercise to show that

$$\begin{aligned}
\left[H_0, c^\dagger_{\mathbf{k}+\mathbf{q},\sigma} c_{\mathbf{k},\sigma}\right] &= \left(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}}\right) c^\dagger_{\mathbf{k}+\mathbf{q},\sigma} c_{\mathbf{k},\sigma} \\
\left[H_V, c^\dagger_{\mathbf{k}+\mathbf{q},\sigma} c_{\mathbf{k},\sigma}\right] &= \sum_{\mathbf{q}'} V_{\mathbf{q}'} \left(c^\dagger_{\mathbf{k}+\mathbf{q}+\mathbf{q}',\sigma} c_{\mathbf{k},\sigma} - c^\dagger_{\mathbf{k}+\mathbf{q},\sigma} c_{\mathbf{k}-\mathbf{q}',\sigma}\right)
\end{aligned} \tag{13.25}$$

Observe that because of the second term in (13.25) the equation for the density fluctuation cannot be solved in full form. Thus one has to use some approximation.

Consider now the first quantized version of the density operator $\rho_{\mathbf{q}}$ which is given by

$$\rho_{\mathbf{q}} = \frac{1}{V}\sum_n e^{i\mathbf{q}\cdot\mathbf{r}_n} \tag{13.26}$$

where $\mathbf{r}_n$ is the position of the n^{th} electron (you can easily show that (13.26) is correct by the direct Fourier transform of $\rho(\mathbf{r}) = \sum_n \delta(\mathbf{r} - \mathbf{r}_n)))$. Therefore, in the r.h.s. of the second equation in (13.25) we see that $\rho_{\mathbf{q}+\mathbf{q}'}$ appears, which is first quantized form is again

$$\rho_{\mathbf{q}+\mathbf{q}'} = \frac{1}{V}\sum_n e^{i(\mathbf{q}+\mathbf{q}')\cdot\mathbf{r}_n} . \tag{13.27}$$

Observe that if the electrons are (statistically) randomly distributed in the system the above sum only gives a finite result if $\mathbf{q} = -\mathbf{q}'$ because the sum involves random phases which add destructively. In RPA we approximate (13.25) by taking only the $\mathbf{q}' = -\mathbf{q}$:

$$\left[H_V, c^\dagger_{\mathbf{k}+\mathbf{q},\sigma}c_{\mathbf{k},\sigma}\right] \approx V_{-\mathbf{q}}\left(c^\dagger_{\mathbf{k},\sigma}c_{\mathbf{k},\sigma} - c^\dagger_{\mathbf{k}+\mathbf{q},\sigma}c_{\mathbf{k}+\mathbf{q},\sigma}\right) \tag{13.28}$$

which now lead to a simple solution for the equation of motion in (13.24) by Fourier transform in time:

$$c^\dagger_{\mathbf{k}+\mathbf{q},\sigma}c_{\mathbf{k},\sigma} = V_{-\mathbf{q}}(\omega)\frac{\overline{n}_{\mathbf{k},\sigma} - \overline{n}_{\mathbf{k}+\mathbf{q},\sigma}}{\hbar\omega - \epsilon_{\mathbf{k}+\mathbf{q}} + \epsilon_{\mathbf{k}}} \tag{13.29}$$

where $\overline{n}_{\mathbf{k}}$ is the Fermi-Dirac occupation number. From (13.22), we get:

$$\langle \rho_{\mathbf{q},\sigma}(\omega)\rangle = V_{-\mathbf{q}}(\omega)\sum_{\mathbf{k}}\frac{\bar{n}_{\mathbf{k},\sigma} - \bar{n}_{\mathbf{k}+\mathbf{q},\sigma}}{\hbar\omega - \epsilon_{\mathbf{k}+\mathbf{q}} + \epsilon_{\mathbf{k}}} . \tag{13.30}$$

Eq. (13.30) can be rewritten in a slightly different way in terms of the charge density distribution

$$\delta\rho_{\mathbf{q}}(\omega) = V_{-\mathbf{q}}(\omega)\Pi(\mathbf{q},\omega) \tag{13.31}$$

where

$$\Pi(\mathbf{q},\omega) = -\sum_{\mathbf{k},\sigma}\frac{\bar{n}_{\mathbf{k},\sigma} - \bar{n}_{\mathbf{k}+\mathbf{q},\sigma}}{\hbar\omega - \epsilon_{\mathbf{k}+\mathbf{q}} + \epsilon_{\mathbf{k}} + i\eta} \tag{13.32}$$

is the so-called polarization function and depends on the electronic system alone. It is important to notice that the positive background of charge (associated with $n_{q=0}$) is subtracted to (13.21) and therefore the sum in (13.32) has to be understood as the principal value. This can be accomplished by introducing a small imaginary part $\eta \rightarrow 0$ in the denominator. Thus, the polarization function has actually a real and a imaginary part. Indeed from (13.32) we can write

$$\begin{aligned}
\Re\{\Pi(\mathbf{q},\omega)\} &= -\mathcal{P}\sum_{\mathbf{k},\sigma}\frac{\bar{n}_{\mathbf{k},\sigma}-\bar{n}_{\mathbf{k}+\mathbf{q},\sigma}}{\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}}+\epsilon_{\mathbf{k}}} \\
&= -\mathcal{P}\sum_{\mathbf{k},\sigma}\bar{n}_{\mathbf{k},\sigma}\left[\frac{1}{\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}}+\epsilon_{\mathbf{k}}}-\frac{1}{\hbar\omega-\epsilon_{\mathbf{k}}+\epsilon_{\mathbf{k}+\mathbf{q}}}\right] \\
\Im\{\Pi(\mathbf{q},\omega)\} &= \pi\sum_{\mathbf{k},\sigma}\left(\bar{n}_{\mathbf{k},\sigma}-\bar{n}_{\mathbf{k}+\mathbf{q},\sigma}\right)\delta\left(\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}}+\epsilon_{\mathbf{k}}\right) \\
&= \pi\sum_{\mathbf{k}}\bar{n}_{\mathbf{k},\sigma}\left[\delta\left(\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}}+\epsilon_{\mathbf{k}}\right)-\delta\left(\hbar\omega-\epsilon_{\mathbf{k}}+\epsilon_{\mathbf{k}+\mathbf{q}}\right)\right]
\end{aligned} \tag{13.33}$$

where where $\mathcal{P}$ means the principal value of the integral and in the last line we have changed $\mathbf{k} \rightarrow -\mathbf{k}-\mathbf{q}$ and used the fact that $\bar{n}_{-\mathbf{k}-\mathbf{q},\sigma} = \bar{n}_{\mathbf{k}+\mathbf{q},\sigma}$ and $\epsilon_{-\mathbf{k}-\mathbf{q}} = \epsilon_{\mathbf{k}+\mathbf{q}}$.

We can now substitute the result (13.31) into the Poisson equation (13.12)

$$\begin{aligned}
V_{\mathbf{q}}(\omega) &= -\frac{4\pi e^2}{q^2}\left(\rho_{ext}(\mathbf{q},\omega)+\delta\rho(\mathbf{q},\omega)\right) \\
&= -\frac{4\pi e^2}{q^2}\left(\rho_{ext}(\mathbf{q},\omega)+eV_{-\mathbf{q}}(\omega)\Pi(\mathbf{q},\omega)\right)
\end{aligned} \tag{13.34}$$

assuming $V_{\mathbf{q}}(\omega) = V_{-\mathbf{q}}(\omega)$ we find

$$V(\mathbf{q},\omega) = \frac{V_{ext}(\mathbf{q},\omega)}{1+\frac{4\pi e}{q^2}\Pi(\mathbf{q},\omega)} \tag{13.35}$$

which by comparison with (13.7) leads to

$$\epsilon_{RPA}(\mathbf{q},\omega) = 1+\frac{4\pi e}{q^2}\Pi(\mathbf{q},\omega) \tag{13.36}$$

which is the RPA expression for the dielectric function. Observe that RPA gives a frequency dependence to the polarization function which is not present in the simple Thomas-Fermi result (13.17). This happens because the Thomas-Fermi result is purely static, that is, it is valid at $\omega = 0$.

In order to check if RPA can reproduce the Thomas-Fermi result let us investigate the static limit of (13.36). From the definition (13.32) at $T = 0$ and assuming a spherical Fermi surface one has

$$\Re\{\Pi(\mathbf{q},0)\} = -2\mathcal{P}\int \frac{d^3k}{(2\pi)^3}\frac{\Theta(k_F-k)-\Theta(k_F-|\mathbf{k}+\mathbf{q}|)}{k^2/(2m)-(\mathbf{k}+\mathbf{q})^2/(2m)} \quad (13.37)$$

This integral can be simplified if we take the limit of $q \to 0$ in which case we can write $|\mathbf{k}+\mathbf{q}| \approx k + q\cos(\theta)$ where θ is the angle between $\mathbf{k}$ and $\mathbf{q}$ and therefore $\Theta(k_F - |\mathbf{k}+\mathbf{q}|) \approx \Theta(k_F - k) - q\cos(\theta)\delta(k_F - k)$ (since $\delta(k) = d\Theta(k)/dk$). Thus, to leading order in q we have

$$\begin{aligned}\Re\{\Pi(\mathbf{q},0)\} &\approx 4m\mathcal{P}\int \frac{d^3k}{(2\pi)^3}\frac{q\cos(\theta)\delta(k_F-k)}{2qk\cos(\theta)} \\ &\approx \frac{mk_F}{\pi^2}\end{aligned} \quad (13.38)$$

which when substituted in (13.36) leads to

$$\lim_{q\to 0}\epsilon_{RPA}(\mathbf{q},\omega=0) = 1 + \frac{4me^2k_F}{\pi q^2} \quad (13.39)$$

which is identical to the Thomas-Fermi result (13.17). Thus, the Thomas-Fermi approach is a special limit of the RPA result when $\omega = 0$ and $q \to 0$. This implies that the RPA result has more information about the screening process in a electron gas than the simple Thomas-Fermi approach.

It should be clear now that the real part of the dielectric function (which is simply related to the real part of the polarization function in the RPA approach) is related to the screening processes that go on in the electron gas. The screening process is a coherent process that involves the displacement of electrons in the system. By now you should be curious about the meaning of the imaginary part of the dielectric function and to what physical process it describes. In order to understand its meaning it is instructive to look at the frequency-dependent electrical conductivity of the electron gas, $\sigma(\mathbf{k},\omega)$. As we have seen in Chapter 6 in a disordered environment the electron gas will have a finite conductivity or resistivity due to the *elastic* scattering with static impurities. But this is not the only source of scattering since the electrons interact with each other. By definition the conductivity of the system is defined by the equation (7.6), $\mathbf{J} = \sigma\mathbf{E}$, where $\mathbf{J}$ is the electric current density. This current is related to the particle current density $\mathbf{j}$ by $\mathbf{J} = -e\mathbf{j}$ and thus

$$\mathbf{j}(\mathbf{k},\omega) = -\frac{1}{e}\sigma(\mathbf{k},\omega)\mathbf{E}(\mathbf{k},\omega)\,. \tag{13.40}$$

On the other hand the number of electrons in the system has to be conserved in the scattering and therefore the current and the density are related by current conservation equation

$$\frac{\partial}{\partial t}n(\mathbf{r},t) + \nabla\cdot\mathbf{j}(\mathbf{r},t) = 0\,. \tag{13.41}$$

We are only interested in the fluctuations of the system around the equilibrium particle density ρ_0, that is, we write $n(\mathbf{r},t) = \rho_0 + \delta\rho(\mathbf{r},t)$ and thus

$$\omega\ \delta\rho_{\mathbf{k}}(\omega) = \mathbf{k}\cdot\mathbf{j}(\mathbf{k},\omega)\,. \tag{13.42}$$

Using that $\mathbf{E}(\mathbf{r},t) = -\nabla\phi(\mathbf{r},t) = \nabla V(\mathbf{r},t)/e$, (13.40) and (13.42) we find that

$$\delta\rho(\mathbf{k},\omega) = i\sigma(\mathbf{k},\omega)\frac{\mathbf{k}^2V(\mathbf{k},\omega)}{e\omega}\,. \tag{13.43}$$

Using $V_{ext}(\mathbf{k},\omega) = -4\pi e^2\rho_{ext}(\mathbf{k},\omega)/k^2$, (13.5) and (13.7) it is easy to show that

$$\epsilon(\mathbf{k},\omega) = 1 + \frac{4\pi i\sigma(\mathbf{k},\omega)}{\omega} \tag{13.44}$$

which gives the relationship between the dielectric function and the conductivity. Direct comparison between (13.44) and (13.36) shows that in RPA we have

$$\sigma_{RPA}(\mathbf{k},\omega) = -ie\frac{\omega}{k^2}\Pi(\mathbf{k},\omega)\,. \tag{13.45}$$

Observe therefore that the real part of the conductivity which is related to the dissipative process in the system is related to the imaginary part of the polarization function. Or more generally, from (13.44) the dissipative processes are related to the imaginary part of the dielectric function. Indeed, from (13.44) one can write

$$\begin{aligned}\Re\{\epsilon(\mathbf{k},\omega)\} &= 1-\frac{4\pi\Im\{\sigma(\mathbf{k},\omega)\}}{\omega}\\ \Im\{\epsilon(\mathbf{k},\omega)\} &= \frac{4\pi\Re\{\sigma(\mathbf{k},\omega)\}}{\omega}\end{aligned} \tag{13.46}$$

which relates these two functions. Observe that in experiments we always measure the real part of these functions and through the relations above one can get the imaginary parts as well. Thus the physical meaning of the real and imaginary part are clear now. Moreover, the static conductivity (the one which is measured when a static field is applied to the system) can be obtained from the equations above by taking the limit of $\omega \to 0$. However, a word of caution is in place at this point. In calculating that static conductivity one has to take the limit of $q \to 0$ before we take the limit of $\omega \to 0$. The opposite limit, that is ,$\omega \to 0$ first with q finite describes a static electric field which is periodic in space with characteristic wavelength $1/q$. In this case the charge distribution will not be uniform since it will try to follow the periodicity in the field. Thus, in calculating the static conductivity one has always to set $q \to 0$ first.

13.2.1 Response of a one-dimensional electron gas

Let us apply the technology developed in the last section to study the one-dimensional electron gas. In this case the integrals for the polarization function are easier to evaluate. Indeed, using (13.33) we have

$$\begin{aligned}\Re\{\Pi(q,\omega)\} &= \frac{1}{\pi}\int_{-k_F}^{k_F} dk\left(\frac{1}{\hbar\omega-\frac{\hbar^2kq}{m}-\frac{\hbar^2q^2}{2m}}-\frac{1}{\hbar\omega+\frac{\hbar^2kq}{m}+\frac{\hbar^2q^2}{2m}}\right)\\ &= \frac{m}{\hbar^2\pi q}\ln\left|\frac{\left(k_F+\frac{q}{2}\right)^2-\left(\frac{m\omega}{\hbar q}\right)^2}{\left(k_F-\frac{q}{2}\right)^2-\left(\frac{m\omega}{\hbar q}\right)^2}\right|.\end{aligned} \tag{13.47}$$

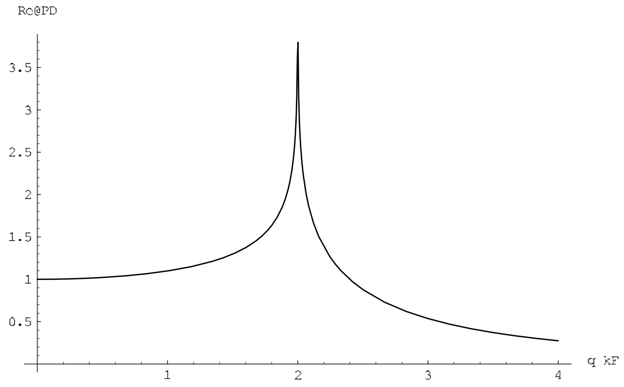

Figure 13.1: *Real part of the polarization function for the one dimensional electron gas as a function of q for $\omega = 0$.*

$\Re\{\Pi(q,\omega)\}$ is depicted in Fig.13.1 for $\omega = 0$. Observe that $\Re\{\Pi(q,\omega)\}$ diverges when $q = 2k_F$ for $\omega = 0$. This divergence comes from what is called the *nesting* of the Fermi surface.

Nesting it is related with the fact that in some systems it is possible to find a vector $\mathbf{k}$ such that $\epsilon_{\mathbf{q}+\mathbf{k}} = \epsilon_{\mathbf{k}}$ for a fixed $\mathbf{q}$. In this case, from (13.32), there is a point in the sum which is divergent. If this is an isolated point then it is not important for the behavior of the polarization function. In one-dimension, however, the Fermi surface is made out of two points, $+k_F$ and $-k_F$ and therefore the vector $q = \pm 2k_F$ connects all the points in the Fermi surface and leads to the divergence in (13.47). In higher dimensions we need a finite density of points at the Fermi surface which are nested, otherwise their contribution to (13.32) is a set of measure zero. One of the classic cases where a nesting condition happens is the half-filled tight binding model in two space dimensions where the Fermi surface has the shape shown in Fig.13.2 and can be connected by a wave-vector $(\pi/a, \pi/a)$. Because

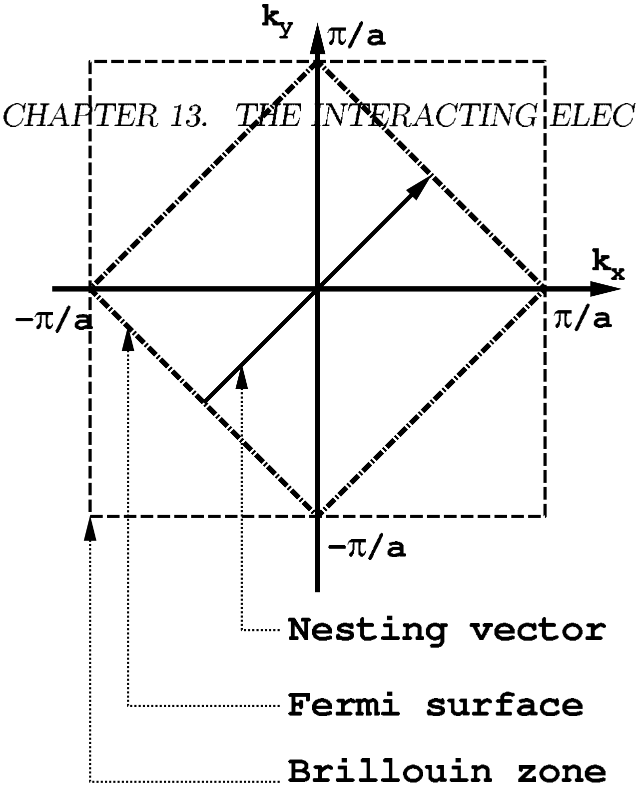

Figure 13.2: *Nesting of the half filled tight binding model in two dimensions.*

response functions, like the polarization function, have denominators which involve $\epsilon_{\mathbf{q}+\mathbf{k}} - \epsilon_{\mathbf{k}}$, nesting leads to instabilities in the electron gas.

Also from (13.33) we have

$$\begin{aligned}\Im\{\Pi(q,\omega)\} &= \int_{-k_F}^{k_F} dk \left[\delta\left(\hbar\omega - \frac{\hbar^2 kq}{m} - \frac{\hbar^2 q^2}{2m}\right) - \delta\left(\hbar\omega + \frac{\hbar^2 kq}{m} + \frac{\hbar^2 q^2}{2m}\right)\right] \\ &= \frac{m}{\hbar^2|q|}\left[\Theta\left(-\omega + \frac{\hbar k_F q}{m} - \frac{\hbar q^2}{2m}\right)\Theta\left(\omega + \frac{\hbar k_F q}{m} + \frac{\hbar q^2}{2m}\right)\right. \\ &- \left.\Theta\left(-\omega + \frac{\hbar k_F q}{m} + \frac{\hbar q^2}{2m}\right)\Theta\left(\omega + \frac{\hbar k_F q}{m} - \frac{\hbar q^2}{2m}\right)\right]. \qquad (13.48)\end{aligned}$$

Observe that $\Im\{\Pi(q,\omega)\}$ has a simple dependence with q (that is, it behaves like $1/q$) but it is not finite in the whole (ω, q) space. Actually it is easy to see that this function is only finite in the shaded area of Fig.13.3. This region is called the *particle-hole continuum* and it is source of dissipation in the system. Notice that the $\Im\{\Pi(q,\omega)\}$ vanishes

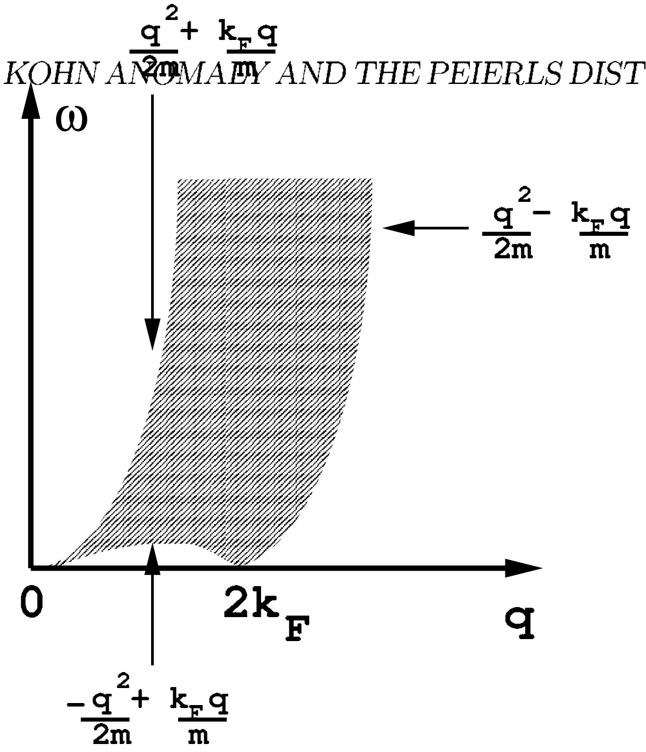

Figure 13.3: *Region of the* (ω, q) *space where* $\Im\{\Pi(q,\omega)\}$ *is finite.*

at $\omega = 0$ for all $0 < q < 2k_F$. We can show that this behavior is very particular of one-dimensional systems and in higher dimensions $\Im\{\Pi(\mathbf{q},\omega)\}$ is actually finite in this domain.

13.3 The Kohn anomaly and the Peierls distortion

We have so far discussed the behavior of an electron gas to an external source. The terminology "external source" is rather loose since the electrons interact with a variety of environmental excitations such as phonons and magnons and also among themselves. Moreover, the electrons interact electrostatically with the ions in the crystal which, from a broad point of view, are an external source. Indeed, let us consider again the electron-phonon problem under this new light. In Chapter 7 it was shown that the electron-phonon Hamiltonian can be written as

$$H = \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} c^\dagger_{\sigma,\mathbf{k}} c_{\sigma,\mathbf{k}} + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} a^\dagger_{\mathbf{q}} a_{\mathbf{q}} + \sum_{\mathbf{q}} U_{\mathbf{q}} n_{\mathbf{q}} \left(a_{\mathbf{q}} + a^\dagger_{-\mathbf{q}}\right) \tag{13.49}$$

where the electron-phonon coupling is the same as in (9.59). Observe the close resemblance of (13.49) and (13.21) if we define

$$V_{\mathbf{q}} = U_{\mathbf{q}} \left(a_{\mathbf{q}} + a^\dagger_{-\mathbf{q}}\right) . \tag{13.50}$$

This is not just a coincidence since, as we said, the electrons are electrostatically coupled to the lattice. Thus, at least from a perturbative point of view we could see that the electrons respond to the phonons in the system and one would suspect that the response should be somewhat related to the polarization function of the electron gas. Using the polarization function (13.32) we add and subtract $\bar{n}_{\mathbf{k},\sigma}\bar{n}_{\mathbf{k}+\mathbf{q},\sigma}$ in the numerator, regroup the terms together, and change $\mathbf{k} \to -\mathbf{k} - \mathbf{q}$ in order to get:

$$\Pi(\mathbf{q},\omega) = -\sum_{\mathbf{k},\sigma} \bar{n}_{\mathbf{k},\sigma}\left(1 - \bar{n}_{\mathbf{k}+\mathbf{q},\sigma}\right) \left[\frac{1}{\hbar\omega - \epsilon_{\mathbf{k}+\mathbf{q}} + \epsilon_{\mathbf{k}} + i\eta} - \frac{1}{\hbar\omega - \epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}+\mathbf{q}} + i\eta}\right] \tag{13.51}$$

which has the same structure as (9.77). Indeed, let us assume that the coupling between electrons and phonons is weak and use result (13.30) and substitute $n_{\mathbf{q}}$ by $\langle n_{\mathbf{q}} \rangle$ in (13.49) using (13.50) in order to find:

$$H = \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} a^\dagger_{\mathbf{q}} a_{\mathbf{q}} - \sum_{\mathbf{q}} |U_{\mathbf{q}}|^2 \,\Pi(\mathbf{q},\omega_{\mathbf{q}}) \left(a_{-\mathbf{q}} + a^\dagger_{\mathbf{q}}\right) \left(a_{\mathbf{q}} + a^\dagger_{-\mathbf{q}}\right) \tag{13.52}$$

is a purely bosonic Hamiltonian. The electrons have been traced out of the problem and their effect only appears through the polarization function. Notice that in the phonon Hamiltonian we now have operators of the form aa and $a^\dagger a^\dagger$ which do not conserve the number of bosons. This is happening because the electrons are now "hidden" and from the point of view of the bosons every time an electron emits a boson it is as if bosons were being produced from vacuum. The full solution of the problem involves the diagonalization of the Hamiltonian (13.52) which is possible because the problem is quadratic but since we are assuming weak coupling we will neglect the terms which do not conserve the number of bosons and, apart from a constant factor, rewrite (13.52) as

$$H = \sum_{\mathbf{q}} \hbar \Omega_{\mathbf{q}} a^{\dagger}_{\mathbf{q}} a_{\mathbf{q}} \tag{13.53}$$

where

$$\Omega_{\mathbf{q}} \approx \omega_{\mathbf{q}} - 2\left|U_{\mathbf{q}}\right|^2 \Pi(\mathbf{q}, \omega_{\mathbf{q}}) \tag{13.54}$$

where we have used that $\omega_{-\mathbf{q}} = \omega_{\mathbf{q}}$ because of the reflection symmetry of the lattice and that in (13.32) $\Pi(-\mathbf{q}, \omega) = \Pi(\mathbf{q}, \omega)$. Eq. (13.54) shows that the electrons actually modify the bare frequency of the phonons! This should be expected since what is measured experimentally is not the frequency of the phonons isolated from their environment but the effective frequency which takes into account the interaction of the phonons with their surroundings. We observe two effects: the real part of $\Pi(\mathbf{q}, \omega)$ renormalizes the phonon frequency while the imaginary part of $\Pi(\mathbf{q}, \omega)$ produces *damping* or dissipation of the phonon modes, that is, when the bare phonon frequency enters a region where $\Im\{\Pi(\mathbf{q}, \omega)\}$ is finite the phonon mode becomes unstable and decay into the particle-hole continuum.

Let us consider the application of (13.54) to the one dimensional case. Let us consider the renormalization of the phonon frequency using (13.47) for the case of the acoustic mode with $\omega_q = v_s q$ where v_s is the sound velocity. In this case we find

$$\Omega_q = v_s q - \frac{2m\left|U_q\right|^2}{\hbar^2 \pi q} \ln \left| \frac{\left(k_F + \frac{q}{2}\right)^2 - \left(\frac{m v_s}{\hbar}\right)^2}{\left(k_F - \frac{q}{2}\right)^2 - \left(\frac{m v_s}{\hbar}\right)^2} \right| \tag{13.55}$$

which is plotted in Fig.13.4. Observe that (13.55) has a singularity at $q = 2k_F(1 + v_s/v_F) \approx 2k_F$ where $v_F = \hbar k_F/m$ is the Fermi velocity (notice that $v_s \ll v_F$). Because of the logarithmic singularity in (13.55) the phonon frequency vanishes close to $2k_F$ in one dimension. In higher dimensions (13.54) predicts a finite frequency at $2k_F$ with a divergent group velocity ($d\Omega/dk \to \infty$) which leads to the so-called Kohn anomaly in metals. In one dimension the Kohn anomaly

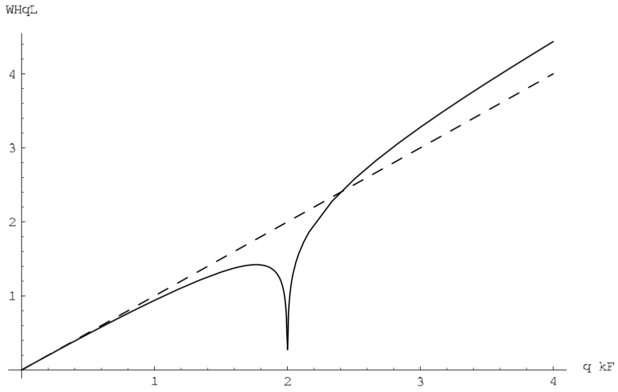

Figure 13.4: *Dashed line: bare phonon dispersion; Continuous line: result from (13.55).*

is more severe and leads to the vanishing of the phonon frequency and has strong consequences.

Observe that in first quantized language we can rewrite (13.53) as

$$H = \sum_{\mathbf{q}} \left(\frac{P_{\mathbf{q}} P_{-\mathbf{q}}}{2M} + \frac{M\Omega_{\mathbf{q}}^2}{2} X_{\mathbf{q}} X_{-\mathbf{q}} \right) \tag{13.56}$$

and therefore the vanishing of $\Omega_{\mathbf{q}}$ for some wave-vector $\mathbf{q} = \mathbf{Q}$ leads to a Hamiltonian of a free particle for that particular mode. A free particle has an unbounded motion. This leads to the conclusion that the vanishing of the phonon frequency is associated to an instability of the lattice. What this result shows is that the lattice becomes "soft" for this particular mode and that there is a gain in energy to produce a distortion with characteristic wavevector $\mathbf{Q}$, that is, the lattice will distort with a modulation given by $\cos(\mathbf{Q} \cdot \mathbf{r})$. In the case of the one dimensional system where $Q = 2k_F$ this distortion is only possible is the electronic density is *commensurate* with the lattice. To understand commensuration recall that $Q = 2N\pi/a$ where N is any integer is a reciprocal lattice vector. Thus, the condition $Q = 2k_F$ implies that $k_F = \pi/(Na)$. In one dimension one has that $k_F = \pi\bar{n}/a$ where $\bar{n} = N/N_s$ is the number of electrons per lattice site. Thus, for the distortion to occur one needs $\bar{n} = 1$ which is the condition for commensuration, that is, the number of lattice sites is a multiple of the number of electrons. The simplest case is $\bar{n} = 1$ that is, the half-filled band. In this case $Q = \pi/a$ and therefore the distortion will be of the form $\cos(\pi x/a)$. In this case the unit cell doubles size as shown in Fig.13.5(a,b). Observe that in this case the unit cell doubles its size going from a to $2a$. This is called the *Peierls distortion* and we say that the system is *dimerized*, that is, transformed to dimers of atoms. This implies that the Brillouin zone has to shrink from $\pm\pi/a$ to $\pm\pi/(2a)$ and a gap has to open at the zone boundary (exactly like in the case of phonons) as shown in Fig.13.5(c,d). It turns out however that the zone boundary is at the Fermi energy and therefore a gap Δ has to open at the Fermi surface and the system should be insulating. The size of the distortion and the magnitude of the gap cannot be discussed in our simple picture because these are non-perturbative effects. This effect, however, is seen in one dimensional systems such as polymers which by

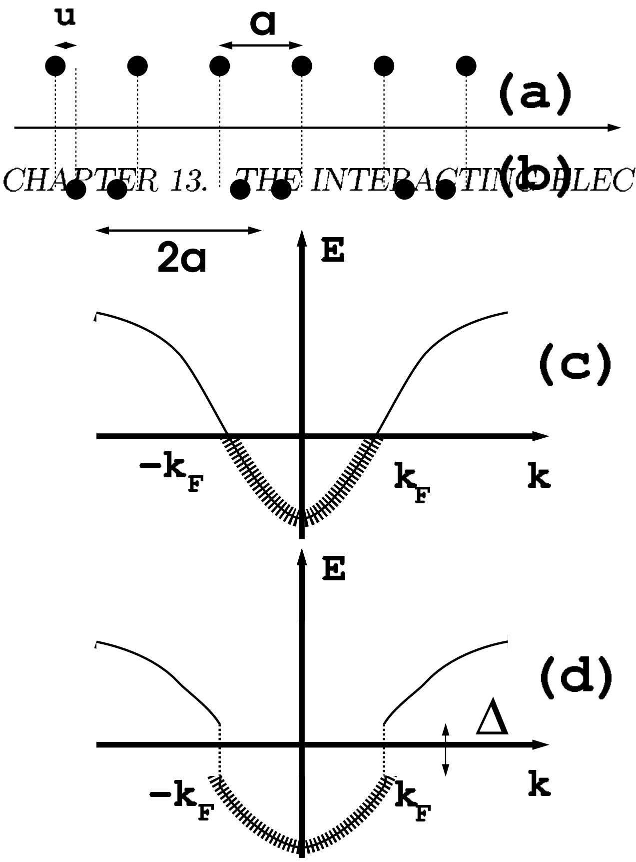

Figure 13.5: *(a) Original Lattice; (b) Peierls distortion; (c) Original electron band; (d) Electron band after Peierls distortion.*

band structure arguments should be conductors but by the effect of the Peierls mechanism are actually insulators.

13.4 Electron-electron interactions

So far we have discussed the problem of an electron gas interacting with external charges or the ion lattice but one important question which is left out is: does our arguments of screening apply to the electron gas itself? Do electrons screen their own Coulomb interaction? On the one hand screening requires the electrons to be indistinguishable from each other and obey the Fermi-Dirac statistics. On the other hand one has to be able to isolate a particular electron in order to apply our argument, that is, we have to be able to distinguish one electron from the others! The problem here is similar to a very familiar puzzle: who was created first, the chicken or the egg? The problem of screening requires one to separate two aspects of the interacting electron gas system: the collective electron motion and the single electron physics. This is a very delicate and complex problem and to my knowledge there is no final answer to it. One usually have to use uncontrolled approximations. Here we will be happy to use a simple mean-field, Hartree-Fock, approach to the electron-electron interaction in three dimensions:

$$H_I = \frac{1}{2V} \sum_{\mathbf{q}} U_q n_{\mathbf{q}} n_{-\mathbf{q}} \tag{13.57}$$

where $U_q = 4\pi e^2/q^2$ (where the factor of 2 is to avoid double counting). In the mean-field approximation one does the usual substitution: $n_{\mathbf{q}} n_{-\mathbf{q}} \to \langle n_{\mathbf{q}} \rangle n_{-\mathbf{q}} + n_{\mathbf{q}} \langle n_{-\mathbf{q}} \rangle$ which changes (13.57) to

$$H_{MF} = \frac{1}{V} \sum_{\mathbf{q}} V_q n_{\mathbf{q}} \tag{13.58}$$

where

$$V_q = U_q \langle n_{\mathbf{q}} \rangle \,. \tag{13.59}$$

Observe that (13.58) has exactly the form of (13.21) for an external potential. In this picture each electron responds to the average charge density. Applying the arguments of the previous sections one would argue that the effective interaction felt by the electrons due to the other electrons would be given (in the static limit) by

$$U_q^{eff} = \frac{U_q}{\epsilon(q,0)} = \frac{4\pi e^2}{q^2 + q_{TF}^2} \tag{13.60}$$

which is the screened Coulomb interaction. Thus, from this point of view the electrons indeed interact via an screened (weaker) interaction than the original long range Coulomb interaction.

13.5 Landau's Theory - An Introduction

In the last sections we have seen that in an electron gas, even if we start with strong long range Coulomb interactions, screening plays a major role and one ends up with only a mild local interaction among the electrons. Since the interactions turned out to be weak, the interacting electron fluid resembles a non-interacting electrons gas. The main problem here is how to incorporate the electron-electron interactions within the properties of the electron gas. Let us imagine that and electron with energy E_F is introduced into the electron fluid as in Fig.13.6(a). As the electron enters the electron gas the other electrons have to move around to screen its charge. In this case a "correlation hole" with positive charge is formed around the electron in such way that, as seen from far away, the electron behaves like a neutral object as in Fig.13.6(b). One imagines that the same picture applies to *all* the electrons in the system (as we did in the mean field theory described previously). In this case the electrons are *dressed* by the interactions with all other electrons in the system. Because of this dressing the elementary excitations in the system are not bare electrons but dressed electrons that we call *quasiparticles* (as shown in Fig.13.6(c)). Although this picture is quite appealing we would like to have a more quantitative description. For instance, one would like to know how interactions affect experimental quantities such as specific heat, magnetic susceptibility and so on.

A major breakthrough in this field was made by Landau in the 40's. Landau's theory of the Fermi liquid is based on two main "intuitive" assumptions:

(1) *There is one-to-one correspondence between the quantum numbers of the non-interacting electron gas and the interacting electron gas.* Thus, the quasiparticles carry one unit of electric charge, they are spin 1/2 excitations and they also carry the momentum quantum number $\mathbf{k}$. Thus, in Landau's theory the Hilbert space for electrons and quasiparticles is the same and the only possible change in the problem is not dynamic but kinematic. This principle is also called the *adiabatic principle* because it assumes that the interactions can be turned on slowly so that nothing tragic happens in the system (in particular, no phase transition occurs!). This principle tells us how the quasiparticles couple to external fields such as the electric and magnetic fields. Since the electric charge is the same as the electrons the electromagnetic field should couple via "minimal coupling" $\mathbf{p}-e\mathbf{A}/c$ plus the Zeeman energy $\mathbf{S}\cdot\mathbf{H}$.

(2)*It is possible to write down an energy functional of the deviations of the quasiparticle occupation relative to the ground state.* As we

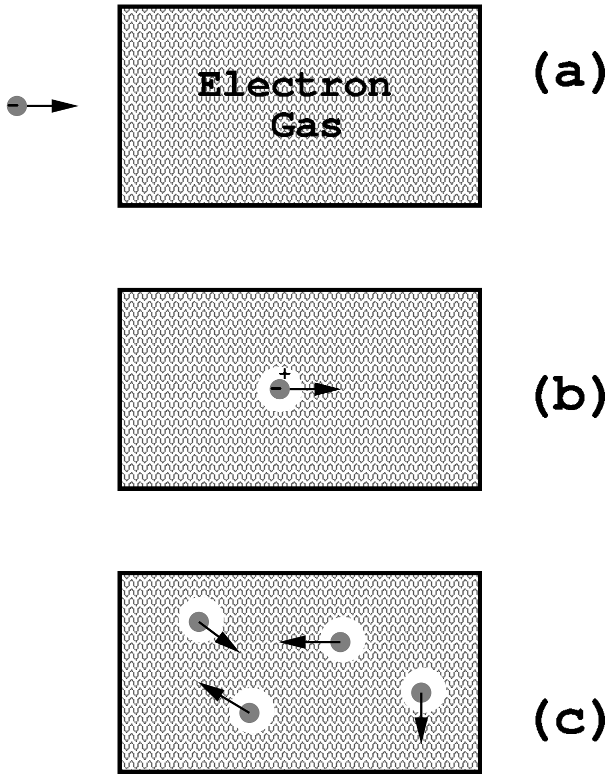

Figure 13.6: *(a) Electron entering the electron gas; (b) Electron plus its correlation hole; (c) Quasiparticle gas.*

have seen before we can create excitations in the electron gas by creating particle-hole excitations around the Fermi surface. Accordingly to Landau the ground state of an interacting Fermi gas is also a Fermi sea of quasiparticles as defined by assumption (1). That is, we can define an occupation number $n_{\mathbf{k},\sigma}$ such that

$$n_{\mathbf{k},\sigma} = \frac{1}{e^{\beta(E_{\mathbf{k},\sigma}-\mu)}+1} \tag{13.61}$$

where $E_{\mathbf{k},\sigma}$ is the quasiparticle energy and μ is the chemical potential of the system. In increasing the temperature or applying a field to a system what one does is to modify the occupation by an amount $\delta n_{\mathbf{k},\sigma}$. In Landau's theory the total energy of the system can be written as an expansion in terms of these deviations:

$$E[\delta n_{\mathbf{k},\sigma}] = E_0 + \frac{1}{V}\sum_{\mathbf{k},\sigma} E^0_{\mathbf{k},\sigma}\delta n_{\mathbf{k},\sigma} + \frac{1}{2V}\sum_{\mathbf{k},\sigma,\mathbf{k}',\sigma'} f_{\mathbf{k},\sigma,\mathbf{k}',\sigma'}\delta n_{\mathbf{k},\sigma}\delta n_{\mathbf{k}',\sigma'} \tag{13.62}$$

plus higher orders in $\delta n_{\mathbf{k},\sigma}$. E_0 is just the ground state energy, $E^0_{\mathbf{k},\sigma}$ is the bare dispersion of the quasiparticles and $f_{\mathbf{k},\sigma,\mathbf{k}',\sigma'}$ is so-called Landau parameter which describes the weak interaction between quasiparticles. Observe that the actual dispersion of the quasiparticles depend on their interaction. Since we can rewrite (13.62) as

$$\begin{aligned} E &= E_0 + \frac{1}{V}\sum_{\mathbf{k},\sigma} E_{\mathbf{k},\sigma}\delta n_{\mathbf{k},\sigma} \\ E_{\mathbf{k},\sigma} &= E^0_{\mathbf{k},\sigma} + \frac{1}{V}\sum_{\mathbf{k},\sigma} f_{\mathbf{k},\sigma,\mathbf{k}',\sigma'}\delta n_{\mathbf{k}',\sigma'} \end{aligned} \tag{13.63}$$

where $E_{\mathbf{k},\sigma}$ is the actual quasiparticle dispersion.

In order to understand the physical meaning and consequences of (13.62) let us consider the problem of the specific heat of the electron gas in Landau's theory. The quasiparticle entropy is given by the usual Boltzmann expression

$$S = -\frac{k_B}{V}\sum_{\mathbf{k},\sigma}\left\{n_{\mathbf{k},\sigma}\ln(n_{\mathbf{k},\sigma}) + (1-n_{\mathbf{k},\sigma})\ln(1-n_{\mathbf{k},\sigma})\right\} . \tag{13.64}$$

A variation $\delta n_{\mathbf{k},\sigma}$ in the distribution function leads to a variation δS in the entropy which is given by

$$\begin{aligned} \delta S &= -\frac{k_B}{V}\sum_{\mathbf{k},\sigma}\delta n_{\mathbf{k},\sigma}\ln\left(\frac{n_{\mathbf{k},\sigma}}{1-n_{\mathbf{k},\sigma}}\right) \\ &= \frac{k_B\beta}{V}\sum_{\mathbf{k},\sigma}\left(E_{\mathbf{k},\sigma}-\mu\right)\delta n_{\mathbf{k},\sigma} \end{aligned} \qquad (13.65)$$

where we used (13.61). What we are interested in is the specific heat which is the variation of the entropy with temperature, that is, $\delta S/\delta T$. Thus, one needs to calculate how the occupation $n_{\mathbf{k},\sigma}$ changes with temperature. This can be easily obtained from (13.61) as

$$\frac{\delta n_{\mathbf{k},\sigma}}{\delta T} = \frac{E_{\mathbf{k},\sigma}-\mu}{T}\left(-\frac{\partial n_{\mathbf{k},\sigma}}{\partial E_{\mathbf{k},\sigma}}\right) . \qquad (13.66)$$

Thus, substituting (13.66) into (13.65) we find

$$\frac{\delta S}{\delta T} = \frac{1}{V}\sum_{\mathbf{k},\sigma}\left(-\frac{\partial n_{\mathbf{k},\sigma}}{\partial E_{\mathbf{k},\sigma}}\right)\left(\frac{E_{\mathbf{k},\sigma}-\mu}{T}\right)^2 . \qquad (13.67)$$

In order to evaluate the sum in (13.67) we transform it into an integral by using the usual definition of the quasiparticle density of states:

$$N(E) = \frac{1}{V}\sum_{\mathbf{k},\sigma}\delta(E-E_{\mathbf{k},\sigma}) \qquad (13.68)$$

and rewrite (13.67) as

$$\frac{\delta S}{\delta T} = \int_{-\infty}^{+\infty} dEN(E)\left(\frac{E-\mu}{T}\right)^2\left(-\frac{\partial n(E)}{\partial E}\right) \qquad (13.69)$$

but observe that the derivative in the expression above is highly peaked around $E=\mu$ (Fermi statistics!) while the rest of the argument is a smooth function around this point. Therefore, with great accuracy we can approximate the above integral as

$$\begin{aligned} \frac{\delta S}{\delta T} &= k_B^2 N(\mu)\int_{-\infty}^{+\infty} dx x^2 \frac{e^x}{(e^x+1)^2} \\ &= \frac{\pi^2}{3}k_B^2 N(\mu) \end{aligned} \qquad (13.70)$$

where we changed variables: $x = \beta(E - \mu)$. The specific heat of the electron gas can be immediately obtained from (13.70) since

$$C_V = T\frac{\delta S}{\delta T} = \frac{\pi^2}{3} k_B^2 N(\mu) T \tag{13.71}$$

which looks identical to the free electron gas result (6.97). The temperature dependence of the specific heat is of course the same as in the free electron gas but the similarity is only apparent because in our definition of the density of states for the quasiparticles (13.68) we have used the actual quasiparticle dispersion $E_{\mathbf{k},\sigma}$ which accordingly to (13.63) also depends on the Landau parameters $f_{\mathbf{k},\sigma,\mathbf{k}',\sigma'}$! Thus, in order to be complete one has to compute $N(\mu)$ as a function of the interaction parameters. First we notice that due to Landau's first assumption the number of electrons and the number of quasiparticles have to be the same. This implies that the Fermi momentum of the quasiparticles is the same as the Fermi momentum of the particles, $k_F = (3\pi n)^{3/2}$, since it depends on the density alone. Let us first go back to the definition of the density of states (13.68) and rewrite it as an integral

$$\begin{aligned} N(\mu) &= \sum_\sigma \int \frac{d^3k}{(2\pi)^3} \delta(\mu - E_{\mathbf{k},\sigma}) \\ &= \sum_\sigma \int \frac{d^3k}{(2\pi)^3} \frac{\delta(k - k_F)}{|\nabla_{\mathbf{k}} E_{\mathbf{k},\sigma}|} \end{aligned} \tag{13.72}$$

since by definition $E_{\mathbf{k}_F,\sigma} = \mu$. Since we are expanding the total energy to second order in $\delta n_{\mathbf{k},\sigma}$ we just keep the quasiparticle energy to *first* order (take a look at (13.63)). In this case we can replace $E_{\mathbf{p},\sigma}$ by $E^0_{\mathbf{p},\sigma}$ in (13.72) which depends on the group velocity of the quasiparticles:

$$\mathbf{v}_{\mathbf{p},\sigma} = \nabla_{\mathbf{p}} E^0_{\mathbf{p},\sigma} \,. \tag{13.73}$$

In a non-interacting Fermi gas the group velocity is simply p_F/m where p_F is the Fermi momentum. By analogy we define the effective mass, m^*, of the quasiparticles as

$$\mathbf{v}_{\mathbf{p},\sigma} = \frac{\mathbf{p}}{m^*} \tag{13.74}$$

when substituted in (13.72) leads to

$$N(\mu) = \frac{m^* p_F}{\pi^2 \hbar^3} \tag{13.75}$$

which is the quasiparticle density of states that depends only on the effective mass of the quasiparticles. Thus, what we have done is transferring the problem of calculating the density of states to the problem of calculating the effective mass. But life is simpler because the mass is a kinematical quantity which reflects the inertia of the system. In the case of the interacting electron gas the effective mass depends on the interaction between the electrons since as one electron moves it has to push the other electrons around, that is, the inertia of the quasiparticle depends on its interaction with the environment.

The simplest way to compute m^* is use an argument due to Landau which assumes Galilean invariance of the system. Consider observing a Fermi gas from a moving frame with velocity $\mathbf{V}$. If the interactions do not depend on the velocity of the particle (as in the case of the Coulomb interactions) then the only change in the Hamiltonian of the system is in kinetic energy which changes from

$$K = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}$$

to

$$K = \sum_{i=1}^{N} \frac{(\mathbf{p}_i - m\mathbf{V})^2}{2m} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - \mathbf{V} \cdot \sum_{i=1}^{N} \mathbf{p}_i + \frac{Nm}{2} \mathbf{V}^2 \tag{13.76}$$

since the velocities have to change from $\mathbf{v}_i$ to $\mathbf{v}_i - \mathbf{V}$ due to Galilean invariance. Thus, the total energy and momentum of the system in the moving frame will be

$$\begin{aligned} E_{mov} &= E - \mathbf{P} \cdot \mathbf{V} + \frac{Nm}{2} \mathbf{V}^2 \\ \mathbf{P}_{mov} &= \mathbf{P} - Nm\mathbf{V} \end{aligned} \tag{13.77}$$

where $\mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i$ is the total momentum in the rest frame of the electron gas. Consider now adding a quasiparticle with momentum $\mathbf{p}$

in the rest frame. This will lead to an increase in the total mass of the system by m and the total momentum of the system by $\mathbf{p}$. Thus, from (13.77) we see that momentum of the quasiparticle, as seen from the moving frame is, $\mathbf{p} - m\mathbf{V}$ while its energy will be

$$\begin{aligned} E_{mov,\mathbf{p}-m\mathbf{V},\sigma} &= E_{\mathbf{p},\sigma} - \mathbf{p}\cdot\mathbf{V} + m\frac{\mathbf{V}^2}{2} \\ E_{mov,\mathbf{p},\sigma} &= E_{\mathbf{p}+m\mathbf{V},\sigma} - \mathbf{p}\cdot\mathbf{V} - m\frac{\mathbf{V}^2}{2}\,. \end{aligned} \tag{13.78}$$

Now assume that $\mathbf{V}$ is very small and expand (13.78) to first order in $\mathbf{V}$:

$$E_{mov,\mathbf{p},\sigma} \approx E_{\mathbf{p},\sigma} + \mathbf{V}\cdot(m\nabla_{\mathbf{p}}E_{\mathbf{p},\sigma} - \mathbf{p}) \tag{13.79}$$

which depends on the quasiparticle energy $E_{\mathbf{p},\sigma}$. Using (13.73) and (13.74) in (13.79) leads to

$$E_{mov,\mathbf{p},\sigma} \approx E_{\mathbf{p},\sigma} + \frac{m-m^*}{m^*}\mathbf{p}\cdot\mathbf{V}\,. \tag{13.80}$$

On the other hand, from the moving frame the distribution function of the quasiparticles has to change as

$$\begin{aligned} n_{mov,\mathbf{p},\sigma} &= n_{\mathbf{p}+m\mathbf{V},\sigma} \approx n_{\mathbf{p},\sigma} + m\mathbf{V}\cdot\nabla_{\mathbf{p}}n_{\mathbf{p},\sigma} \\ &= n_{\mathbf{p},\sigma} + m\mathbf{V}\cdot\nabla_{\mathbf{p}}E_{\mathbf{p},\sigma}\frac{\partial n_{\mathbf{p},\sigma}}{\partial E_{\mathbf{p},\sigma}} \\ &= n_{\mathbf{p},\sigma} + \frac{m}{m^*}\mathbf{V}\cdot\mathbf{p}\frac{\partial n_{\mathbf{p},\sigma}}{\partial E_{\mathbf{p},\sigma}}\,. \end{aligned} \tag{13.81}$$

From the change of the occupation we can calculate the energy of the quasiparticle in the moving frame from (13.63)

$$E_{mov,\mathbf{p},\sigma} = E_{\mathbf{p},\sigma} + \frac{1}{V}\sum_{\mathbf{p}',\sigma'} f_{\mathbf{p},\sigma,\mathbf{p}',\sigma'}\frac{m}{m^*}\mathbf{V}\cdot\mathbf{p}'\frac{\partial n_{\mathbf{p}',\sigma}}{\partial E_{\mathbf{p}',\sigma}} \tag{13.82}$$

which has to be compared with (13.80). At this point the comparison is not straightforward because we have to evaluate the integral in (13.82). In dealing with an isotropic system and therefore a spherical Fermi surface we have an extra symmetry which is the rotations in momentum space. This implies that in the scattering between two quasiparticles with momentum $\mathbf{p}$ and $\mathbf{p}'$ the interaction parameter $f_{\mathbf{p},\sigma,\mathbf{p}',\sigma'}$ only depends on the angle $\theta(\mathbf{p},\mathbf{p}')$ between $\mathbf{p}$ and $\mathbf{p}'$. In this case we can expand $f_{\mathbf{p},\sigma,\mathbf{p}',\sigma'}$ in Legendre polynomials, $P_l(\cos(\theta))$ as

$$f_{\mathbf{p},\sigma,\mathbf{p}',\sigma'} = \sum_{l=0}^{\infty} f_{l,\sigma,\sigma'} P_l(\cos(\theta(\mathbf{p},\mathbf{p}'))) \tag{13.83}$$

which can be inverted due to the orthogonality between the Legendre polynomials as

$$\begin{aligned} f_{l,\sigma,\sigma'} &= \frac{2l+1}{2}\int_0^{\pi} d\theta(\mathbf{p},\mathbf{p}')\sin(\theta(\mathbf{p},\mathbf{p}'))P_l(\cos(\theta(\mathbf{p},\mathbf{p}')))f_{\mathbf{p},\sigma,\mathbf{p}',\sigma'} \\ &= \frac{2l+1}{2}\int_{-1}^{+1} du(\mathbf{p},\mathbf{p}')P_l(u(\mathbf{p},\mathbf{p}'))f_{\mathbf{p},\sigma,\mathbf{p}',\sigma'} \end{aligned} \tag{13.84}$$

where $u=\cos(\theta)$. Direct substitution of (13.83) into (13.82) leads to

$$\begin{aligned} E_{mov,\mathbf{p},\sigma} &= E_{\mathbf{p},\sigma} - \frac{m}{m^*}\sum_{\sigma',l} f_{l,\sigma,\sigma'}\int \frac{d^3p'}{(2\pi\hbar)^3}\left(-\frac{\partial n_{\mathbf{p},\sigma}}{\partial E_{\mathbf{p},\sigma}}\right)P_l(\cos(\theta))\mathbf{V}\cdot\mathbf{p}' \\ &= E_{\mathbf{p},\sigma} - \frac{m}{m^*}N(0)\sum_{\sigma'}\frac{f_{l,\sigma,\sigma'}}{6}\mathbf{V}\cdot\mathbf{p} \\ &= E_{\mathbf{p},\sigma} - \frac{m}{m^*}\frac{F_1^s}{3}\mathbf{V}\cdot\mathbf{p} \end{aligned} \tag{13.85}$$

where we have defined

$$\begin{aligned} F_l^s &= N(0)\,\frac{f_{l,\sigma,\sigma}+f_{l,\sigma,-\sigma}}{2} \\ F_l^a &= N(0)\,\frac{f_{l,\sigma,\sigma}-f_{l,\sigma,-\sigma}}{2} \end{aligned} \tag{13.86}$$

the symmetric and anti-symmetric Landau parameters. Direct comparison of (13.85) with (13.80) we find

$$\frac{m^*}{m} = 1 + \frac{F_1^s}{3} \tag{13.87}$$

which gives the renormalization of the mass in terms of the interactions. The density of states can now be easily obtained from (13.75).

It is clear that many properties of the interacting electron gas can be directly calculated from Landau's assumptions. In this case the Landau parameters enter into the theory as phenomenological functions which describe the physics of the interacting Fermi gas. It is possible, therefore, to make many predictions about the physical quantities of interest and check experimentally. The simplicity and power of Landau's approach should be clear and its success in explaining the physical properties of many systems such as He^3 and simple metals made it the standard approach to study interacting electron systems.

13.6 Problems

1. Consider a system of electrons moving on a plane. Use a system of coordinates where the three dimensional vectors can be written as $\mathbf{R} = (\mathbf{r}, z)$ where $\mathbf{r}$ is the vector in the plane. (*i*) Using the Thomas-Fermi approximation show that the Thomas-Fermi screening length is the Bohr radius a_0 and does not depend on the density. (*ii*) Calculate the effective potential for a charge Q sitting at the origin of the plane ($\rho_{ext}(\mathbf{r}) = Q\delta(z)\delta(\mathbf{r})$) and show that at long distances ($r \gg a_0$) the effective potential behaves like

   $$V(r) \approx -\frac{4\pi^2 a_0^2 eQ}{r^3}.$$

   In this case the potential does not decay exponentially contrary to the problem in three dimensions.

2. Use (13.51) to calculate the polarization function for a three dimensional electron gas with a spherical Fermi surface. *Hint: you can find the full solution in Fetter and Walecka, "Quantum Theory of Many-Particle systems" (McGraw-Hill, New York, 1971), pg.158.*

3. Calculate the polarization function of a two dimensional electron gas in the RPA approximation. (*i*) Plot $\Re\{\Pi(q, \omega = 0)$ and show that it does not diverge at $q = 2k_F$. (*ii*) In what region of the (ω, q) space $\Im\{\Pi(q, \omega)\}$ is finite. (*iii*) How does the dielectric function compares with the result of question (2)?

4. Consider the Hamiltonian (13.52). (*i*) Calculate the commutator of $a_{\mathbf{q}}$ with the Hamiltonian and show that the operators $a_{\mathbf{q}}$ mixes with the operator $a^{\dagger}_{-\mathbf{q}}$. (*ii*) Consider the unitary transformation

   $$b_{\mathbf{q}} = u_{\mathbf{q}} a_{\mathbf{q}} + v_{\mathbf{q}} a^{\dagger}_{-\mathbf{q}}$$

   what is the condition on $u_{\mathbf{q}}$ and $v_{\mathbf{q}}$ in order to have canonical commutation relations? (*iii*) Show that the Hamiltonian can be completely diagonalized by the transformation above. What are the new phonon frequencies in this case?

5. Consider a one-dimensional electron gas at half filling with hopping matrix element t_0. Consider the case where the system undergoes a Peierls distortion of size u (that is, the size of the distortion in Fig.13.5). (*i*) Assume that wavefunction of the electron in each atom has an exponential form, $\psi(x) \sim e^{-|x|/a_0}$ where a_0 is the lattice spacing. Show that there is a change in hopping matrix element in the system from t_0 to $t_0 \pm 2\alpha u$ depending on the site (α is a constant).

   (*ii*) From your result above show that in the tight binding approximation the Hamiltonian for the electrons of the problem can be written as

   $$H_e = -\sum_n \left(t_0 + 2\alpha u(-1)^n\right)\left(c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n\right) . \qquad (13.88)$$

   (*iii*) Show based on general arguments that the elastic energy due to the Peierls distortion can be written as

   $$H_d = 2NKu^2 \qquad (13.89)$$

   where N is the number of atoms and K is the spring constant.

   (*iv*) Fourier transform (13.88) and show that it can be written as

   $$H_e = \sum_k \left[\epsilon_k \left(b_k^\dagger b_k - a_k^\dagger a_k\right) + 2\alpha u \sin(ka_0)\left(b_k^\dagger a_k + a_k^\dagger b_k\right)\right] (13.90)$$

   where $\epsilon_k = -2t_0 \cos(ka_0)$, $a_k = c_k$ and $b_k = -ic_{k\pm Q}$ (with $Q = \pi/a$) and the sum over k goes from $-Q/2$ to $Q/2$ (that is, the new Brillouin zone).

   (*v*) Observe that (13.90) is quadratic and can be diagonalized. Define the following unitary transformation

   $$\begin{aligned} \alpha_k &= u_k a_k + v_k b_k \\ \beta_k &= u_k b_k - v_k a_k \end{aligned} \qquad (13.91)$$

   where u_k and v_k are constants. Show that $u_k^2 + v_k^2 = 1$. Use (13.91) to diagonalize (13.90) and show that the new Hamiltonian can be written as

   $$H_e = \sum_k E_k \left(\beta_k^\dagger \beta_k - \alpha_k^\dagger \alpha_k\right) \qquad (13.92)$$

where $E_k = \sqrt{\epsilon_k^2 + \Delta_k^2}$ and

$$\Delta_k = 4\alpha u \sin(k a_0)\,. \tag{13.93}$$

Make a plot of $\pm E_k$ and show that a gap opens at $k = \pi/(2a)$. Give a physical meaning to the operators β_k and α_k.

(*vi*) Show that

$$\begin{aligned} u_k &= \sqrt{\frac{1}{2}\left(1+\frac{\epsilon_k}{E_k}\right)} \\ v_k &= \sqrt{\frac{1}{2}\left(1-\frac{\epsilon_k}{E_k}\right)} sgn(k) \end{aligned}$$

where $sgn(k) = +1(-1)$ if $k > 0(k < 0)$.

(*v*) Assume that the electron system is half filled and show that the total energy of the system (electron+distortion) is given by

$$\frac{E(u)}{N} = -\frac{4t_0}{\pi}\mathbf{E}\left[1-\left(\frac{2\alpha u}{t_0}\right)^2\right] + 2Ku^2 \tag{13.94}$$

where $\mathbf{E}[x] = \int_0^{\pi/2} dt\sqrt{1 - x\sin^2(t)}$ is an Elliptic integral.

(*vi*) Show that for $u \ll t_0/\alpha$ the energy of the system can be written as

$$\frac{E(u)}{N} \approx -\frac{4t_0}{\pi} + \left[2K + \frac{4\alpha^2}{\pi t_0} - \frac{8\alpha^2}{\alpha t_0}\ln\left(\frac{2t_0}{\alpha u}\right)\right]u^2\,. \tag{13.95}$$

What happens when $u \to \infty$? From these two results prove that no matter how small α there is always a value of $u = u_0 \neq 0$ for which the energy is minimum. Thus, you just proved that, no matter how small the coupling constant α, the one dimensional system is always dimerized (Peierls theorem).

(*vii*) Using (13.95) show that

$$u_0 \approx \frac{2t_0}{\alpha} e^{-1-\frac{\pi t_0 K}{4\alpha^2}}$$

for $u \ll t_0/\alpha$. Observe that u_0 is not an analytic function of α!

6. In this exercise we are going to consider the compressibility of the electron gas in the presence of interactions. The physical quantity of interest is the compressibility, κ (or bulk modulus). The compressibility is defined as

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial P} = \frac{1}{n^2}\frac{\partial n}{\partial mu}$$

where V is the volume, P is pressure, $n = N/V$ is the particle density and μ is the chemical potential. Thus, in order to calculate κ one has to consider the change in the quasiparticle occupation, $\delta n_{\mathbf{k},\sigma}$ in respect to the chemical potential.

(*i*) Using (13.61) show that

$$\delta n_{\mathbf{k},\sigma} = (\delta E_{\mathbf{k},\sigma} - \delta\mu)\frac{\partial n_{\mathbf{k},\sigma}}{\partial E_{\mathbf{k},\sigma}} \,. \tag{13.96}$$

(*ii*) Show that

$$\delta E_{\mathbf{k},\sigma} = \frac{1}{V}\sum_{\mathbf{k}',\sigma'} f_{\mathbf{k},\sigma,\mathbf{k}',\sigma'}\delta n_{\mathbf{k}',\sigma'} \tag{13.97}$$

and from that prove that

$$\delta E_{\mathbf{k},\sigma} = \frac{F_0^s}{N(\mu)}\delta n$$

where $\delta n = \frac{1}{V}\sum_{\mathbf{k},\sigma}\delta n_{\mathbf{k},\sigma}$ is the total variation in the number of quasiparticles.

(*iii*) Using the results of item (*i*) and (*ii*) show that

$$\kappa = \frac{1}{n^2}\frac{N(\mu)}{1+F_0^s} \,.$$

What is the physical meaning of this result?

7. In the exercise you will calculate the magnetic susceptibility of the interacting electron gas in the Landau approach. Let us consider only the Zeeman energy which is given by

$$H_z = -g\mu_B\sum_{i=1}^{N}\mathbf{S}_i\cdot\mathbf{H}$$

where **S** is the spin of the quasiparticles which, according to Landau's assumption, is $\pm\hbar/2$.

(i) What is the change in the quasiparticle energy in the presence of the field? What is the difference from (13.97)?

(ii) The change in the occupation is still given by (13.96). Notice however that the change in the chemical potential cannot depend on the direction of the field **H** and therefore can only be of order $\mathbf{H}^2$. Thus, neglecting the change in the chemical potential due to the field and using the result of item (i) show that

$$\delta n_\sigma = \frac{N(\mu) g \mu_B}{2(1+F_0^a)} \sigma H_z$$

where $\delta n_\sigma = \frac{1}{V}\sum_{\mathbf{k}} \delta n_{\mathbf{k},\sigma}$, and H_z is the z-component of the magnetic field. From the above result calculate the total magnetization of the electron gas and show that the magnetic susceptibility is given by

$$\chi = \frac{N(\mu)(g\mu_B)^2}{1+F_0^a}.$$

What is the physical meaning of this result if $F_0^a < 0$?

Chapter 14

Superconductivity

We have shown in Chapter 7 that phonons can induce an attractive interaction among the electrons. This retarded interaction can lead to the phenomenon of Cooper pairing where electrons with opposite momenta close to the Fermi surface can form a bound state. This bound state was called Cooper pair. Because of that the electron gas is unstable and cannot be the ground state of the system at low temperatures. On the other hand the long range Coulomb interaction can prevent the electrons from forming these pairs since it is a repulsive interaction. In the previous chapter we have argued that the Coulomb interaction is actually screened by the other electrons in the system and can be effectively weak within the many-body system. Thus, if the attraction is strong enough so that it overcomes the screened repulsive Coulomb interaction the electron gas is indeed unstable to the formation of Cooper pairs with a binding energy

$$\Delta \approx 2\hbar\omega_D e^{-\frac{1}{N(\mu)U}} \tag{14.1}$$

where ω_D is the Debye frequency of the phonons, $N(\mu)$ the density of state of the electron gas and U the effective attractive potential (including the Coulomb interaction) between the electrons.

It is clear that the free electron gas being unstable it cannot describe the nature of these new state with Cooper pairs. The Cooper argument tells us that the system is unstable but it does not tell us what is the nature of the actual ground state. However it gives us important clues such as it is made of pairs with total zero momentum. In what follows we are going to consider also the case where the pairs have zero spin projection as well since it is simpler (states with finite spin projection are actually possible). Consider making a state with a pair of electrons with zero momentum in the vacuum:

$$|\Psi_{\mathbf{k}}\rangle = c^\dagger_{\mathbf{k},\sigma} c^\dagger_{-\mathbf{k},-\sigma}|0\rangle \tag{14.2}$$

one would suspect that the actual ground state of the system to be made of superposition of states of the form (14.2). One has to remember, however, that pairing only occur for electron states with momentum close to the Fermi surface. Electron states deep inside of the Fermi sea will not be affected by the attraction because retardation effects are quite weak for such electrons and the Pauli principle "protect" them from the interactions which result in pairing. Thus, the pairs must be formed only close to the Fermi surface and not all the electrons will pair up.

14.1 BCS theory

In what follows we are going to discuss the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity in its simplest form. We have seen that the generic Hamiltonian for electron-electron interaction can be written in the form

$$H_I = \int d\mathbf{r} \int d\mathbf{r}' \sum_{\sigma,\sigma'} U_{\sigma,\sigma'}(\mathbf{r}-\mathbf{r}') \psi^\dagger_\sigma(\mathbf{r}) \psi_\sigma(\mathbf{r}) \psi^\dagger_{\sigma'}(\mathbf{r}') \psi_{\sigma'}(\mathbf{r}') \,. \tag{14.3}$$

Since we will be discussing the pairing mechanism it is convenient to reduce (14.3) to simpler Hamiltonian which contains the essential physics of the problem. Assuming that there is an attractive interaction for electrons with opposite momenta (close to the Fermi surface) and assuming the spins to be opposite we choose

$$U_{\sigma,\sigma'}(\mathbf{r}-\mathbf{r}') = -\frac{U(E)}{2}\delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma,-\sigma'} \tag{14.4}$$

where $U(E)$ is the interaction energy which is only finite for energies close to the Fermi surface ($|E-\mu| < \hbar\omega_D$). In this case (14.3) simplifies to

$$H_I = -\frac{U}{2}\int d\mathbf{r}\sum_{\sigma}\psi^{\dagger}_{\sigma}(\mathbf{r})\psi^{\dagger}_{-\sigma}(\mathbf{r})\psi_{-\sigma}(\mathbf{r})\psi_{\sigma}(\mathbf{r}) \tag{14.5}$$

where we rearranged the operators in a slightly different form. Notice that to (14.5) one has to add the kinetic energy of the electrons as well which turns the whole problem into a very complicated one. Instead, we are going to follow the tips given to us by the Cooper argument and consider the problem in a mean field picture. Since pairs of electrons have a wavefunction of the form (14.2) we factorize the interaction term as

$$\begin{aligned}\psi^{\dagger}_{\sigma}(\mathbf{r})\psi^{\dagger}_{-\sigma}(\mathbf{r})\psi_{-\sigma}(\mathbf{r})\psi_{\sigma}(\mathbf{r}) &\rightarrow \psi^{\dagger}_{\sigma}(\mathbf{r})\psi^{\dagger}_{-\sigma}(\mathbf{r})\langle\psi_{-\sigma}(\mathbf{r})\psi_{\sigma}(\mathbf{r})\rangle \\ &+ \langle\psi^{\dagger}_{\sigma}(\mathbf{r})\psi^{\dagger}_{-\sigma}(\mathbf{r})\rangle\psi_{-\sigma}(\mathbf{r})\psi_{\sigma}(\mathbf{r})\end{aligned}$$

where the average now is supposed to be taken in the actual ground state. Observe that it implies from this decoupling that the function

$$\Delta(\mathbf{r}) = U\langle\psi_{\uparrow}(\mathbf{r})\psi_{\downarrow}(\mathbf{r})\rangle = -U\langle\psi_{\downarrow}(\mathbf{r})\psi_{\uparrow}(\mathbf{r})\rangle \tag{14.6}$$

has to be different of zero in the ground state. Observe that in the free electron gas the function Δ is zero because the total number of particles is fixed in the non-interacting ground state. Thus, Δ is the order parameter of the superconducting state. You must find this strange because at this point we have talked only about states which conserve the number of particles and therefore one would naively expect that $\Delta = 0$ for any state with fixed number of particles. The difficult here lies in the fact that the paired state is actually very different from the unpaired state which is still present in the system (all those electrons deep inside the Fermi sea). The situation here is very similar to the problem of two fluids in thermodynamic equilibrium. In this case the number of particles between the two fluids is fluctuating all the time but their chemical potential is the same. Thus, in order to discuss this situation it is better to consider the problem in the grand-canonical ensemble where the number of particles is not fixed. Notice, however, that even in the grand-canonical ensemble $\Delta = 0$ for the electron gas. Thus, Δ is indeed the order parameter of the problem.

The full Hamiltonian of the problem can be written as

$$\begin{aligned} H &= \int d\mathbf{r} \left\{ \sum_{\sigma} \psi^{\dagger}_{\sigma}(\mathbf{r})(E(-i\hbar\nabla) - \mu)\psi_{\sigma}(\mathbf{r}) + \Delta(\mathbf{r})\psi^{\dagger}_{\uparrow}(\mathbf{r})\psi^{\dagger}_{\downarrow}(\mathbf{r}) \right. \\ &+ \left. \Delta^{*}(\mathbf{r})\psi_{\downarrow}(\mathbf{r})\psi_{\uparrow}(\mathbf{r}) \right\} \end{aligned} \tag{14.7}$$

where $E(-i\hbar\nabla)$ is $E_{\mathbf{k}}$ with $\mathbf{k}$ replaced by $-i\hbar\nabla$. (14.7) is the effective Hamiltonian which describes the physics of pairing. Observe that, as any mean field Hamiltonian, it is quadratic in the electron operators and therefore can be diagonalized by a transformation. It is instructive to define the spinor

$$\Psi(\mathbf{r}) = \begin{pmatrix} \psi_{\uparrow}(\mathbf{r}) \\ \psi^{\dagger}_{\downarrow}(\mathbf{r}) \end{pmatrix} \tag{14.8}$$

and the Hamiltonian matrix

$$[\mathcal{H}(\mathbf{r})] = \begin{bmatrix} E(-i\hbar\nabla) - \mu & \Delta(\mathbf{r}) \\ \Delta^{*}(\mathbf{r}) & -E(-i\hbar\nabla) + \mu \end{bmatrix} \tag{14.9}$$

in which case the Hamiltonian becomes

$$\begin{aligned} H &= \int d\mathbf{r} \left\{ \psi^{\dagger}_{\uparrow}(\mathbf{r})(E(-i\hbar\nabla) - \mu)\psi_{\uparrow}(\mathbf{r}) + \psi^{\dagger}_{\downarrow}(\mathbf{r})(E(-i\hbar\nabla) - \mu)\psi_{\downarrow}(\mathbf{r}) \right. \\ &+ \left. \Delta(\mathbf{r})\psi^{\dagger}_{\uparrow}(\mathbf{r})\psi^{\dagger}_{\downarrow}(\mathbf{r}) + \Delta^{*}(\mathbf{r})\psi_{\downarrow}(\mathbf{r})\psi_{\uparrow}(\mathbf{r}) \right\} \\ &= E_0 + \int d\mathbf{r} \left\{ \psi^{\dagger}_{\uparrow}(\mathbf{r})(E(-i\hbar\nabla) - \mu)\psi_{\uparrow}(\mathbf{r}) - \psi_{\downarrow}(\mathbf{r})(E(-i\hbar\nabla) - \mu)\psi^{\dagger}_{\downarrow}(\mathbf{r}) \right. \\ &+ \left. \Delta(\mathbf{r})\psi^{\dagger}_{\uparrow}(\mathbf{r})\psi^{\dagger}_{\downarrow}(\mathbf{r}) + \Delta^{*}(\mathbf{r})\psi_{\downarrow}(\mathbf{r})\psi_{\uparrow}(\mathbf{r}) \right\} \\ &= E_0 + \int d\mathbf{r}\Psi^{\dagger}(\mathbf{r})[\mathcal{H}(\mathbf{r})]\Psi(\mathbf{r}) \end{aligned} \tag{14.10}$$

where E_0 is a constant. Observe that the definition (14.8) and the Hamiltonian (14.10) has the same form as the Hamiltonian we used to study antiferromagnetic spin waves (12.49) and (12.48) with the difference that we are dealing with fermion operators instead of bosons. As before we look for a transformation U such that

$$\Psi(\mathbf{r}) = \sum_{n} \mathcal{U}_n(\mathbf{r})\Phi_n \tag{14.11}$$

where

$$\Phi_n = \begin{pmatrix} \gamma_{n,\uparrow} \\ \gamma^{\dagger}_{n,\downarrow} \end{pmatrix} \tag{14.12}$$

where $\gamma_{n,\sigma}$ are fermion operators ($\{\gamma_{n,\sigma}, \gamma^{\dagger}_{m,\sigma'}\} = \delta_{n,m}\delta_{\sigma,\sigma'}$). On the other hand one must have

$$\Phi_n = \int d\mathbf{r}\, \mathcal{U}_n^{-1}(\mathbf{r})\Psi(\mathbf{r}) \tag{14.13}$$

which implies the orthogonality relations

$$\begin{aligned} \sum_n \mathcal{U}_n^{-1}(\mathbf{r})\mathcal{U}_n(\mathbf{r}') &= \delta(\mathbf{r}-\mathbf{r}')I\,, \\ \int d\mathbf{r}\, \mathcal{U}_n^{-1}(\mathbf{r})\mathcal{U}_m(\mathbf{r}) &= \delta_{n,m}I \end{aligned} \tag{14.14}$$

where I is the identity matrix. Moreover, due to the anti-commutation relations between the operators it is easy to show that

$$[\mathcal{U}_n(\mathbf{r})] = \begin{bmatrix} u_n(\mathbf{r}) & -v_n^*(\mathbf{r}) \\ v_n(\mathbf{r}) & u_n^*(\mathbf{r}) \end{bmatrix}. \tag{14.15}$$

Moreover, due to (14.14) we can easily show that

$$\int d\mathbf{r}\left(|u_n(\mathbf{r})|^2 + |v_n(\mathbf{r})|^2\right) = 1 \tag{14.16}$$

which is the normalization condition on the coefficients of the matrix $\mathcal{U}$. Furthermore, observe that $\mathcal{U}$ is unitary ($\mathcal{U}^{-1} = \mathcal{U}^{\dagger}$).

The objective of the unitary transformation is to diagonalize the Hamiltonian in (14.10) and reduce it to the form

$$\begin{aligned} H &= \sum_{n,\sigma} \epsilon_n \gamma^{\dagger}_{n,\sigma}\gamma_{n,\sigma} \\ &= E_0 + \sum_n \left[\gamma^{\dagger}_{n,\uparrow}\gamma_{n,\uparrow} - \gamma_{n,\downarrow}\gamma^{\dagger}_{n,\downarrow}\right] \\ &= E_0 + \sum_n \epsilon_n \Phi^{\dagger}_n \sigma_z \Phi_n \end{aligned} \tag{14.17}$$

where ϵ_n are the eigenvalues of the problem, σ_z is the Pauli matrix and E_0 is a constant. Notice that the σ_z matrix appears because of the unusual form of the vector operator (spinor). Substituting (14.11) into (14.10) we find

$$H = \int d\mathbf{r} \sum_{n,m} \Phi_n^\dagger \mathcal{U}_n^{-1}(\mathbf{r})[\mathcal{H}(\mathbf{r})]\mathcal{U}_m(\mathbf{r})\Phi_m\,. \tag{14.18}$$

Comparing the above equation with (14.17) we see that in order to diagonalize the problem we have to require

$$\int d\mathbf{r}\mathcal{U}_n^{-1}(\mathbf{r})[\mathcal{H}(\mathbf{r})]\mathcal{U}_m(\mathbf{r}) = \epsilon_n \delta_{n,m}\sigma_z \tag{14.19}$$

or with the help of the orthogonality relations (14.14)

$$[\mathcal{H}(\mathbf{r})]\mathcal{U}_n(\mathbf{r}) = \epsilon_n \sigma_z \mathcal{U}_n(\mathbf{r})\,. \tag{14.20}$$

Using (14.15) we find

$$\begin{aligned} (E(-i\hbar\nabla) - \mu)\, u_n(\mathbf{r}) + \Delta(\mathbf{r}) v_n(\mathbf{r}) &= \epsilon_n u_n(\mathbf{r}) \\ -\,(E(-i\hbar\nabla) - \mu)\, v_n(\mathbf{r}) + \Delta^*(\mathbf{r}) u_n(\mathbf{r}) &= \epsilon_n v_n(\mathbf{r}) \end{aligned} \tag{14.21}$$

which determines u_n, v_n and ϵ_n. Observe that we have mapped the pairing problem into a problem of free fermions or "quasiparticles" given by Hamiltonian (14.17). From these results we immediately know how the ground state looks like since we just have to fill up all the fermion states up to the chemical potential. Naturally the occupation number of the problem is given by

$$f_n = \langle \gamma_{n,\sigma}^\dagger \gamma_{n,\sigma} \rangle = \frac{1}{e^{\beta\epsilon_n} + 1}\,. \tag{14.22}$$

Observe that averages of the type $\langle \gamma_{n,\sigma}\gamma_{m,\sigma'} \rangle$ vanish in the new representation.

Any operator in the electronic language can now be rewritten in the quasiparticle language. For instance, the number of electrons in the system can be written as

$$\begin{aligned} N &= \int d\mathbf{r} \sum_\sigma \psi_\sigma^\dagger(\mathbf{r})\psi_\sigma(\mathbf{r}) = N_s + \int d\mathbf{r}\Psi^\dagger(\mathbf{r})\sigma_z\Psi(\mathbf{r}) \\ &= N_s + \int d\mathbf{r} \sum_n \Phi_n^\dagger(\mathbf{r})\mathcal{U}_n^\dagger(\mathbf{r})\sigma_z\mathcal{U}_n(\mathbf{r})\Phi_n(\mathbf{r}) \\ &= N_s + \sum_n \int d\mathbf{r} \left\{ \left(|u_n(\mathbf{r})|^2 - |v_n(\mathbf{r})|^2\right) \sum_\sigma \left(\gamma_{n,\sigma}^\dagger\gamma_{n,\sigma} - \frac{1}{2}\right) \right. \\ &- \left. 2u_n(\mathbf{r})v_n(\mathbf{r})\gamma_{n,\downarrow}\gamma_{n,\uparrow} - 2u_n^*(\mathbf{r})v_n^*(\mathbf{r})\gamma_{n,\downarrow}^\dagger\gamma_{n,\uparrow}^\dagger \right\} \end{aligned} \tag{14.23}$$

and therefore, in average,

$$\begin{aligned}
\langle N \rangle &= N_s + 2\sum_n \int d\mathbf{r}\left(|u_n(\mathbf{r})|^2 - |v_n(\mathbf{r})|^2\right)\left(f_n - \frac{1}{2}\right) \\
&= N_s + 2\sum_n \left[\left(f_n - \frac{1}{2}\right) - 2\int d\mathbf{r}|v_n(\mathbf{r})|^2 \left(f_n - \frac{1}{2}\right)\right] \\
&= 2\sum_n f_n + 2\sum_n \int d\mathbf{r}|v_n(\mathbf{r})|^2 \tanh\left(\frac{\beta\epsilon_n}{2}\right) \qquad (14.24)
\end{aligned}$$

where N_s is the number of sites in the system and we have used (14.16).

The problem has not been fully solved yet since the order parameter has not been determined. Notice that the order parameter of the problem has to be obtained self-consistently from its definition (14.6). Substituting the transformation (14.11) into (14.6) and using the results above we find

$$\begin{aligned}
\Delta(\mathbf{r}) &= U\langle \Psi^\dagger(\mathbf{r})\sigma^- \Psi(\mathbf{r})\rangle \\
&= U\sum_n u_n(\mathbf{r})v_n^*(\mathbf{r})(1-2f_n) \\
&= U\sum_n u_n(\mathbf{r})v_n^*(\mathbf{r})\tanh\left(\frac{\beta\epsilon_n}{2}\right) . \qquad (14.25)
\end{aligned}$$

Observe that the full solution of the problem depends on the solution of the coupled equations (14.21) in the presence of the self-consistent condition (14.25). It should be obvious that in most cases this is highly non-linear problem.

14.1.1 The nature of the ground state

At this point one should worry if the mean field theory we are using indeed describes a ground state made out of Cooper pairs as in (14.2). In order to answer this question let us consider what happens at $T = 0$. According to (14.22) the number of "quasiparticles" vanishes at $T = 0$, in order words, the ground state $|G\rangle$ is defined as the state without quasiparticles, that is,

$$\gamma_{n,\sigma}|G\rangle = 0 . \qquad (14.26)$$

Let us consider for simplicity the case with $\sigma =\uparrow$. From the transformation (14.13) we find

$$\gamma_{n,\uparrow} = \int d\mathbf{r} \left(u_n^*(\mathbf{r})\psi_\uparrow(\mathbf{r}) + v_n^*(\mathbf{r})\psi_\downarrow^\dagger(\mathbf{r}) \right) . \tag{14.27}$$

It is convenient to Fourier transform (14.27) to

$$\gamma_{n,\uparrow} = \sum_{\mathbf{k}} \left(u_n^*(\mathbf{k}) a_{\mathbf{k},\uparrow} + v_n^*(\mathbf{k}) a_{-\mathbf{k},\downarrow}^\dagger \right) \tag{14.28}$$

where

$$\begin{aligned} \psi_\sigma(\mathbf{k}) &= \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \; a_{\mathbf{k},\sigma} \\ u_n(\mathbf{k}) &= \frac{1}{\sqrt{V}} \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} u_n(\mathbf{r}) \end{aligned} \tag{14.29}$$

and similarly to $v_n(\mathbf{k})$. Observe that the condition (14.26) implies that

$$\left(u_n^*(\mathbf{k}) a_{\mathbf{k},\uparrow} + v_n^*(\mathbf{k}) a_{-\mathbf{k},\downarrow}^\dagger \right) |G\rangle = 0 \tag{14.30}$$

which is the equation that determines the ground state. We want to construct the ground state starting from the vacuum $|0\rangle$. For that we have to recall that

$$\begin{aligned} a_{\mathbf{k},\sigma}|0\rangle &= 0 \,, \\ a_{\mathbf{k},\sigma}^\dagger a_{\mathbf{k},\sigma}^\dagger |0\rangle &= 0 \,, \\ a_{\mathbf{k},\sigma} a_{\mathbf{k},\sigma}^\dagger |0\rangle &= |0\rangle \,. \end{aligned} \tag{14.31}$$

Observe that the filled Fermi sea which is described by

$$|FS\rangle \propto \prod_{\mathbf{k},\sigma}^{k<k_F} a_{\mathbf{k},\sigma}^\dagger |0\rangle \tag{14.32}$$

is not the the ground state because the condition (14.30) is not fulfilled. As a next tentative let us use (14.2) which we write in a more general form

$$|CP\rangle = \prod_{\mathbf{k}',n} \alpha_{\mathbf{k}',n}^* a_{\mathbf{k}',\uparrow}^\dagger a_{-\mathbf{k}',\downarrow}^\dagger |0\rangle \tag{14.33}$$

where $\alpha^*_{\mathbf{k},n}$ are complex numbers. First observe that

$$\begin{aligned} a_{\mathbf{k},\uparrow}|CP\rangle &= \left[\prod_{\mathbf{k}'\neq\mathbf{k},n} \alpha^*_{\mathbf{k}',n} a^\dagger_{\mathbf{k}',\uparrow} a^\dagger_{-\mathbf{k}',\downarrow}\right] \alpha^*_{\mathbf{k},n} a_{\mathbf{k},\uparrow} a^\dagger_{\mathbf{k},\uparrow} a^\dagger_{-\mathbf{k},\downarrow}|0\rangle \\ &= \left[\prod_{\mathbf{k}'\neq\mathbf{k},n} \alpha^*_{\mathbf{k}',n} a^\dagger_{\mathbf{k}',\uparrow} a^\dagger_{-\mathbf{k}',\downarrow}\right] \alpha^*_{\mathbf{k},n} (1 - a^\dagger_{\mathbf{k},\uparrow} a_{\mathbf{k},\uparrow}) a^\dagger_{-\mathbf{k},\downarrow}|0\rangle \\ &= \left[\prod_{\mathbf{k}'\neq\mathbf{k}} \alpha^*_{\mathbf{k}',n} a^\dagger_{\mathbf{k}',\uparrow} a^\dagger_{-\mathbf{k}',\downarrow}\right] \alpha^*_{\mathbf{k},n} a^\dagger_{-\mathbf{k},\downarrow}|0\rangle \end{aligned} \tag{14.34}$$

where we have used (14.31). Moreover,

$$\begin{aligned} a^\dagger_{-\mathbf{k},\downarrow}|CP\rangle &= \left[\prod_{\mathbf{k}'\neq\mathbf{k},n} \alpha^*_{\mathbf{k}',n} a^\dagger_{\mathbf{k}',\uparrow} a^\dagger_{-\mathbf{k}',\downarrow}\right] \alpha^*_{\mathbf{k},n} a^\dagger_{-\mathbf{k},\downarrow} a^\dagger_{\mathbf{k},\uparrow} a^\dagger_{-\mathbf{k},\downarrow}|0\rangle \\ &= -\left[\prod_{\mathbf{k}'\neq\mathbf{k},n} \alpha^*_{\mathbf{k}',n} a^\dagger_{\mathbf{k}',\uparrow} a^\dagger_{-\mathbf{k}',\downarrow}\right] \alpha^*_{\mathbf{k},n} a^\dagger_{\mathbf{k},\uparrow} a^\dagger_{-\mathbf{k},\downarrow} a^\dagger_{-\mathbf{k},\downarrow}|0\rangle \\ &= 0 \end{aligned} \tag{14.35}$$

where we have used (14.31). The conclusion is that (14.33) is also not the ground state! What have we done wrong? The problem here is that $a^\dagger_{-\mathbf{k},\downarrow}$ annihilates $|CP\rangle$ while it does not annihilate $|0\rangle$ while $a_{\mathbf{k},\uparrow}$ annihilates $|0\rangle$ but does not annihilate $|CP\rangle$. Thus, we try to generalize (14.33) to a more generic form which includes $|0\rangle$

$$|BCS\rangle = \prod_{\mathbf{k}',n} \left(\beta^*_{\mathbf{k}',n} + \alpha^*_{\mathbf{k}',n}\; a^\dagger_{\mathbf{k}',\uparrow} a^\dagger_{-\mathbf{k}',\downarrow}\right)|0\rangle \tag{14.36}$$

which is known as the BCS wave-function. It is very simple to show using (14.34) and (14.35) that

$$\begin{aligned} \left(u^*_n(\mathbf{k}) a_{\mathbf{k},\uparrow} + v^*_n(\mathbf{k}) a^\dagger_{-\mathbf{k},\downarrow}\right)|BCS\rangle = &\left[\prod_{\mathbf{k}'\neq\mathbf{k},m\neq n} \left(\beta^*_{\mathbf{k}',m} + \alpha^*_{\mathbf{k}',m} a^\dagger_{\mathbf{k}',\uparrow} a^\dagger_{-\mathbf{k}',\downarrow}\right)\right] \\ &\times \left(u^*_n(\mathbf{k})\alpha^*_{\mathbf{k},n} - v^*_n(\mathbf{k})\beta^*_{\mathbf{k},n}\right) a^\dagger_{-\mathbf{k},\downarrow}|0\rangle \end{aligned} \tag{14.37}$$

which, in order to obey (14.30), requires that $u^*_n(\mathbf{k})\alpha^*_{\mathbf{k},n} = v^*_n(\mathbf{k})\beta^*_{\mathbf{k},n}$ or $\alpha_{\mathbf{k},n} = Cv_n(\mathbf{k})$ and $\beta_{\mathbf{k},n} = Cu_n(\mathbf{k})$ where C is a constant. Thus, we can rewrite (14.36) as

$$|BCS\rangle = C\prod_{\mathbf{k},n}\left(u_n(\mathbf{k}) + v_n(\mathbf{k})a^{\dagger}_{\mathbf{k},\uparrow}a^{\dagger}_{-\mathbf{k},\downarrow}\right)|0\rangle \tag{14.38}$$

which is the ground state of the problem. The reader can easily show that the normalization condition $\langle BCS|BCS\rangle = 1$ leads to $|C| = 1$.

Observe that (14.38) gives a well defined physical meaning to the coefficients u and v, that is, $|v_n(\mathbf{k})|^2$ is nothing but the probability of a state with a pair of electrons with opposite momenta and spin in a state n to be occupied while $|u_n(\mathbf{k})|^2$ gives the probability of this pair to be unoccupied. Since the number of pairs in the system is half of the number of electrons N we must have

$$\langle N\rangle = 2\sum_{n,\mathbf{k}}|v_n(\mathbf{k})|^2 \tag{14.39}$$

which is identical to (14.24) at $T = 0$. Since we are working with a fixed chemical potential but not a fixed number of particles we can calculate the deviations from the mean value. The reader can show (after some algebra) that at $T = 0$ we must have

$$\begin{aligned}(\delta\langle N\rangle)^2 &= \langle(N - \langle N\rangle)^2\rangle = \langle N^2\rangle - (\langle N\rangle)^2\\ &= 4\sum_{n,\mathbf{k}} u_n^2(\mathbf{k})v_n^2(\mathbf{k})\end{aligned} \tag{14.40}$$

which is zero if the occupancy of the pair states is discontinuous. However, we will see that this is not the case and that δN is finite but $\delta\langle N\rangle/\langle N\rangle$ actually vanishes when $\langle N\rangle \to \infty$ in most cases. If this is true we can actually forget about fluctuations in the number of particles in the system.

Therefore one would suspect that the ground state $|BCS\rangle$ is not an eigenstate of the number operator. Formally speaking the BCS wavefunction does not have a well-defined number of particles. Another way to see how this is so is to reconsider (14.38) by taking the product seriously, that is, it is obvious that (14.38) can be written as

$$|BCS\rangle = \sum_M \sum_{\mathbf{k}_1,\ldots,\mathbf{k}_M} C(\mathbf{k}_1,\mathbf{k}_2,\ldots,\mathbf{k}_M)a^{\dagger}_{\mathbf{k}_1,\uparrow}a^{\dagger}_{-\mathbf{k}_1,\downarrow}\ldots a^{\dagger}_{\mathbf{k}_M,\uparrow}a^{\dagger}_{-\mathbf{k}_M,\downarrow}|0\rangle \tag{14.41}$$

where

$$C(\mathbf{k}_1, \mathbf{k}_2, ..., \mathbf{k}_M) = \prod_{\mathbf{k},n} u_n(\mathbf{k}) \prod_{\mathbf{k}',n} v_n(\mathbf{k}') \tag{14.42}$$

are constants where $\mathbf{k}$ runs over the unoccupied states and $\mathbf{k}'$ over the occupied states. In this expression M is the number of states available for $\mathbf{k}$ (if this is coming from a simple band the number of states is just the number of atoms in the system which is usually larger than the number of electrons). Thus, we have $N/2$ states occupied by pairs and $M - N/2$ states which are unoccupied. If all $u_n(\mathbf{k})$ and $v_n(\mathbf{k})$ are finite there is a finite probability of any N going from 0 to $2M$, that is, the state $|BCS\rangle$ is not an eigenstate of the number operator. This is in complete accordance of our discussion of the result (14.40). Observe therefore that we can rewrite (14.41) in the form

$$|BCS\rangle = \sum_N C_N |N\rangle \tag{14.43}$$

where $|N\rangle$ are states with well defined **even** number N of particles and $N/2$ pairs. Thus, $|C_N|^2$ is the probability of having such a state (and thus, $\sum_N |C_N|^2 = 1$). Observe that $|C_N|^2$ will be largest for $N \approx \langle N \rangle$ which is the average number of electrons in the system but it will have a spread (or variance) of size $\delta\langle N \rangle$ which can be large or small depending on the properties of the superconducting state.

We know from quantum mechanics that when an operator has a large variance then there is always another operator which is conjugated to the first which has a small variance, that is, Heisenberg's uncertainty principle. It is not clear from our discussion what operator it should be. In order to address this problem it is worth take another look at the order parameter $\Delta(\mathbf{r})$ which is defined in (14.6). First of all $\Delta(\mathbf{r})$ is complex which implies that it can always be written as

$$\Delta(\mathbf{r}) = |\Delta(\mathbf{r})| e^{i\varphi(\mathbf{r})} \tag{14.44}$$

where $\varphi(\mathbf{r})$ is the phase of the order parameter and $|\Delta(\mathbf{r})|$ its amplitude. We can physical interpret the phase of the order parameter as the phase of the Cooper pairs in which case we rewrite (14.38) as

$$|\varphi\rangle = \prod_{\mathbf{k},n} \left(|u_n(\mathbf{k})| + |v_n(\mathbf{k})| e^{i\varphi} a^\dagger_{\mathbf{k},\uparrow} a^\dagger_{-\mathbf{k},\downarrow} \right) |0\rangle \tag{14.45}$$

which is a state with well defined phase. Observe that if we try to write (14.45) in the same form of (14.41) one would obtain constants of the form

$$\begin{aligned} C(\mathbf{k}_1, \mathbf{k}_2, ..., \mathbf{k}_M) &= \prod_{\mathbf{k},n} |u_n(\mathbf{k})| \prod_{\mathbf{k}',n} e^{i\varphi} |v_n(\mathbf{k}')| \\ &= e^{i\frac{N}{2}\varphi} \prod_{\mathbf{k},n} |u_n(\mathbf{k})| \prod_{\mathbf{k}',n} |v_n(\mathbf{k}')| \qquad (14.46) \end{aligned}$$

which is equivalent to write (14.43) as

$$|\varphi\rangle = \sum_N e^{i\frac{N}{2}\varphi} |C_N| |N\rangle \qquad (14.47)$$

which gives the state with a well defined phase as a linear combination of states with well defined number. The above expression can be inverted since

$$\int_{-\pi}^{\pi} \frac{d\varphi}{2\pi} e^{-i\frac{N'}{2}\varphi} |\varphi\rangle = \sum_N \delta_{N,N'} |C_N| |N\rangle \qquad (14.48)$$

that is,

$$\begin{aligned} |N\rangle &= \frac{1}{|C_N|} \int_{-\pi}^{\pi} \frac{d\varphi}{2\pi} e^{-i\frac{N}{2}\varphi} |\varphi\rangle \\ &= \frac{1}{|C_N|} \int_{-\pi}^{\pi} \frac{d\varphi}{2\pi} e^{-i\frac{N}{2}\varphi} \prod_{\mathbf{k},n} \left(|u_n(\mathbf{k})| + |v_n(\mathbf{k})| e^{i\varphi} a^\dagger_{\mathbf{k},\uparrow} a^\dagger_{-\mathbf{k},\downarrow} \right) |0\rangle \qquad (14.49) \end{aligned}$$

The physical interpretation of this expression is very simple, by integrating over φ we make its value completely uncertain and because of that the number of particles becomes fixed. Thus, the Heisenberg uncertainty relation is

$$\delta N \delta\varphi > 1\,. \qquad (14.50)$$

What this relation implies is that we can see the superconducting phase as an operator which is canonically conjugated with the number operator, that is,

$$[N, \varphi] = 1 \qquad (14.51)$$

from which we can easily derive (14.50). Observe that the BCS state has well defined phase and ill defined number of particles. This characteristic of the BCS state is very important and will discuss it further.

14.2 The translational invariant problem

Let us first consider the problem of a translational invariant system in which case $\Delta(\mathbf{r}) = \Delta_0$ is independent of the position. The quantum numbers in this case are just the momentum, that is, $n = \mathbf{k}$ and the Hamiltonian (14.17) is simply

$$H = \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} \gamma^{\dagger}_{\mathbf{k},\sigma} \gamma_{\mathbf{k},\sigma} \tag{14.52}$$

where the spectrum can be obtained by (14.21) by observing that the solution can be written in terms of a Fourier transform, that is,

$$\begin{aligned} u_{\mathbf{k}}(\mathbf{r}) &= \frac{1}{\sqrt{V}} u_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \\ v_{\mathbf{k}}(\mathbf{r}) &= \frac{1}{\sqrt{V}} v_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \end{aligned} \tag{14.53}$$

where the coefficients $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are determined by the equations

$$\begin{aligned} (E_{\mathbf{k}} - \mu - \epsilon_{\mathbf{k}}) u_{\mathbf{k}} + \Delta_0 v_{\mathbf{k}} &= 0 \\ \Delta_0^* u_{\mathbf{k}} + (-E_{\mathbf{k}} + \mu - \epsilon_{\mathbf{k}}) v_{\mathbf{k}} &= 0 \end{aligned} \tag{14.54}$$

which a simple matrix equation of the form

$$\begin{bmatrix} E_{\mathbf{k}} - \mu - \epsilon_{\mathbf{k}} & \Delta_0 \\ \Delta_0^* & -E_{\mathbf{k}} + \mu - \epsilon_{\mathbf{k}} \end{bmatrix} \begin{pmatrix} u_{\mathbf{k}} \\ v_{\mathbf{k}} \end{pmatrix} = 0 \,. \tag{14.55}$$

Thus, in order to avoid the trivial solution ($u_{\mathbf{k}} = v_{\mathbf{k}} = 0$) we must impose

$$\epsilon^{\pm}_{\mathbf{k}} = \pm \epsilon_{\mathbf{k}} = \pm \sqrt{(E_{\mathbf{k}} - \mu)^2 + |\Delta_0|^2} \,, \tag{14.56}$$

which gives the dispersion of the excitations in the problem. When $\Delta_0 = 0$ (normal state) we have $\epsilon^{\pm}_{\mathbf{k}} = \pm |E_{\mathbf{k}} - \mu|$ which are shown as the dashed lines in Fig.14.1. Observe that the overturn of the dispersion from the normal $E_{\mathbf{k}} - \mu$ is due to the ordering of the operators in the spinor (14.8) as can be explicit seen on (14.17) (this overturn is related with the appearance of the matrix σ_z). When $\Delta_0 \neq 0$ we observe that

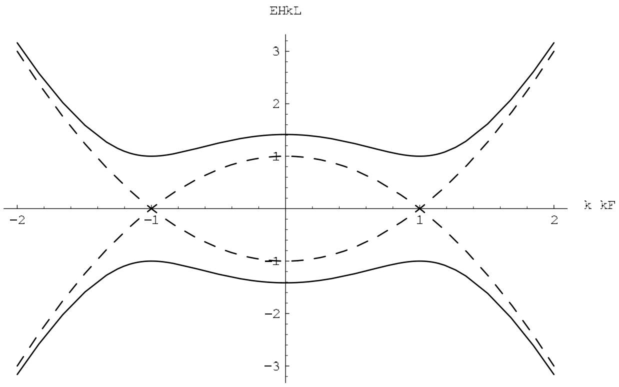

Figure 14.1: *Quasiparticle dispersion in BCS theory: Dashed line - normal state; Continuous line: superconducting state.*

a gap of size $|\Delta_0|$ opens exactly at the Fermi surface of the system as shown in Fig.14.1. Moreover, from (14.54) and the normalization condition $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$ one finds

$$\begin{aligned} u^{\pm}_{\mathbf{k}} &= \cos\theta^{\pm}_{\mathbf{k}} = \sqrt{\frac{1}{2}\left(1 \pm \frac{E_{\mathbf{k}} - \mu}{\epsilon_{\mathbf{k}}}\right)} \\ v^{\pm}_{\mathbf{k}} &= \sin\theta^{\pm}_{\mathbf{k}} = \sqrt{\frac{1}{2}\left(1 \mp \frac{E_{\mathbf{k}} - \mu}{\epsilon_{\mathbf{k}}}\right)}. \end{aligned} \tag{14.57}$$

The superconducting gap is given by (14.25):

$$\begin{aligned} \Delta_0 &= \frac{1}{V}\sum_{\mathbf{k}} U\Delta_0 \frac{\tanh\left(\frac{\beta\epsilon_{\mathbf{k}}}{2}\right)}{\epsilon_{\mathbf{k}}} \\ 1 &= \int \frac{d^d k}{(2\pi)^d} U \frac{\tanh\left(\frac{\beta\sqrt{(E_{\mathbf{k}}-\mu)^2+|\Delta_0|^2}}{2}\right)}{\sqrt{(E_{\mathbf{k}} - \mu)^2 + |\Delta_0|^2}} \end{aligned}$$

$$1 = \int_{-\infty}^{+\infty} dE U(E) N(E) \frac{\tanh\left(\frac{\beta\sqrt{(E-\mu)^2+|\Delta_0|^2}}{2}\right)}{\sqrt{(E-\mu)^2+|\Delta_0|^2}} \tag{14.58}$$

which is the equation that determines $|\Delta_0(T)|$ ($N(E)$ is the density of states of electron gas). Since $U(E)$ is finite only in the shell $|E-\mu| < \hbar\omega_D$, and in this shell the density of states is constant and equals to $N(\mu)$ we rewrite (14.58) (change variables to $\epsilon = E - \mu$) as

$$1 = UN(\mu) \int_0^{\hbar\omega_D} d\epsilon \frac{\tanh\left(\frac{\beta\sqrt{\epsilon^2+|\Delta_0(T)|^2}}{2}\right)}{\sqrt{\epsilon^2+|\Delta_0(T)|^2}} . \tag{14.59}$$

Consider first the case of zero temperature where the equation becomes

$$\begin{aligned} 1 &= UN(\mu) \int_0^{\hbar\omega_D} \frac{d\epsilon}{\sqrt{\epsilon^2+|\Delta_0(0)|^2}} \\ 1 &= UN(\mu) \ln\left(\frac{\hbar\omega_D}{|\Delta_0(0)|} + \sqrt{\left(\frac{\hbar\omega_D}{|\Delta_0(0)|}\right)^2 + 1}\right) \end{aligned} \tag{14.60}$$

which for $|\Delta_0(0)| << \hbar\omega_D$ reduces to

$$|\Delta_0(0)| \approx 2\hbar\omega_D e^{-\frac{1}{UN(\mu)}} \tag{14.61}$$

which is identical to the Cooper solution (14.1). It is also clear from (14.59) that there is a temperature $T = T_c$ above which $|\Delta_0(T)|$ vanishes. This is the critical temperature of the problem. This temperature can be obtained from (14.59) as (using that $|\Delta_0(T_c+\eta)| = 0$ for $\eta \to 0^+$)

$$\begin{aligned} 1 &= UN(\mu) \int_0^{\hbar\omega_D} d\epsilon \frac{\tanh\left(\frac{\beta_c\epsilon}{2}\right)}{\epsilon} \\ 1 &= UN(\mu) \int_0^{\beta_c\hbar\omega_D/2} dx \frac{\tanh x}{x} \\ 1 &= UN(\mu) \left[\tanh\left(\frac{\beta_c\hbar\omega_D}{2}\right) \ln\left(\frac{\beta_c\hbar\omega_D}{2}\right)\right. \\ &- \left.\int_0^{\beta_c\hbar\omega_D/2} dx\ sech^2 x \ln x\right] \end{aligned} \tag{14.62}$$

where the last integral cannot be obtained analytically. Let us assume that $\hbar\omega_D >> k_B T_c$ in which case we find

$$\begin{aligned} 1 &= UN(\mu)\left[\ln\left(\frac{\beta_c \hbar\omega_D}{2}\right) - \int_0^\infty dx\ sech^2 x \ln x\right] \\ 1 &= UN(\mu)\left[\ln\left(\frac{\beta_c \hbar\omega_D}{2}\right) + \ln\left(\frac{4e^\gamma}{\pi}\right)\right] \end{aligned} \tag{14.63}$$

where $\gamma \approx 0.5772$ is the Euler's constant. From the equation above we immediately derive

$$k_B T_c \approx \frac{2e^\gamma \hbar\omega_D}{\pi} e^{-\frac{1}{UN(\mu)}} . \tag{14.64}$$

Observe that $k_B T_c$ and $|\Delta_0(0)|$ are not the same. Indeed,

$$\frac{|\Delta_0(0)|}{k_B T_c} = \pi e^{-\gamma} \approx 1.76 \tag{14.65}$$

which is a universal number independent of the material properties. The whole function $|\Delta_0(T)|$ can be obtained from (14.59) and one can easily show that for $T << T_c$ we have

$$|\Delta_0(T)| \approx |\Delta_0(0)| - \sqrt{2\pi|\Delta_0(0)|k_B T} e^{-\beta|\Delta_0(0)|} \tag{14.66}$$

and for $|T - T_c| << T_c$

$$|\Delta_0(T)| \approx k_B T_c \sqrt{\frac{8\pi^2}{7\zeta(3)}} \left(1 - \frac{T}{T_c}\right)^{1/2} \tag{14.67}$$

which shows that as in any good phase transition the order parameter vanishes at $T = T_c$ with an exponent of $1/2$.

In face of the discussions in the last subsection of this chapter it is interesting to consider the problem of the number of electrons in the system. From (14.24) and (14.53) we have (at $T = 0$)

$$\langle N \rangle = \frac{2}{V} \sum_{\mathbf{k}} |v_{\mathbf{k}}|^2 . \tag{14.68}$$

Before going into the calculation of this quantity we observe that it has a deep meaning. The average number of particles in the electron representation can be written as

$$\langle N \rangle = \frac{1}{V} \sum_{\mathbf{k},\sigma} \langle a^\dagger_{\mathbf{k},\sigma} a_{\mathbf{k},\sigma} \rangle \,. \tag{14.69}$$

Since, in average, the number of electrons in the superconducting state is the same as in the normal state we must have

$$\langle a^\dagger_{\mathbf{k},\sigma} a_{\mathbf{k},\sigma} \rangle = |v_{\mathbf{k}}|^2 = \frac{1}{2}\left(1 - \frac{E_{\mathbf{k}} - \mu}{\sqrt{(E_{\mathbf{k}} - \mu)^2 + |\Delta_0|^2}}\right) \tag{14.70}$$

which can actually be obtained directly from the unitary transformation (14.11). In order to check that this is indeed the distribution function for the electrons in the normal state let us take $\Delta_0 \to 0$ in (14.70) and find

$$\langle a^\dagger_{\mathbf{k},\sigma} a_{\mathbf{k},\sigma} \rangle = \frac{1}{2}\left(1 - sgn(E_{\mathbf{k}} - \mu)\right) = \Theta(\mu - E_{\mathbf{k}}) \tag{14.71}$$

which has a discontinuity at the Fermi surface ($E_{\mathbf{k}_F} = \mu$ and it is the Fermi-Dirac distribution at $T = 0$. Observe, however, that for any finite Δ_0 the distribution function is continuous across the Fermi surface, indeed, at the Fermi surface

$$\langle a^\dagger_{\mathbf{k}_F,\sigma} a_{\mathbf{k}_F,\sigma} \rangle = \frac{1}{2} \,. \tag{14.72}$$

This shows that because of the opening of the superconducting gap there is a redistribution of the electrons in momentum space. The width of this redistribution can be obtained directly from (14.70). Assume that $E_k = \hbar^2 k^2/(2m)$ observe that the spread of the distribution is of order $E_k - \mu \approx \Delta_0$, that is $k^2 - k_F^2 = (k - k_F)(k + k_F) \approx (2m\Delta_0)/\hbar^2$ since we have $k \approx k_F$ we find

$$\delta k = k - k_F \approx \frac{m\Delta_0}{\hbar^2 k_F} = \frac{\Delta_0}{\hbar v_F} \tag{14.73}$$

where $v_F = \hbar k_F/m$ is the Fermi velocity. Associated with δk we have a characteristic length scale through the uncertainty relation $\delta k \delta x \approx 1$.

Thus, the superconducting problem has a characteristic length scale which is

$$\xi_0 \propto \frac{\hbar v_F}{\Delta_0} \tag{14.74}$$

which is called the superconducting correlation length. Observe that $\xi_0 \sim \lambda_F(E_F/\Delta_0)$ where λ_F is the Fermi wavelength. Thus, $\xi_0 \gg \lambda_F$ since $E_F \gg \Delta_0$. At this point there is no direct physical interpretation for ξ_0. In order to understand its physical meaning consider a Cooper pair of electrons which are situated at positions $\mathbf{r}$ and $\mathbf{r}'$. These pair of electrons is described by the order parameter (14.6). Instead of (14.6) consider the more general correlator

$$\begin{aligned}
\langle\psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r}')\rangle &= \sum_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r})v^*_{\mathbf{k}}(\mathbf{r}') \\
&= \frac{\Delta_0}{V}\sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}}{\sqrt{(E_{\mathbf{k}}-\mu)^2+\Delta_0^2}}
\end{aligned} \tag{14.75}$$

where we have used (14.53). Transforming the sum into an integral it is easy to show that

$$\begin{aligned}
\langle\psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r}')\rangle &= \Delta_0 \int \frac{d\mathbf{k}}{(2\pi)^3}\int \frac{d\omega}{\pi}\frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}}{\omega^2+(E_{\mathbf{k}}-\mu)^2+\Delta_0^2} \\
&= \frac{m\Delta_0}{\pi^3\hbar^2 R}\int_{-\infty}^{+\infty} d\omega \int_0^\infty \frac{k\sin(kR)}{(k^2-k_F^2)^2+\left(\frac{2m}{\hbar^2}\right)^2(\omega^2+\Delta_0^2)} \\
&= \frac{m\Delta_0}{2\pi^3\hbar^2 R}\left(-\frac{\partial}{\partial R}\right)\int_{-\infty}^{+\infty} d\omega \int_{-\infty}^\infty \frac{\cos(kR)}{(k^2-k_F^2)^2+\left(\frac{2m}{\hbar^2}\right)^2(\omega^2+\Delta_0^2)} \\
&= \frac{m\Delta_0}{2\pi^3\hbar^2 R}\left(-\frac{\partial}{\partial R}\right)\int_{-\infty}^{+\infty} d\omega \int_{-\infty}^\infty \frac{e^{ikR}}{(k^2-k_F^2)^2+\left(\frac{2m}{\hbar^2}\right)^2(\omega^2+\Delta_0^2)} \\
&= \frac{m\Delta_0}{2k_F^3\pi^3\hbar^2 R}\left(-\frac{\partial}{\partial R}\right)\int_{-\infty}^{+\infty} d\omega \int_{-\infty}^\infty \frac{e^{ik_F Rx}}{(x^2-1)^2+\frac{(\omega^2+\Delta_0^2)}{E_F^2}}
\end{aligned} \tag{14.76}$$

where $R = |\mathbf{r}-\mathbf{r}'|$. Observe that the integral in x has poles at $x = \pm z_0$ and $x = \pm z_0^*$ where $z_0 = \sqrt{1+i\sqrt{\omega^2+\Delta_0^2}/E_F}$. Since E_F is a large energy scale and the behavior of the integral is dominated by the small ω part we can rewrite

$$z_0 \approx 1 + i\left(\frac{\Delta_0}{2E_F} + \frac{\omega^2}{4E_F\Delta_0}\right) \tag{14.77}$$

in which case the integral simplifies tremendously and it is easy to show that for $R >> \xi_0$

$$\langle\psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r}')\rangle \sim \Delta_0 \left(\frac{\xi_0}{R}\right)^{3/2} e^{-R/\xi_0} \tag{14.78}$$

which shows that the pair wavefunction extends over a region of size ξ_0. Since the Fermi wavelength is small compared to the correlation length there are many electrons in which a Cooper exists. The number of electrons in this region is simply $N \propto (\xi_0/\lambda_F)^3 \sim 10(E_F/\Delta_0)^3$. Since in ordinary superconductors the gap energy is order of $1-5$K and the Fermi energies are of order of 10^4K we see that there are in average 10^{13} electrons in the region of a Cooper pair! This is related to the fact that the BCS theory the pairing occurs in momentum space and it is rather delocalized.

Let us now proceed with the actual calculation of the average number of electrons in the system. We first use the definition of the density of states $N(E)$ and write

$$\frac{\langle N\rangle}{V} = \int_{-\infty}^{+\infty} dE N(E)\frac{1}{2}\left(1 - \frac{E-\mu}{\sqrt{(E-\mu)^2 + |\Delta_0|^2}}\right). \tag{14.79}$$

For simplicity we are going to use a flat density of states

$$N(E) = \frac{N_s/V}{W}\theta(W - |E|) \tag{14.80}$$

where N_s is the number of unit cells in the system and $2W$ is the electron bandwidth (observe that the density of states is normalized so that $\int_{-\infty}^{+\infty} dE N(E) = 2N_s/V$ is the total number of states). Substituting (14.80) into (14.79) we find

$$\langle N\rangle = \frac{N_s}{2W}\int_{-W}^{W} dE \left(1 - \frac{E-\mu}{\sqrt{(E-\mu)^2 + |\Delta_0|^2}}\right)$$

$$
\begin{aligned}
&= N_s\left(1-\frac{1}{2W}\int_{-W-\mu}^{W-\mu} d\epsilon \frac{\epsilon}{\sqrt{\epsilon^2+|\Delta_0|^2}}\right) \\
&= N_s\left[1-\left(\frac{\sqrt{(W-\mu)^2+|\Delta_0|^2}-\sqrt{(W+\mu)^2+|\Delta_0|^2}}{2W}\right)\right] \qquad (14.81)
\end{aligned}
$$

which is shown in Fig.14.2. Observe that in the normal state ($\Delta_0 = 0$) we find

$$
\begin{aligned}
\langle N\rangle &= N_s\left[1-\left(\frac{|W-\mu|-|W+\mu|}{2W}\right)\right] \\
&= N_s\left(1+\frac{\mu}{W}\right) \qquad (14.82)
\end{aligned}
$$

for $\mu < W$. Observe that this is indeed the expect result since at $\mu = -W$ the band is empty ($\langle N\rangle = 0$) and at $\mu = W$ the band is completely full ($\langle N\rangle = 2N_s$). In the superconducting state (since it does not conserve the number of particles) there is occupation even when $|\mu| > W$.

Let us now consider the problem of the fluctuation in the number of particles in the superconducting state. From (14.40) we have

$$
\begin{aligned}
(\delta\langle N\rangle)^2 &= \sum_{\mathbf{k}}\left(1-\frac{(E_{\mathbf{k}}-\mu)^2}{(E_{\mathbf{k}}-\mu)^2+|\Delta_0|^2}\right) \\
&= V\int_{-\infty}^{+\infty} dEN(E)\frac{|\Delta_0|^2}{(E-\mu)^2+|\Delta_0|^2} \\
&= \frac{N_s|\Delta_0|^2}{2W}\int_{-W-\mu}^{W-\mu} d\epsilon\frac{d\epsilon}{\epsilon^2+|\Delta_0|^2} \\
&= \frac{N_s|\Delta_0|}{2W}\left[\arctan\left(\frac{W-\mu}{|\Delta_0|}\right)+\arctan\left(\frac{W+\mu}{|\Delta_0|}\right)\right] \qquad (14.83)
\end{aligned}
$$

which is shown on Fig.14.3. Observe that for $\Delta_0 = 0$ we obtain $\delta\langle N\rangle = 0$ showing that there are no fluctuations in the number of particles in the normal state. In the superconducting state, however, the fluctuations are centered around $\mu = 0$ (half-filled band) where the variance in the number of particles is maximum. Indeed, at $\mu = 0$ we find,

$$
(\delta\langle N\rangle)^2 = \frac{N_s|\Delta_0|}{W}\arctan\left(\frac{W}{|\Delta_0|}\right) \qquad (14.84)
$$

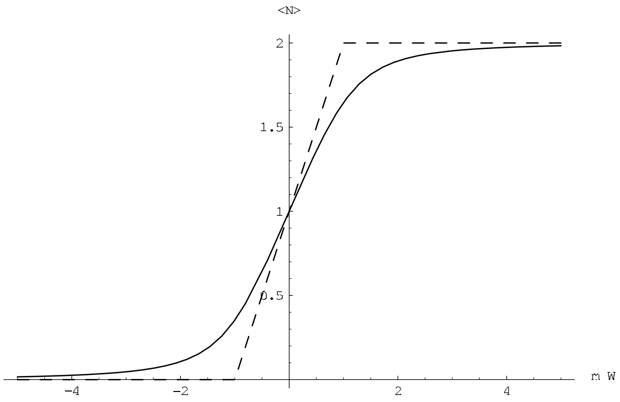

Figure 14.2: *Average number of electrons: Dashed line is the normal state ($\Delta_0 = 0$) the continuous line is the superconducting state.*

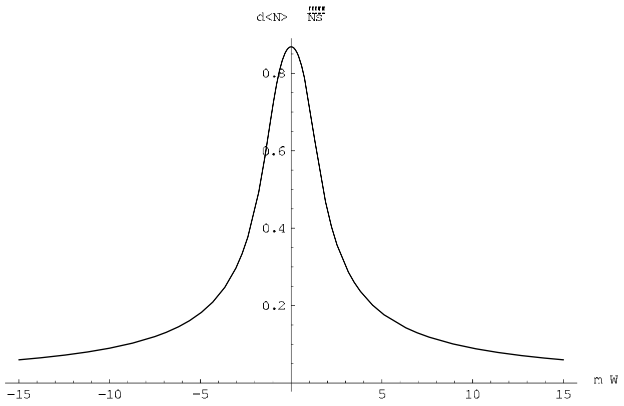

Figure 14.3: *Variance of the number of particles in the superconducting state.*

while, from (14.81), we have $\langle N \rangle = N_s$ and therefore

$$\frac{\delta \langle N \rangle}{\langle N \rangle} = \sqrt{\frac{|\Delta_0|}{N_s W} \arctan\left(\frac{W}{|\Delta_0|}\right)} \tag{14.85}$$

which is shown on Fig.14.4. Observe that the variance scales like $1/\sqrt{N_s}$ and therefore vanishes in the thermodynamic limit.

14.2.1 Thermodynamics

We would like to discuss other properties of the superconducting transition such as the specific heat. For that we need the Free energy of the system. Instead of using the usual route let us first prove a theorem due to Feynman and Hellman. Consider a system described by a Hamiltonian

$$H(\lambda) = H_0 + \lambda H_1 \tag{14.86}$$

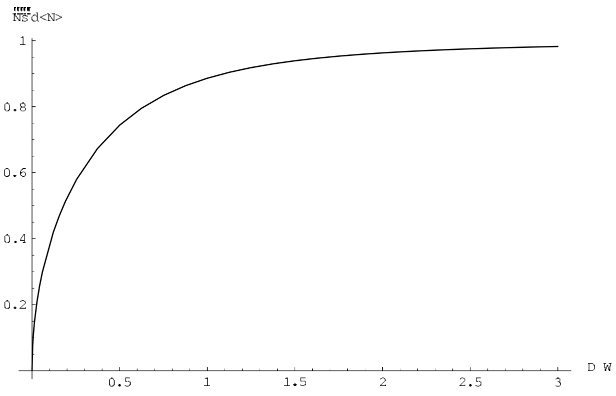

Figure 14.4: *Relative variance in the number of particles in the superconducting state at* $\mu = 0$*.*

where λ is a parameter we put by hand. The problem we want to solve has actually $\lambda = 1$. The partition function of the problem can be written as

$$\begin{aligned} Z(\lambda) &= e^{-\beta F(\lambda)} = tr\left(e^{-\beta H(\lambda)}\right) \\ &= \sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} tr\left(H_0 + \lambda H_1\right)^n . \end{aligned} \tag{14.87}$$

Observe the interesting property of this expression as we take its derivative

$$\begin{aligned} \frac{\partial Z(\lambda)}{\partial \lambda} &= \sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!} n tr\left[\left(H_0 + \lambda H_1\right)^{n-1} H_1\right] \\ &= -\beta \sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} tr\left[\left(H_0 + \lambda H_1\right)^n H_1\right] \\ &= -\beta tr\left[e^{-\beta H(\lambda)} H_1\right] \\ &= -\frac{\beta Z(\lambda)}{\lambda} \langle \lambda H_1 \rangle . \end{aligned} \tag{14.88}$$

On the other hand, from (14.86), we have

$$\frac{\partial F(\lambda)}{\partial \lambda} = -\frac{1}{\beta Z(\lambda)} \frac{\partial Z(\lambda)}{\partial \lambda} . \tag{14.89}$$

From (14.88) and (14.89) we find

$$\frac{\partial F(\lambda)}{\partial \lambda} = \frac{1}{\lambda} \langle \lambda H_1 \rangle \tag{14.90}$$

which can be integrated

$$F = F_0 + \int_0^1 d\lambda \frac{1}{\lambda} \langle \lambda H_1 \rangle \tag{14.91}$$

where $F = F(\lambda = 1)$ is the total free energy, $F_0 = F(\lambda = 0)$ is the free energy associated with the Hamiltonian H_0. Thus (14.91) allows to write the change in the free energy of the system due to a new term in the Hamiltonian.

Let us apply (14.91) to the superconducting problem where H_1 is given by (14.5) with $\lambda = U$. Thus, from (14.91), we would have

$$\begin{aligned} F &= F_0 - \int_0^U \frac{du}{u} \int d\mathbf{r} \frac{u}{2V} \sum_\sigma \langle \psi^\dagger_\sigma(\mathbf{r}) \psi^\dagger_{-\sigma}(\mathbf{r}) \psi_{-\sigma}(\mathbf{r}) \psi_\sigma(\mathbf{r}) \rangle \\ &= F_0 - \int_0^U \frac{du}{u^2} \int d\mathbf{r} |\Delta(\mathbf{r}, u)|^2 \end{aligned} \tag{14.92}$$

where F_0 is the electron gas free energy and we have used the mean field decoupling. Observe that the dependence of the gap on the coupling constant u is given by the equation (14.25).

In what follows we will consider the homogeneous problem. In this case the dependence of the gap on the coupling constant u is given in (14.59). Notice however that we can look at (14.59) as an equation for $\Delta(\mathbf{r}, u)$ as a function of $1/u$. Thus it is convenient to change variables in the above equation as $\delta(u) = |\Delta(T, u)|$ in order to get

$$\begin{aligned} \frac{F - F_0}{V} &= \int_0^{|\Delta_0(T,U)|} d\delta \delta^2 \frac{du^{-1}}{d\delta} \\ &= N(\mu) \int_0^{|\Delta_0(T,U)|} d\delta \delta^2 \frac{d}{d\delta} \left[\int_0^{\hbar\omega_D} d\epsilon \frac{\tanh\left(\frac{\beta\sqrt{\epsilon^2 + |\Delta_0(T,U)|^2}}{2}\right)}{\sqrt{\epsilon^2 + |\Delta_0(T,U)|^2}} \right] . \end{aligned}$$

Evaluating the integral by parts we find

$$\begin{aligned} \frac{F - F_0}{V} &= N(\mu) \int_0^{\hbar\omega_D} d\epsilon \left[\frac{|\Delta_0(T,U)|^2}{\sqrt{\epsilon^2 + |\Delta_0(T,U)|^2}} \tanh\left(\frac{\beta\sqrt{\epsilon^2 + |\Delta_0(T,U)|^2}}{2} \right) \right. \\ &- \left. 2 \int_0^{\hbar\omega_D} d\epsilon \int_0^{|\Delta_0(T,U)|} d\delta \frac{\delta}{\sqrt{\epsilon^2 + \delta^2}} \tanh\left(\frac{\beta\sqrt{\epsilon^2 + \delta^2}}{2} \right) \right] . \end{aligned}$$

Observe that the first integral is nothing but the one that appears in the gap equation (14.59) and that the second integral can be easily evaluated with a change of variables $x = \sqrt{\epsilon^2 + \delta^2}$:

$$\frac{F - F_0}{V} = \frac{|\Delta_0(T)|^2}{U} - \frac{4N(\mu)}{\beta} \int_0^{\hbar\omega_D} d\epsilon \ln \left[\frac{\cosh\left(\frac{\beta\sqrt{\epsilon^2 + |\Delta_0(T)|^2}}{2} \right)}{\cosh\left(\frac{\beta\epsilon}{2}\right)} \right] .$$

This equation can also be written as

$$
\begin{aligned}
\frac{F-F_0}{V} &= \frac{|\Delta_0(T)|^2}{U} + \frac{4N(\mu)}{\beta}\int_0^{\hbar\omega_D} d\epsilon \ln\left(1+e^{-\beta\epsilon}\right) \\
-\frac{4N(\mu)}{\beta}\int_0^{\hbar\omega_D} d\epsilon & \left[\ln\left(1+e^{-\beta\sqrt{\epsilon^2+|\Delta_0(T)|^2}}\right) + \frac{\beta(\sqrt{\epsilon^2+|\Delta_0(T)|^2}-\epsilon)}{2}\right]
\end{aligned}
\tag{14.93}
$$

Let us now consider the limit of $T << T_c << \hbar\omega_D/k_B$. In this case, each integral in (14.93) approximate with great accuracy. Indeed the first integral is simply

$$
\int_0^{\hbar\omega_D} d\epsilon \ln\left(1+e^{-\beta\epsilon}\right) \approx \int_0^{\infty} d\epsilon \ln\left(1+e^{-\beta\epsilon}\right) = \frac{\pi^2}{12\beta}.
$$

Moreover,

$$
\begin{aligned}
\int_0^{\hbar\omega_D} d\epsilon\sqrt{\epsilon^2+|\Delta_0(T)|^2} &= \frac{|\Delta_0(T)|^2}{2}\left[\frac{\hbar\omega_D}{|\Delta_0(T)|}\sqrt{\left(\frac{\hbar\omega_D}{|\Delta_0(T)|}\right)^2+1}\right. \\
&+ \left.\ln\left(\frac{\hbar\omega_D}{|\Delta_0(T)|}+\sqrt{\left(\frac{\hbar\omega_D}{|\Delta_0(T)|}\right)^2+1}\right)\right] \\
&\approx \frac{(\hbar\omega_D)^2}{2} + \frac{|\Delta_0(T)|^2}{4} + \frac{|\Delta_0(T)|^2}{2}\ln\left(\frac{2\hbar\omega_D}{|\Delta_0(T)|}\right) \\
&= \frac{(\hbar\omega_D)^2}{2} + \frac{|\Delta_0(T)|^2}{4} + \frac{|\Delta_0(T)|^2}{2N(\mu)U} \\
&+ \frac{|\Delta_0(T)|^2}{2}\ln\left(\frac{|\Delta_0(T=0)|}{|\Delta_0(T)|}\right)
\end{aligned}
\tag{14.94}
$$

where we used (14.1). Furthermore,

$$
\begin{aligned}
\int_0^{\hbar\omega_D} d\epsilon \ln\left(1+e^{-\beta\sqrt{\epsilon^2+|\Delta_0(T)|^2}}\right) &\approx \int_0^{\infty} d\epsilon \ln\left(1+e^{-\beta\sqrt{\epsilon^2+|\Delta_0(T=0)|^2}}\right) \\
&\approx \int_0^{\infty} d\epsilon e^{-\beta\sqrt{\epsilon^2+|\Delta_0|^2}} \\
&\approx e^{-\beta|\Delta_0|}\int_0^{\infty} d\epsilon e^{-\frac{\beta}{2|\Delta_0|}\epsilon} \\
&= \sqrt{\frac{\pi|\Delta_0|}{2\beta}}e^{-\beta|\Delta_0|}
\end{aligned}
$$

Putting all the results together we find

$$\begin{aligned}\frac{\delta F(T)}{V} &\approx -\frac{1}{2}N(\mu)|\Delta_0(T)|^2 - N(\mu)|\Delta_0(T)|^2 \ln\left(\frac{|\Delta_0|}{|\Delta_0(T)|}\right) + \frac{\pi^2}{3\beta^2}N(\mu) \\ &- 2N(\mu)\sqrt{\frac{2\pi|\Delta_0|}{\beta^3}}e^{-\beta|\Delta_0(0)|} \end{aligned} \tag{14.95}$$

which is the change in the free energy. Observe that for the electron gas in the normal state is simply

$$\frac{F_N(T)}{V} \approx E_0 - \frac{\pi^2}{3\beta^2}N(\mu) \tag{14.96}$$

where E_0 is the ground state energy. Thus, the free energy of the superconducting state is

$$\frac{F_S(T)}{V} \approx E_0 - \frac{1}{2}N(\mu)|\Delta_0|^2 - 2N(\mu)\sqrt{\frac{2\pi|\Delta_0|}{\beta^3}}e^{-\beta|\Delta_0|}. \tag{14.97}$$

Observe that there is a major change in the free energy of the system as it goes from the normal state to the superconducting state. This is can be readily seen if we calculate the specific heat. In the normal state we have the well-known result

$$\frac{C_{V,N}}{V} = \frac{2\pi^2}{3}N(\mu)k_B^2T \tag{14.98}$$

while the superconducting specific heat is

$$\frac{C_{V,S}}{V} \approx 2N(\mu)|\Delta_0|k_B\sqrt{\frac{2\pi|\Delta_0(0)|^3}{(k_BT)^3}}e^{-\beta|\Delta_0|} \tag{14.99}$$

which vanishes exponentially at $T \to 0$.

14.2.2 Electromagnetic response

Let us consider the electromagnetic response of a superconductor at zero temperature. The starting point, as always, is the Hamiltonian of the problem which in absence of the electromagnetic field is given by H_{BCS} in (14.7). In the presence of an electromagnetic field the momentum of the electrons is shifted by $\mathbf{p} \to \mathbf{p} - e\mathbf{A}/c$ where $\mathbf{A}(\mathbf{r})$ is the vector potential. Thus, in the first quantized language the kinetic energy is modified as

$$\frac{\mathbf{p}^2}{2m} \to \frac{\mathbf{p}^2}{2m} - \frac{e}{2mc}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2}{2mc^2}\mathbf{A}^2 . \qquad (14.100)$$

At this point it is interesting to consider the problem of gauge invariance in a superconductor. As you know well the vector potential is defined up to a gradient, that is, we can replace $\mathbf{A}$ by $\mathbf{A} + \nabla\chi$ where χ is an arbitrary function, without changing the electromagnetic fields. Since the momentum operator has the same structure of the gradient operator we know that this change in the vector potential can be completely absorbed into the definition of the electron operator

$$\psi_\sigma(\mathbf{r}) \to \psi_\sigma(\mathbf{r}) e^{\frac{ie}{\hbar c}\chi(\mathbf{r})} \qquad (14.101)$$

Indeed, this transformation does not affect the anti-commutation rules, the form of the kinetic energy or the electron-electron interactions described by (14.3). Thus, as expect in general ground the original Hamiltonian is *invariant* under the gauge transformation. Observe, however, that our mean field Hamiltonian (14.7) **is not** gauge invariant, indeed the order parameter defined in (14.6) transforms according to

$$\Delta(\mathbf{r}) = U\langle\psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r})\rangle \to \Delta(\mathbf{r}) e^{\frac{2ie}{\hbar c}\chi(\mathbf{r})} \qquad (14.102)$$

and therefore is not gauge invariant! Furthermore, in the equations (14.21) we see that the gauge transformation lead to

$$\begin{aligned} u_n(\mathbf{r}) &\to u_n(\mathbf{r}) e^{\frac{ie}{\hbar c}\chi(\mathbf{r})} \\ v_n(\mathbf{r}) &\to v_n(\mathbf{r}) e^{\frac{ie}{\hbar c}\chi(\mathbf{r})} \end{aligned} \qquad (14.103)$$

while the energies ϵ_n are still gauge invariant. Actually, if we use the representation (14.44) we observe that under the gauge transformation we have

$$\Delta(\mathbf{r}) \to |\Delta(\mathbf{r})| e^{i\left(\varphi(\mathbf{r}) + \frac{2e}{\hbar c}\chi(\mathbf{r})\right)} . \qquad (14.104)$$

Observe that under the gauge transformation the phase of the superconducting order parameter changes like

$$\varphi(\mathbf{r}) \to \varphi(\mathbf{r}) + \frac{2e}{\hbar c}\chi(\mathbf{r}) \tag{14.105}$$

and therefore we can define a gauge invariant vector

$$\mathbf{g}(\mathbf{r}) = \nabla\varphi(\mathbf{r}) - \frac{2e}{\hbar c}\mathbf{A}(\mathbf{r})\,. \tag{14.106}$$

Notice that because of gauge invariance we are free to choose any gauge we wish. For instance we could impose that

$$\chi(\mathbf{r}) = -\frac{\hbar c}{2e}\varphi(\mathbf{r}) \tag{14.107}$$

which actually is a way to *fix the gauge*. This is not a unique choice, as usual. The particular choice given above is the so-called London gauge. The bottom line here is that in a superconductor the gauge symmetry is *broken*. As we are going to see this leads to amazing consequences to the electromagnetic properties of superconductors.

14.2.3 Linear response

In what follows we are going to consider the linear response of the system, that is, we are going to think the electromagnetic field as a weak perturbation and consider the changes in the system to first order in $\mathbf{A}$. In second quantized language the Hamiltonian will have the form

$$\begin{aligned} H &= H_{BCS} + H_F \\ H_F &= \frac{ei\hbar}{2mc}\int d\mathbf{r}\sum_{\sigma}\psi^{\dagger}_{\sigma}(\mathbf{r})\left(\mathbf{A}(\mathbf{r})\cdot\nabla + \nabla\cdot\mathbf{A}(\mathbf{r})\right)\psi_{\sigma}(\mathbf{r}) \end{aligned} \tag{14.108}$$

We are not really interested in solving the full problem (14.108) but we would like to know the solution of th problem to first order in $\mathbf{A}$. To zeroth order the problem is given by the equations (14.21). To first order one expects that

$$\begin{aligned} u_n(\mathbf{r}) &\approx u_n^{(0)}(\mathbf{r}) + u_n^{(1)}(\mathbf{r}) \\ v_n(\mathbf{r}) &\approx v_n^{(0)}(\mathbf{r}) + v_n^{(1)}(\mathbf{r}) \\ \Delta(\mathbf{r}) &\approx \Delta^{(0)}(\mathbf{r}) + \Delta^{(1)}(\mathbf{r}) \end{aligned} \tag{14.109}$$

where the upper script (0) refers to the unperturbed state and (1) to the leading order correction. In particular we can write

$$\Delta^{(1)}(\mathbf{r}) = \int d\mathbf{r}'\mathbf{G}(\mathbf{r},\mathbf{r}')\cdot\mathbf{A}(\mathbf{r}') \tag{14.110}$$

where $\mathbf{G}(\mathbf{r},\mathbf{r}')$ is the kernel which depends only on the properties of the unperturbed system. In an isotropic, homogeneous system, this kernel depends only on the relative distance $\mathbf{R} = \mathbf{r} - \mathbf{r}'$. Our first reaction would be to simply substitute the above equations in (14.21) and calculate. We can be smarter, however, and use the fact that we have not fixed the gauge yet. Indeed, from (14.102) we have to first order in χ,

$$\Delta^{(1)}(\mathbf{r}) = \frac{2ie}{\hbar c}\Delta^{(0)}(\mathbf{r})\chi(\mathbf{r}) \tag{14.111}$$

on the other hand $\Delta^{(0)}(\mathbf{r})$ is determined in the absence of fields. In this case $\mathbf{A}(\mathbf{r}) = \nabla\chi(\mathbf{r})$ is the so-called pure gauge. Thus, from the above equations we find

$$\int d\mathbf{r}'\mathbf{G}(\mathbf{r}-\mathbf{r}')\cdot\nabla\chi(\mathbf{r}') = \frac{2ie}{\hbar c}\Delta^{(0)}(\mathbf{r})\chi(\mathbf{r}) \tag{14.112}$$

which can be understood as the equation that fixes the gauge. Integrating the above equation by parts assuming that $\chi(\mathbf{r})$ vanishes at large distances we find

$$\frac{2ie}{\hbar c}\Delta^{(0)}(\mathbf{r})\chi(\mathbf{r}) = -\int d\mathbf{r}'\chi(\mathbf{r}')\nabla\cdot\mathbf{G}(\mathbf{r}-\mathbf{r}') \tag{14.113}$$

which requires that

$$\nabla\cdot\mathbf{G}(\mathbf{r}-\mathbf{r}') = -\frac{2ie}{\hbar c}\Delta^{(0)}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \tag{14.114}$$

From now on we are going to assume a translationally invariant solution for the unperturbed system $\Delta^{(0)}(\mathbf{r}) = \Delta^{(0)}$ in which case the above equation can be solved at once

$$\begin{aligned} \mathbf{G}(\mathbf{r}-\mathbf{r}') &= \frac{2ie}{\hbar c}\Delta^{(0)}\nabla\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right) \\ &= -\frac{2ie}{\hbar c}\Delta^{(0)}\frac{(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} \end{aligned} \tag{14.115}$$

since $\nabla^2(1/|\mathbf{r}-\mathbf{r}'|) = \delta(\mathbf{r}-\mathbf{r}')$ in three dimensions. Going back to (14.110) we have

$$\begin{aligned}
\Delta^{(1)}(\mathbf{r}) &= \frac{2ie}{\hbar c}\Delta^{(0)}\int d\mathbf{r}'\nabla\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right)\cdot\mathbf{A}(\mathbf{r}') \\
&= -\frac{2ie}{\hbar c}\Delta^{(0)}\left[\int d\mathbf{r}'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\nabla\cdot\mathbf{A}(\mathbf{r}')\right. \\
&- \left.\int d\mathbf{S}'\frac{\mathbf{A}(\mathbf{r}')\cdot\mathbf{n}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right] \qquad (14.116)
\end{aligned}$$

where $\mathbf{S}'$ is the area of the sample and $\mathbf{n}(\mathbf{r}')$ the unit vector normal to it. In the Coulomb gauge and assuming $\mathbf{A}$ parallel to the surface, that is,

$$\begin{aligned}
\nabla\cdot\mathbf{A}(\mathbf{r}) &= 0 \\
\mathbf{A}(\mathbf{r}')\cdot\mathbf{n}(\mathbf{r}') &= 0 \qquad (14.117)
\end{aligned}$$

we find that $\Delta^{(1)}(\mathbf{r}) = 0$. Thus, this choice of gauge simplifies the calculations a lot since we do not have to calculate the change in the order parameter due to the electromagnetic field.

Substituting (14.109) and (14.108) into (14.21) we find that up to first order we must have

$$\begin{aligned}
(\epsilon_n - E(\nabla) - \mu)\,u_n^{(1)}(\mathbf{r}) - \Delta_0 v_n^{(1)}(\mathbf{r}) &= \frac{ei\hbar}{mc}\mathbf{A}(\mathbf{r})\cdot\nabla u_n^{(0)}(\mathbf{r}) \\
(\epsilon_n + E(\nabla) + \mu)\,v_n^{(1)}(\mathbf{r}) - \Delta_0 u_n^{(1)}(\mathbf{r}) &= \frac{ei\hbar}{mc}\mathbf{A}(\mathbf{r})\cdot\nabla v_n^{(0)}(\mathbf{r}) \qquad (14.118)
\end{aligned}$$

where $u_n^{(0)}(\mathbf{r})$ and $v_n^{(0)}(\mathbf{r})$ are given in (14.53). In this case (14.118) becomes

$$\begin{aligned}
(\epsilon_{\mathbf{k}} - E(\nabla) - \mu)\,u_{\mathbf{k}}^{(1)}(\mathbf{r}) - \Delta_0 v_{\mathbf{k}}^{(1)}(\mathbf{r}) &= -\frac{e\hbar}{mc}\mathbf{A}(\mathbf{r})\cdot\mathbf{k}u_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}} \\
(\epsilon_{\mathbf{k}} + E(\nabla) + \mu)\,v_{\mathbf{k}}^{(1)}(\mathbf{r}) - \Delta_0 u_{\mathbf{k}}^{(1)}(\mathbf{r}) &= -\frac{e\hbar}{mc}\mathbf{A}(\mathbf{r})\cdot\mathbf{k}v_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}} \qquad (14.119)
\end{aligned}$$

This set of equations is linear and can be solved if we expand $u_{\mathbf{k}}^{(1)}(\mathbf{r})$ and $v_{\mathbf{k}}^{(1)}(\mathbf{r})$ in a Fourier series

$$u_{\mathbf{k}}^{(1)}(\mathbf{r}) = \sum_{\mathbf{k}'} a_{\mathbf{k},\mathbf{k}'}e^{i\mathbf{k}'\cdot\mathbf{r}}$$

$$v^{(1)}_{\mathbf{k}}(\mathbf{r}) \;=\; \sum_{\mathbf{k}'} b_{\mathbf{k},\mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{r}} \qquad (14.120)$$

so that (14.119) becomes

$$\begin{aligned}
\left(\epsilon_{\mathbf{k}} - \xi_{\mathbf{k}'}\right) a_{\mathbf{k},\mathbf{k}'} - \Delta_0 b_{\mathbf{k},\mathbf{k}'} &= -\frac{e\hbar}{mc}\mathbf{A}_{\mathbf{k}'-\mathbf{k}}\cdot\mathbf{k}u_{\mathbf{k}} \\
\left(\epsilon_{\mathbf{k}} + \xi_{\mathbf{k}'}\right) b_{\mathbf{k},\mathbf{k}'} - \Delta_0 a_{\mathbf{k},\mathbf{k}'} &= -\frac{e\hbar}{mc}\mathbf{A}_{\mathbf{k}'-\mathbf{k}}\cdot\mathbf{k}v_{\mathbf{k}} \qquad (14.121)
\end{aligned}$$

where $\mathbf{A}_{\mathbf{k}}$ is the Fourier transform of the vector potential and we have defined

$$\xi_{\mathbf{k}} = E_{\mathbf{k}} - \mu\,. \qquad (14.122)$$

The equations above can be easily solve to find

$$\begin{aligned}
a_{\mathbf{k},\mathbf{k}'} &= -\frac{e\hbar}{mc}\mathbf{A}_{\mathbf{k}'-\mathbf{k}}\cdot\mathbf{k}\frac{\left[\left(\epsilon_{\mathbf{k}} + \xi_{\mathbf{k}'}\right) u_{\mathbf{k}} + \Delta_0 v_{\mathbf{k}}\right]}{\xi^2_{\mathbf{k}} - \xi^2_{\mathbf{k}'}} \\
b_{\mathbf{k},\mathbf{k}'} &= -\frac{e\hbar}{mc}\mathbf{A}_{\mathbf{k}'-\mathbf{k}}\cdot\mathbf{k}\frac{\left[\left(\epsilon_{\mathbf{k}} - \xi_{\mathbf{k}'}\right) v_{\mathbf{k}} + \Delta_0 u_{\mathbf{k}}\right]}{\xi^2_{\mathbf{k}} - \xi^2_{\mathbf{k}'}}\,. \qquad (14.123)
\end{aligned}$$

When an electromagnetic field is applied to the system it will induce a current. The current density operator is given by

$$\begin{aligned}
\mathbf{J}(\mathbf{r}) &= -\frac{e\hbar}{2mi}\sum_{\sigma}\left[\psi^\dagger(\mathbf{r})_\sigma \nabla\psi_\sigma(\mathbf{r}) - \left(\nabla\psi^\dagger(\mathbf{r})_\sigma\right)\psi_\sigma(\mathbf{r})\right] \\
&- \frac{e^2}{mc}\sum_{\sigma}\psi^\dagger(\mathbf{r})_\sigma \mathbf{A}(\mathbf{r})\psi_\sigma(\mathbf{r}) \qquad (14.124)
\end{aligned}$$

where the last term is obtained by the substitution of $-i\hbar\nabla$ by $-i\hbar\nabla - e\mathbf{A}/c$ in the usual way. The electron operators can be replaced by the quasiparticle as in (14.11)

$$\begin{aligned}
\psi_\uparrow(\mathbf{r}) &= \sum_{\mathbf{k}}\left(u_{\mathbf{k}}(\mathbf{r})\gamma_{\mathbf{k},\uparrow} - v^*_{\mathbf{k}}(\mathbf{r})\gamma^\dagger_{\mathbf{k},\downarrow}\right) \\
\psi^\dagger_\uparrow(\mathbf{r}) &= \sum_{\mathbf{k}}\left(u^*_{\mathbf{k}}(\mathbf{r})\gamma^\dagger_{\mathbf{k},\uparrow} - v_{\mathbf{k}}(\mathbf{r})\gamma_{\mathbf{k},\downarrow}\right) \\
\psi_\downarrow(\mathbf{r}) &= \sum_{\mathbf{k}}\left(v^*_{\mathbf{k}}(\mathbf{r})\gamma^\dagger_{\mathbf{k},\uparrow} + u_{\mathbf{k}}(\mathbf{r})\gamma_{\mathbf{k},\downarrow}\right) \\
\psi_\uparrow(\mathbf{r}) &= \sum_{\mathbf{k}}\left(v_{\mathbf{k}}(\mathbf{r})\gamma_{\mathbf{k},\uparrow} + u^*_{\mathbf{k}}(\mathbf{r})\gamma^\dagger_{\mathbf{k},\downarrow}\right)\,. \qquad (14.125)
\end{aligned}$$

Although the substitution of the above transformation into the expression for the current density leads to many terms we are going to simplify the calculation by taking the zero temperature limit. In this limit all the average values of quadratic forms of the γ operators vanish except $\langle\gamma_{\mathbf{k},\sigma}\gamma^\dagger_{\mathbf{k}',\sigma'}\rangle = \delta_{\sigma,\sigma'}\delta_{\mathbf{k},\mathbf{k}'}$. It is convenient to separate the current into two components a diamagnetic and a paramagnetic part. The diamagnetic part is given by

$$\begin{aligned}\langle\mathbf{J}_D(\mathbf{r})\rangle &= -\frac{e^2}{mc}\sum_\sigma\langle\psi^\dagger(\mathbf{r})_\sigma\mathbf{A}(\mathbf{r})\psi_\sigma(\mathbf{r})\rangle \\ &= -\frac{e^2}{mc}\mathbf{A}(\mathbf{r})\frac{2}{V}\sum_{\mathbf{k}}|v_{\mathbf{k}}|^2 \\ &= -\frac{e^2\langle N\rangle}{mcV}\mathbf{A}(\mathbf{r}) \qquad (14.126)\end{aligned}$$

we have used (14.39). The paramagnetic current is slightly more complicated and it is defined as

$$\begin{aligned}\langle\mathbf{J}_P(\mathbf{r})\rangle &= -\frac{e\hbar}{2mi}\sum_\sigma\langle\left[\psi^\dagger(\mathbf{r})_\sigma\nabla\psi_\sigma(\mathbf{r}) - \left(\nabla\psi^\dagger(\mathbf{r})_\sigma\right)\psi_\sigma(\mathbf{r})\right]\rangle \\ &= -\frac{e\hbar}{mi}\sum_{\mathbf{k}}\left(v_{\mathbf{k}}(\mathbf{r})\nabla v^*_{\mathbf{k}}(\mathbf{r}) - v^*_{\mathbf{k}}(\mathbf{r})\nabla v_{\mathbf{k}}(\mathbf{r})\right) . \qquad (14.127)\end{aligned}$$

In accord to (14.109) we have

$$\begin{aligned}\langle\mathbf{J}_P(\mathbf{r})\rangle &\approx -\frac{e\hbar}{mi}\sum_{\mathbf{k}}\Big(v^{(0)}_{\mathbf{k}}(\mathbf{r})\nabla v^{(1)^*}_{\mathbf{k}}(\mathbf{r}) + v^{(1)}_{\mathbf{k}}(\mathbf{r})\nabla v^{(0)^*}_{\mathbf{k}}(\mathbf{r}) \\ &- v^{(0)^*}_{\mathbf{k}}(\mathbf{r})\nabla v^{(1)}_{\mathbf{k}}(\mathbf{r}) - v^{(1)^*}_{\mathbf{k}}(\mathbf{r})\nabla v^{(0)}_{\mathbf{k}}(\mathbf{r})\Big) \qquad (14.128)\end{aligned}$$

which is correct to first order in the vector potential $\mathbf{A}$ (notice that the zeroth order term vanishes since there is no net current in the absence of an electromagnetic field). Using (14.53), (14.120) and (14.123) we find

$$\langle\mathbf{J}_P(\mathbf{r})\rangle \approx \frac{e\hbar}{m}\sum_{\mathbf{k},\mathbf{k}'} v_{\mathbf{k}}\left(b_{\mathbf{k},\mathbf{k}'} - b^*_{-\mathbf{k},-\mathbf{k}'}\right)(\mathbf{k}+\mathbf{k}')\,e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} . \qquad (14.129)$$

From (14.123) we easily find $b^*_{-\mathbf{k},-\mathbf{k}'} = -b_{\mathbf{k},\mathbf{k}'}$ and using (14.53) we get

$$\langle \mathbf{J}_P(\mathbf{r})\rangle \approx -\frac{1}{c}\left(\frac{e\hbar}{m}\right)^2 \sum_{\mathbf{k},\mathbf{k}'} (\mathbf{k}+\mathbf{k}')\,\mathbf{k}\cdot\mathbf{A}_{\mathbf{k}'-\mathbf{k}} \frac{[(\epsilon_{\mathbf{k}}-\xi_{\mathbf{k}'})(\epsilon_{\mathbf{k}}-\xi_{\mathbf{k}})+\Delta_0^2]}{\epsilon_{\mathbf{k}}\left(\xi_{\mathbf{k}}^2-\xi_{\mathbf{k}'}^2\right)} e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \tag{14.130}$$

Observe that the Fourier transform of the paramagnetic current

$$\langle \mathbf{J}_P(\mathbf{q})\rangle \approx -\frac{1}{c}\left(\frac{e\hbar}{m}\right)^2 \sum_{\mathbf{k}} (2\mathbf{k}+\mathbf{q})\,\mathbf{k}\cdot\mathbf{A}_{\mathbf{q}} \frac{[(\epsilon_{\mathbf{k}}-\xi_{\mathbf{k}+\mathbf{q}})(\epsilon_{\mathbf{k}}-\xi_{\mathbf{k}})+\Delta_0^2]}{\epsilon_{\mathbf{k}}\left(\xi_{\mathbf{k}}^2-\xi_{\mathbf{k}+\mathbf{q}}^2\right)} \tag{14.131}$$

where we have used the Coulomb gauge $\mathbf{q}\cdot\mathbf{A}_{\mathbf{q}} = 0$. Changing the sum over $\mathbf{k}$ in (14.131) to $\mathbf{k}-\mathbf{q}/2$ we get

$$\langle \mathbf{J}_P(\mathbf{q})\rangle \approx -\frac{2}{c}\left(\frac{e\hbar}{m}\right)^2 \sum_{\mathbf{k}} \mathbf{k}(\mathbf{k}\cdot\mathbf{A}_{\mathbf{q}}) \frac{\left[(\epsilon_{\mathbf{k}-\mathbf{q}/2}-\xi_{\mathbf{k}+\mathbf{q}/2})(\epsilon_{\mathbf{k}-\mathbf{q}/2}-\xi_{\mathbf{k}-\mathbf{q}/2})+\Delta_0^2\right]}{\epsilon_{\mathbf{k}-\mathbf{q}/2}\left(\xi_{\mathbf{k}-\mathbf{q}/2}^2-\xi_{\mathbf{k}+\mathbf{q}/2}^2\right)} \tag{14.132}$$

while changing the sum in (14.131) to $-\mathbf{k}-\mathbf{q}/2$ we find

$$\langle \mathbf{J}_P(\mathbf{q})\rangle \approx \frac{2}{c}\left(\frac{e\hbar}{m}\right)^2 \sum_{\mathbf{k}} \mathbf{k}(\mathbf{k}\cdot\mathbf{A}_{\mathbf{q}}) \frac{\left[(\epsilon_{\mathbf{k}+\mathbf{q}/2}-\xi_{\mathbf{k}-\mathbf{q}/2})(\epsilon_{\mathbf{k}+\mathbf{q}/2}-\xi_{\mathbf{k}+\mathbf{q}/2})+\Delta_0^2\right]}{\epsilon_{\mathbf{k}+\mathbf{q}/2}\left(\xi_{\mathbf{k}+\mathbf{q}/2}^2-\xi_{\mathbf{k}-\mathbf{q}/2}^2\right)} \tag{14.133}$$

where we have used that $\epsilon_{\mathbf{k}} = \epsilon_{-\mathbf{k}}$ and $\xi_{\mathbf{k}} = \xi_{-\mathbf{k}}$. Adding (14.132) and (14.133) and using that $\xi_{\mathbf{k}+\mathbf{q}/2}^2 - \xi_{\mathbf{k}-\mathbf{q}/2}^2 = \epsilon_{\mathbf{k}+\mathbf{q}/2}^2 - \epsilon_{\mathbf{k}-\mathbf{q}/2}^2$ we finally get

$$\langle \mathbf{J}_P(\mathbf{q})\rangle \approx \frac{1}{c}\left(\frac{e\hbar}{m}\right)^2 \sum_{\mathbf{k}} \mathbf{k}(\mathbf{k}\cdot\mathbf{A}_{\mathbf{q}}) \frac{\left(\Delta_0^2+\xi_{\mathbf{k}+\mathbf{q}/2}\xi_{\mathbf{k}-\mathbf{q}/2}-\epsilon_{\mathbf{k}+\mathbf{q}/2}\epsilon_{\mathbf{k}-\mathbf{q}/2}\right)}{\epsilon_{\mathbf{k}+\mathbf{q}/2}\epsilon_{\mathbf{k}-\mathbf{q}/2}\left(\epsilon_{\mathbf{k}+\mathbf{q}/2}+\epsilon_{\mathbf{k}-\mathbf{q}/2}\right)} \tag{14.134}$$

which is the final expression for the paramagnetic current. Putting together (14.126) and (14.134) we find

$$\langle J_\mu(\mathbf{q})\rangle \approx \sum_\nu S_{\mu,\nu}(\mathbf{q}) A_{\nu,\mathbf{q}} \tag{14.135}$$

where $\mu,\nu = x,y,z$ and

$$\begin{aligned} S_{\mu,\nu}(\mathbf{q}) &= \frac{1}{c}\left(\frac{e\hbar}{m}\right)^2 \sum_{\mathbf{k}} k_\mu k_\nu \frac{\left(\Delta_0^2+\xi_{\mathbf{k}+\mathbf{q}/2}\xi_{\mathbf{k}-\mathbf{q}/2}-\epsilon_{\mathbf{k}+\mathbf{q}/2}\epsilon_{\mathbf{k}-\mathbf{q}/2}\right)}{\epsilon_{\mathbf{k}+\mathbf{q}/2}\epsilon_{\mathbf{k}-\mathbf{q}/2}\left(\epsilon_{\mathbf{k}+\mathbf{q}/2}+\epsilon_{\mathbf{k}-\mathbf{q}/2}\right)} \\ &- \frac{e^2\langle N\rangle}{mcV}\delta_{\mu,\nu}\,. \end{aligned} \tag{14.136}$$

Observe that in real space (14.135) becomes

$$\langle J_\mu(\mathbf{r})\rangle \approx \int d\mathbf{r}' \sum_\nu S_{\mu,\nu}(\mathbf{r}-\mathbf{r}')A_{\nu,\mathbf{r}'} \tag{14.137}$$

which represents the response of the system, that is, the production of a current, in the presence of an external electromagnetic field. In particular, for a homogeneous magnetic field we take the limit of $q \to 0$ in (14.136) in which case

$$S_{\mu,\nu}(\mathbf{q}\to 0) = -\frac{e^2\langle N\rangle}{mcV}\delta_{\mu,\nu} \tag{14.138}$$

since the contribution from the paramagnetic current vanishes in this limit. This result shows that in a superconductor the response of the system is purely diamagnetic. This is to be contrasted with the normal metal which has both paramagnetic and diamagnetic response. In this limit we can rewrite (14.137) as

$$\langle \mathbf{J}(\mathbf{r})\rangle = -\frac{e^2\rho}{mc}\mathbf{A}(\mathbf{r}) \tag{14.139}$$

which is the so-called London equation ($\rho = \langle N\rangle/V$). In the BCS theory at $T = 0$ the electron density is just the density of superconducting electrons ρ_s while the current is the super-current, $\mathbf{J}_s$ so that (14.139) can be rewritten

$$\langle \mathbf{J}_s(\mathbf{r})\rangle = -\frac{e^2\rho_s}{mc}\mathbf{A}(\mathbf{r})\,. \tag{14.140}$$

The above expression was calculated in the in the Coulomb gauge $\nabla\cdot\mathbf{A} = 0$.

In order to understand the implications of equation (14.139) consider the static Maxwell equations for the magnetic field

$$\begin{aligned} \nabla\times\mathbf{H} &= \frac{4\pi}{c}\mathbf{J} \\ \nabla\cdot\mathbf{H} &= 0 \end{aligned} \tag{14.141}$$

where $\mathbf{H} = \nabla\times\mathbf{A}$. Using (14.139) we find

$$\nabla\times\mathbf{H} = -\frac{4\pi e^2\rho_s}{mc^2}\mathbf{A}$$

$$\begin{aligned}\nabla \times \nabla \times \mathbf{H} &= -\frac{4\pi e^2 \rho_s}{mc^2}\mathbf{H} \\ \nabla^2 \mathbf{H} &= \frac{\mathbf{H}}{\lambda^2}\end{aligned} \tag{14.142}$$

where we have used the second equation in (14.141) and defined

$$\lambda = \sqrt{\frac{mc^2}{4\pi e^2 \rho_s}} \tag{14.143}$$

which is called the penetration length of the superconductor. To understand the physical meaning of this length consider a semi-infinite superconductor located at $x > 0$ in a applied field H_0 in the y direction. Outside the superconductor (that is, at $x < 0$) the field is simply H_0 but for $x > 0$ we have to solve (14.142). Because the symmetry of the problem we have

$$\frac{d^2 H}{dx^2} = \frac{H}{\lambda^2} \tag{14.144}$$

which has a solution $H(x) = Ae^{-x/\lambda} + Be^{x/\lambda}$. The solution with a increasing exponential is unphysical can should be discarded and therefore with the boundary condition $H(x = 0) = H_0$ we see that $H(x) = H_0 e^{-x/\lambda}$. Thus, the magnetic field only penetrates the superconductor a distance λ and this is the reason it is called the penetration length. In a metal the magnetic field penetrates completely the system but a superconductor is a perfect diamagnet. This amazing effect is called the Meissner effect.

Consider now another simple problem of a superconductor slab of width d subject to a magnetic field. Again we have to use (14.144) with the boundary conditions $H(x = \pm d/2) = H_0$. The solution of this problem is simply

$$H(x) = H_0 \frac{\cosh\left(\frac{x}{\lambda}\right)}{\cosh\left(\frac{d}{2\lambda}\right)} . \tag{14.145}$$

Notice that the induction field in the superconductor is

$$B = \int_{-d/2}^{d/2} \frac{dx}{d} H(x) = H_0 \frac{2\lambda}{d} \tanh\left(\frac{d}{2\lambda}\right) \tag{14.146}$$

while the magnetization M of the system is defined in electromagnetism as

$$B = H_0 + 4\pi M\,. \tag{14.147}$$

Therefore, for $d \gg \lambda$,

$$\begin{aligned} B &\approx 0 \\ M &\approx -\frac{H_0}{4\pi} \end{aligned} \tag{14.148}$$

which is perfect diamagnetism. In the opposite limit, that is $d \ll \lambda$, we have

$$\begin{aligned} B &\approx H_0\left(1 - \frac{d^2}{12\lambda^2}\right) \\ M &\approx -\frac{d^2}{12\lambda^2}\frac{H_0}{4\pi}\,. \end{aligned} \tag{14.149}$$

When a magnetic field is applied to a superconductor its energy is raised by

$$\frac{\delta E(H)}{V} = -\int_0^H dH'M(H') \tag{14.150}$$

If this energy is larger than the gain in energy δF for the system become a superconductor then the superconductor has to have a transition to the normal state. The magnetic field at which this happens is called the critical field H_c. In the bulk superconductor ($d \gg \lambda$) the change in energy is given by (14.148) and (14.150)

$$\frac{\delta E(H_c)}{V} = \frac{H_c^2}{8\pi} \tag{14.151}$$

This change in energy can now be compared with the change in the free energy at low temperatures given in (14.95)

$$\begin{aligned} -\frac{\delta F}{V} &= \frac{\delta E}{V} \\ \frac{N(\mu)\Delta_0^2}{2} - \frac{\pi^2 N(0)(k_BT)^2}{3} &= \frac{H_c^2}{8\pi} \end{aligned} \tag{14.152}$$

which leads to

$$H_c(T) = H_c(0)\left[1 - \frac{e^{2\gamma}}{3}\left(\frac{T}{T_c}\right)^2\right] \tag{14.153}$$

where $H_c(0) = \sqrt{4\pi N(\mu)\Delta_0^2}$ and we have used (14.65). Equation (14.153) shows that the critical field decreases with increasing temperature. The reason for that is that the superconducting gap decreases with increasing temperature and therefore the magnetic energy required to suppress the superconducting state becomes smaller. As the temperature increases we must have $H_c(T_c) = 0$, naturally.

Another interesting consequence of the existence of a critical magnetic field in a superconductor is that there is also a critical current I_c above which superconductivity vanishes. Consider, for instance, a cylindrical superconductor of radius R carrying a current I. The current produces a magnetic field which is given by

$$H = \frac{2I}{cR} \tag{14.154}$$

and therefore when $H > H_c$ superconductivity disappears. The critical current can be obtained from (14.153

$$I_c(T) = \frac{Rc}{2}H_c(T) \tag{14.155}$$

and therefore a critical current density

$$J_c = \frac{I_c}{2\pi R\lambda} = \frac{c}{4\pi}\frac{H_c}{\lambda}\,. \tag{14.156}$$

14.2.4 Flux quantization

The electromagnetic properties of superconductors lead to the most amazing effects. Consider for instance a superconducting ring which is much thicker than the penetration depth λ. Suppose a magnetic field is applied to the center of the ring (using a solenoid, for instance). Accordingly to our results the magnetic field only penetrates the ring in a region of size λ. Inside the superconducting ring the magnetic field vanishes and therefore $\nabla \times \mathbf{A} = 0$ in this region. This implies that $\mathbf{A} \propto \nabla\chi(\mathbf{r})$ in that region where χ is an arbitrary function. This arbitrariness is lost by gauge fixing. Let us consider the London gauge discussed in the context of equation (14.107). As we showed before we can write down a gauge invariant vector $\mathbf{g}(\mathbf{r})$ which is defined in (14.106). Inside the ring we have $\mathbf{g}(\mathbf{r}) = 0$ everywhere since $\mathbf{A}(\mathbf{r}) \sim \nabla\varphi(\mathbf{r})$ where φ is the phase of the superconducting order parameter, that is, $\Delta(\mathbf{r}) = |\Delta(\mathbf{r})|e^{i\varphi(\mathbf{r})}$. Consider now the line integral of this quantity around a loop inside of the superconductor

$$\int_C d\mathbf{l} \cdot \left(\nabla\varphi(\mathbf{r}) - \frac{2e}{\hbar c}\mathbf{A}(\mathbf{r})\right) = 0 \tag{14.157}$$

which is an identity. On the one hand, we observe that by Stokes theorem

$$\begin{aligned} \int_C d\mathbf{l} \cdot \mathbf{A}(\mathbf{r}) &= \int d\mathbf{S} \cdot \nabla \times \mathbf{A} \\ &= \int d\mathbf{S} \cdot \mathbf{H} = \phi \end{aligned} \tag{14.158}$$

is the total magnetic flux through the ring. On the other hand,

$$\int_C d\mathbf{l} \cdot \nabla\varphi(\mathbf{r}) = \delta\varphi \tag{14.159}$$

is the total change of the superconducting phase around the ring. Since the superconducting order parameter is a physical quantity and therefore single valued we must have $\delta\varphi = 2\pi n$ where n is an integer. Substituting these two conditions on (14.157) we find

$$\begin{aligned} \phi &= n\Phi_0 \\ \Phi_0 &= \frac{ch}{2e} \end{aligned} \tag{14.160}$$

that is, the magnetic flux through a superconducting ring has to be quantized in units of ϕ_0 which is called the flux quantum. Observe that this flux quantum is different from the flux quantum we obtained in Chapter 4 in studying the Bohm-Aharonov effect where we showed that, due to gauge invariance, for a close electronic orbit orbit the amount of flux enclosed by the orbit is $2\Phi_0$! The reason for this difference is that the Cooper pairs have charge $2e$ instead of e.

14.3 Ginzburg-Landau approach

Consider a homogeneous superconductor where the superconducting order parameter is the same everywhere, that is, $\Delta(\mathbf{r}) = \Delta$. Using the methods given in this chapter we can determine $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ and without enforcing self-consistency like in (14.30) we could calculate the free energy as a function of Δ as in subsection (1.2.1). Assuming that T is close to T_c, that is, that Δ is small we can write the free energy as a power series expansion in Δ:

$$\frac{\delta F}{V} = A(T)|\Delta|^2 + \frac{B(T)}{2}|\Delta|^4 + h.o.t. \tag{14.161}$$

where $A(T)$ are coefficients which depend only on the temperature. Observe that the Free energy as a function of temperature looks like the free energy for the Ising magnet we studied in Chapter 9 (take a look on Fig.11.4). In particular, when $T > T_c$ we have $A > 0$ and for $T < T_c$ we have $A < 0$. Moreover, because the free energy is bounded when $|\Delta| \to \infty$ we must have $B > 0$ for all T. Observe that A must be an odd function of $T - T_c$ and for $T - T_c << T_c$ we can make a series expansion

$$A(T) = a\frac{T - T_c}{T_c} \tag{14.162}$$

where $a > 0$ is a constant. Moreover, we assume B to be temperature independent. In order to obtain the lowest energy state one has to minimize (14.161) with respect to Δ and we find that either $|\Delta| = 0$ (which describes the normal state or

$$|\Delta_0|^2 = -\frac{A}{B} = \frac{a}{B}\frac{T_c - T}{T_c} \tag{14.163}$$

which predicts that the order parameter vanishes with exponent 1/2 at $T = T_c$ as in the BCS theory (see (14.67). Observe that in the case of (14.163) we find

$$\frac{\delta F}{V} = -\frac{A^2}{2B} = -\frac{a^2}{2B}\left(\frac{T - T_c}{T_c}\right)^2 . \tag{14.164}$$

Since (14.164) is the required energy for a magnetic field to make superconductivity disappear at $T < T_c$, that is, $\delta F/V = -H_c^2/(8\pi)$ we immediately get

$$H_c(T) = 2a\sqrt{\frac{\pi}{B}}\frac{T_c - T}{T_c} \tag{14.165}$$

which predicts that the critical magnetic field vanishes linearly with temperature at $T = T_c$.

Let us now consider the case where we allow the order parameter to vary in space. Assuming that this variation is very slow we can make a gradient expansion of the free energy. Because the problem has symmetry of inversion the free energy cannot contain terms which are first derivatives of the order parameter. The fist allowed term has the form $|\nabla\Delta|^2$. Thus, the free energy has the form

$$\begin{aligned}\delta F &= \int d\mathbf{r}A(T)|\Delta(\mathbf{r})|^2 + \frac{B}{2}|\Delta(\mathbf{r})|^4 + C\left(\left|\frac{\partial\Delta(\mathbf{r})}{\partial x}\right|^2 + \left|\frac{\partial\Delta(\mathbf{r})}{\partial y}\right|^2 + \left|\frac{\partial\Delta(\mathbf{r})}{\partial z}\right|^2\right) \\ &= A(T)|\Delta(\mathbf{r})|^2 + \frac{B}{2}|\Delta(\mathbf{r})|^4 + C\,|\nabla\Delta(\mathbf{r})|^2 \qquad (14.166)\end{aligned}$$

where $C > 0$ is a constant. Moreover, gauge invariance requires that the free energy is invariant under $\mathbf{A} \to \mathbf{A} + \nabla\chi$. Since the order parameter changes from $\Delta(\mathbf{r})$ to $\Delta(\mathbf{r})e^{2ie\chi/(\hbar c)}$ we find that in the presence of an electromagnetic field we must have

$$\begin{aligned}\delta F &= \int d\mathbf{r}A(T)|\Delta(\mathbf{r})|^2 + \frac{B}{2}|\Delta(\mathbf{r})|^4 + C\left|\left(-i\nabla - \frac{e^*\mathbf{A}(\mathbf{r})}{\hbar c}\right)\Delta(\mathbf{r})\right|^2 \\ &+ \frac{H^2(\mathbf{r})}{8\pi} \qquad (14.167)\end{aligned}$$

where $H(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ is the magnetic field and the last term represents the electromagnetic energy in the system and $e^* = 2e$ is the charge of the Cooper pairs. The traditional way to represent (14.167) is to define

$$\Psi(\mathbf{r}) = \sqrt{\frac{2m^*C}{\hbar^2}}\Delta(\mathbf{r})$$

$$\begin{aligned}\alpha(T) &= \frac{\hbar^2}{2m^*}\frac{A(T)}{C} \\ \beta &= \left(\frac{\hbar^2}{2m^*}\right)^2 \frac{B}{C^2}\end{aligned} \tag{14.168}$$

in which case (14.167) becomes

$$\begin{aligned}\delta F &= \int d\mathbf{r}\alpha(T)|\Psi(\mathbf{r})|^2 + \frac{\beta}{2}|\Psi(\mathbf{r})|^4 + \frac{1}{2m^*}\left|\left(-i\hbar\nabla - \frac{e^*\mathbf{A}(\mathbf{r})}{c}\right)\Psi(\mathbf{r})\right|^2 \\ &+ \frac{H^2(\mathbf{r})}{8\pi}\end{aligned} \tag{14.169}$$

where m is arbitrary. The free energy (14.169) was proposed by Landau and Ginzburg well before the BCS theory. In their approach they define the effective charge e^* which we now know to be equal to $2e$ (at that point in time the idea of Cooper pairs had not been formulated) and $m^* = 2m$ the mass of the pairs. When this free energy was proposed the value of e^* and m^* where now known and this were consider microscopic parameters of the model which should be fit by experimental data. It turns out that (14.169) is an extremely useful functional which allows us to predict many different properties of superconductors.

The equilibrium the state of the system is obtained by minimizing the free energy with respect to Ψ^* and $\mathbf{A}$. It is easy to show that

$$\begin{aligned}\frac{\partial F}{\partial \Psi^*(\mathbf{r})} &= 2\alpha(T)\Psi(\mathbf{r}) + 2\beta|\Psi(\mathbf{r})|^2\Psi(\mathbf{r}) + \frac{1}{m^*}\left(-i\hbar\nabla - \frac{e^*\mathbf{A}(\mathbf{r})}{c}\right)^2\Psi(\mathbf{r}) = 0 \\ \frac{\partial F}{\partial A_\nu(\mathbf{r})} &= \frac{1}{4\pi}\left(\nabla\times\nabla\times\mathbf{A}(\mathbf{r})\right)_\nu - \frac{e^*}{2m^*c}\Psi^*(\mathbf{r})\left(-i\hbar\nabla - \frac{e^*\mathbf{A}(\mathbf{r})}{c}\right)_\nu\Psi(\mathbf{r}) \\ &- \frac{e}{mc}\Psi(\mathbf{r})\left(+i\hbar\nabla - \frac{e^*\mathbf{A}(\mathbf{r})}{c}\right)_\nu\Psi^*(\mathbf{r}) = 0\end{aligned} \tag{14.170}$$

which leads to

$$\alpha(T)\Psi(\mathbf{r}) + \beta|\Psi(\mathbf{r})|^2\Psi(\mathbf{r}) + \frac{1}{2m^*}\left(-i\hbar\nabla - \frac{e^*\mathbf{A}(\mathbf{r})}{c}\right)^2\Psi(\mathbf{r}) = 0$$

$$\frac{1}{4\pi}\nabla\times\mathbf{H}(\mathbf{r}) + \frac{ie^*\hbar}{2m^*}\left(\Psi^*(\mathbf{r})\nabla\Psi(\mathbf{r}) - \Psi(\mathbf{r})\nabla\Psi^*(\mathbf{r})\right) + \frac{(e^*)^2}{mc}|\Psi(\mathbf{r})|^2\mathbf{A}(\mathbf{r}) = 0 \tag{14.171}$$

where we used that $\mathbf{H} = \nabla \times \mathbf{A}$. Observe that the current in the system is

$$\begin{aligned} \mathbf{J}(\mathbf{r}) &= \frac{1}{4\pi} \nabla \times \mathbf{H}(\mathbf{r}) = -\frac{ie^*\hbar}{2m^*} \left(\Psi^*(\mathbf{r}) \nabla \Psi(\mathbf{r}) - \Psi(\mathbf{r}) \nabla \Psi^*(\mathbf{r})\right) \\ &- \frac{(e^*)^2}{m^* c} |\Psi(\mathbf{r})|^2 \mathbf{A}(\mathbf{r}) \end{aligned} \tag{14.172}$$

where the first term is the paramagnetic current and the second term is the diamagnetic current.

In order to understand the meaning of the free energy let us study the simplest case first, that is, no external fields and a homogeneous Ψ. In this case the free energy is minimized by $\Psi = 0$ or

$$\Psi_0^2 = \frac{-\alpha}{\beta} \tag{14.173}$$

as we directly obtain from (14.171). The case of $\Psi = 0$ is the non-superconducting state and it is of no interest. Observe that for the solution (14.173) to be a solution we must require that $\alpha < 0$, which according to (14.162) requires that $T < T_c$, as expected. This solution is completely equivalent to (14.163). Thus, like in (14.165) we find

$$H_c = 2\sqrt{\pi} \frac{|\alpha|}{\sqrt{\beta}} . \tag{14.174}$$

Notice that for this solution the current in the system driven by an external vector potential $\mathbf{A}$ is given in (14.172) by

$$\mathbf{J} = -\frac{(e^*)^2}{m^* c} \Psi_0^2 \mathbf{A} \tag{14.175}$$

which is identical to the London equation (14.139) which leads to the Meissner effect. From this relationship we can directly relate Ψ_0 with ρ_s the superfluid density in the system. If we use $e^* = 2e$ and $m^* = 2m$ we see that

$$\Psi_0 = \rho_s^* = \frac{\rho_s}{2} \tag{14.176}$$

which shows that Ψ is the density of Cooper pairs (each Cooper pair has 2 electrons). Moreover, we immediate conclude that the penetration depth in this case is

$$\lambda = \frac{m^* c^2}{4\pi (e^*)^2 \rho_s^*} \tag{14.177}$$

in complete analogy with (14.143). Using (14.173) we can also write:

$$\lambda = \frac{m^* c^2 \beta^{1/2}}{4\pi (e^*)^2 \sqrt{-\alpha}} \, . \tag{14.178}$$

Notice that (14.174) and (14.178) predict that

$$\begin{aligned} H_c(T) &\propto T_c - T \\ \lambda(T) &\propto \frac{1}{\sqrt{T_c - T}} \end{aligned} \tag{14.179}$$

since $\alpha(T) \propto T - T_c$. Observe that λ diverges in the normal phase since the magnetic field can penetrate completely in the sample. Moreover, (14.174) and (14.178) allows us to rewrite the phenomenological constants α and β in terms of the experimentally observable quantities H_c and λ. Indeed, by inverting these two relations we find

$$\begin{aligned} \alpha &= \frac{(e^*)^2}{m^* c^2} H_c^2 \lambda^2 \\ \beta &= \frac{4\pi (e^*)^2}{(m^*)^2 c^4} H_c^2 \lambda^4 \, . \end{aligned} \tag{14.180}$$

Let us now consider another simple case, also in the absence of fields, of a superconductor in contact with vacuum at the surface $x = 0$. In the vacuum we must have $\Psi = 0$ while for $x > 0$ we must have Ψ given by the equations (14.171). In this case (14.171) reduces to

$$-\frac{\hbar^2}{2m^*} \frac{d^2 \Psi}{dx^2} + \alpha \Psi + \beta \Psi^3 = 0 \tag{14.181}$$

which is very similar to the non-linear Schödinger equation we discussed in Chapter 7. There are two trivial solutions of this equation $\Psi = 0$

and $\Psi = \Psi_0 = \sqrt{-\alpha/\beta}$ which were discussed previously. None of these solutions satisfy the boundary conditions at $x = 0$. Notice that far away from the surface we expect $\Psi(x \to +\infty) = \Psi_0$ which is given in (14.173). It is convenient to reparameterize (14.181) as

$$\Psi(x) = \Psi_0 f(x) \tag{14.182}$$

where $f(x \to +\infty) = 1$ and $f(x = 0) = 0$. Substituting the above relation in (14.181) we find

$$-\xi^2 \frac{d^2 f}{dx^2} - f + f^3 = 0 \tag{14.183}$$

where

$$\xi = \sqrt{\frac{\hbar^2}{2m^*(-\alpha)}} \propto \frac{1}{\sqrt{T_c - T}}\,. \tag{14.184}$$

Observe that ξ has dimensions of length and its meaning becomes clear if we realize that the solution of the above equation with the boundary conditions given above is

$$f(x) = \tanh\left(\frac{x}{\sqrt{2}\xi}\right)\,. \tag{14.185}$$

This solution shows that $\Psi(x)$ changes from 0 at the interface to Ψ_0 inside the superconductor in a length scale given by ξ. This is nothing but the superconducting coherence length which measures the way the condensate varies as the order parameter goes to zero. Observe that this length scale has nothing in common with the penetration depth λ which measures the scale in which the order parameter varies in a magnetic field. Moreover, observe that from (14.184) diverges at T_c since the order parameter has to vanish in the interior of the sample.

Therefore the superconductor has two characteristic lengths xi and λ and the types of superconductivity can be classified according to their ratio

$$\begin{aligned}\kappa &= \frac{\lambda(T)}{\xi(T)} \\ &= \frac{mc}{2e\hbar}\sqrt{\frac{\beta}{2\pi}} = \frac{\hbar c}{4Ce}\sqrt{\frac{B}{2\pi}}\end{aligned} \tag{14.186}$$

which is called Landau-Ginzburg parameter. In order to understand the physical meaning of this parameter consider the problem of an infinite superconductor in a homogeneous magnetic field. We will assume that the we are very close to the transition and the field is large enough so that we can disregard the non-linear term in (14.171). In this case the equation is simplified to:

$$\frac{1}{2m^*}\left(-i\hbar\nabla - \frac{e^*\mathbf{A}(\mathbf{r})}{c}\right)^2 \Psi(\mathbf{r}) = -\alpha(T)\Psi(\mathbf{r}) \tag{14.187}$$

which is called the linearized Ginzburg-Landau equation. Observe that this equation has the same form as the Schrödinger equation for a particle in a magnetic field where the energy is replaced by $-\alpha$. In the presence of the field this equation can be solved exactly like the usual Schrödinger equation. Thus, the cyclotron frequency in this case is

$$\Omega_c = \frac{e^*H}{m^*c} \tag{14.188}$$

notice that because $e^* = 2e$ and $m^* = 2m$ the cyclotron frequency of Cooper pairs is the same as ordinary electrons. The eigenenergies of the problem are given by (here we will use the Landau gauge as in the case of the free electron gas):

$$E_n(k) = \hbar\Omega_c\left(n + \frac{1}{2}\right) + \frac{\hbar^2k^2}{2m} \tag{14.189}$$

where k is the momentum in the direction of the field. Observe that in the ground state ($n = k = 0$) the energy is simply $\hbar\Omega_c/2$ which should be equated to $-\alpha$. This implies that there is a special value of the field, H_{c2} such that

$$\begin{aligned} H_{c2} &= -\frac{\alpha mc}{e\hbar} = \frac{\Phi_0}{2\pi\xi^2(T)} \\ &= \frac{a\Phi_0(T_c - T)}{2\pi C T_c} \end{aligned} \tag{14.190}$$

where we used (14.160) and (14.184). Notice that for larger energy states with different n and k we are going to find lower values of H.

The physical meaning of this field becomes clear when we consider the eigenstates of (14.187) that is,

$$\Psi_k(\mathbf{r}) \propto e^{iky} e^{-\frac{(x-x_k)^2}{2\xi^2}} \tag{14.191}$$

where

$$x_k = \frac{k\Phi_0}{2\pi H} \tag{14.192}$$

is the center of the cyclotron orbit and k is the momentum along the y direction. Observe that the order parameter vanishes away from ξ from the center of the orbit. Thus, H_{c2} is the largest value of the magnetic field at which superconductivity can nucleate on a distance ξ inside the superconductor. For fields with value larger than that H_{c2} superconductivity is not possible. Using (14.165) and (14.186) we can rewrite

$$H_{c2} = \sqrt{2}\kappa H_c \tag{14.193}$$

which shows that $H_{c2} > H_c$ if $\kappa > 1/\sqrt{2}$ and $H_{c2} < H_c$ if $\kappa < 1/\sqrt{2}$. In the first case, that is, for $\kappa > 1/\sqrt{2}$ a large magnetic field will start to nucleate superconducting regions before the system reaches a complete Meissner effect at fields $H < H_c$. In the second case when $\kappa < 1/\sqrt{2}$ as we start with very large magnetic fields we have a direct transition to a fully Meissner phase and H_{c2} is irrelevant. Systems such that $\kappa < 1/\sqrt{2}$ are called type I superconductors and the ones for which $\kappa > 1/\sqrt{2}$ are called type II superconductors. Consider the difference between type I and type II superconductors starting from high magnetic fields. In a type I superconductor the magnetization is zero (normal state) until one reaches a critical field H_c where the field is completely expelled from the sample. At this point the magnetization jumps to a value $M = -H_c/(4\pi)$ and increases linearly with the decreasing field in accord with (14.148). In a type II superconductor as one decreases the field starting from high fields one first reaches a field equal to H_{c2} where superconducting regions start to nucleate.

The main problem of our solution is that it disregards completely the non-linear term $\beta\Psi^4$ in the Ginzburg-Landau free energy and therefore it allows for overlapping of the various centers of the superconducting regions to overlap. Since this term grows with the amplitude of the order parameter it is obvious that this term will frustrate large local amplitude of the order parameter in real space. In fact this term breaks the degeneracy of the problem with respect of the position of the center of the orbit making energetically more favorable for the superconducting regions of size ξ to form a periodic structure which clearly has to be the solution of the problem when the system is isotropic and homogeneous. This periodic array of superconducting regions is called the Abrikosov lattice.

In order to understand how the lattice is formed consider along the y direction. In this case the periodic conditions imply that k in (14.191) has to be quantized as

$$k_n = nK \tag{14.194}$$

where n is an integer and K is the wave-vector which determines the periodicity of the lattice which is given by

$$\delta y = \frac{2\pi}{K} . \tag{14.195}$$

The determination of the particular wave-vector depends directly on the type of lattice and the Ginzburg-Landau parameters. Notice, however, that because of (14.194) the position of the center of the superconducting regions given by (14.192) is also quantized by

$$x_n = \frac{nK\Phi_0}{2\pi H} . \tag{14.196}$$

Combining (14.195) and (14.196) we see that

$$\delta y \delta x = \delta y (x_{n+1} - x_n) = \frac{\Phi_0}{H} \tag{14.197}$$

which implies that $H\delta x \delta y = \Phi_0$ implying that in this periodic array of superconducting islands the magnetic flux per plaquette is one quantum of flux. Although this argument shows that flux quantization and periodicity are related it does not provide any information about the geometry of the lattice. Consider, the generic solution of the linear Ginzburg-Landau equation (14.187) which is given by

$$\psi(\mathbf{r}) = \sum_n C_n e^{inKy} e^{-(x-x_n)^2/(2\xi^2)} \tag{14.198}$$

which is not a solution of the general Ginzburg-Landau equation (14.171). This however can be a periodic solution of the linear Ginzburg-Landau equation if we enforce a particular periodic condition. For instance, for the square lattice we would write:

$$\psi(x+\delta x, y) = \psi(x, y+\delta y) = \psi(x, y)\,. \tag{14.199}$$

Application of this condition to (14.198) requires that $C_{n+1} = C_n$, that is, all the constants are equal: $C_n = C_0$ for all n. Knowing this condition we could substitute (14.198) into the general Ginzburg-Landau free energy (14.169) and find the value of C_0 which minimizes the energy. On the other hand, a different lattice with a different symmetry will require different relations between the different coefficients C_n in (14.198).

In order to understand the minimization procedure consider the simple case of the square lattice discussed above in which the wavefunction can be written as $\psi(\mathbf{r}) = C_0\chi(\mathbf{r})$ where $\chi(\mathbf{r})$ is given. Let us assume that the order parameter varies very smoothly over the sample and forget about gradient terms in the (14.169). In this case the free energy becomes

$$\frac{\delta F}{V} = \alpha C_0^2 \left\langle \chi^2 \right\rangle + \frac{C_0^4 \beta}{2} \left\langle \chi^4 \right\rangle \tag{14.200}$$

where

$$\begin{aligned} \left\langle \chi^2 \right\rangle &= \frac{1}{V}\int d\mathbf{r}\chi^2(\mathbf{r}) \\ \left\langle \chi^4 \right\rangle &= \frac{1}{V}\int d\mathbf{r}\chi^4(\mathbf{r}) \end{aligned} \tag{14.201}$$

are averages of the moments of the given function over the sample. We can now minimize the free energy (14.200) with respect to C_0 in order to find

$$C_0 = \frac{-\alpha}{\beta}\frac{\langle \chi^2 \rangle}{\langle \chi^4 \rangle} \tag{14.202}$$

which when substituted back into (14.200) gives

$$\frac{\delta F}{V} = -\frac{\alpha^2}{2\beta}\frac{1}{\beta_A} \tag{14.203}$$

where

$$\beta_A = \frac{\langle \chi^4 \rangle}{\langle \chi^2 \rangle^2} \tag{14.204}$$

is called the Abrikosov parameter. Its physical meaning is simple: if $\chi(\mathbf{r})$ is constant over the volume then $\beta_A = 1$ and the problem reduces to the one studied in the beginning of this section. If however $\chi(\mathbf{r})$ changes then $\beta_A > 1$ when the function χ becomes more localized. Observe that the result (14.203) penalizes functions which have large β_A because the free energy becomes larger (less negative). Thus, the discussion of the problem of minimizing the free energy is directly related with the minimization of β_A for a given Abrikosov lattice. Although the argument given here is correct in its original paper Abrikosov predicted that the lattice with lowest energy would be a square one. In fact, later numerical calculations have shown that the triangular lattice is the one with lowest energy since it has a close-packed structure.

Finally, as one decreases the field more and more superconducting regions are formed but there is no complete Meissner effect because the sample still has normal regions. As one lowers the field further there is a critical field H_{c1} at which the superconducting regions percolate and take over the whole sample. Below this field the Meissner effect is complete. Observe that H_{c1} is not guaranteed to be H_c. How one would calculate H_{c1}? It is clear from our discussion that H_{c1} is the field at which the magnetic field start to enter into the sample. As we showed previously the magnetic flux through a superconductor is quantized in units of Φ_0. Thus, H_{c1} is the field such that one quantum of magnetic flux crosses the sample. Let us consider the case of a extreme type II superconductor where $\lambda >> \xi$. In this case the region where superconductivity is destroyed by the magnetic field (that is, ξ) is insignificant compared with the region for which the field penetrates. Thus, from the point of view of the magnetic properties we can assume that the magnetic flux is infinitesimally sharp and along the z axis.

Thus, the magnetic field caused by this magnetic flux is simply $H_f = \Phi_0 \delta(x)\delta(y)$ (observe that if we integrate in a surface transverse to the flux we have, $\int dSH_f = \Phi_0$ as expected). In this case the magnetic field profile is given by (14.142) with a point source

$$\mathbf{H} - \lambda^2 \nabla^2 \mathbf{H} = \Phi_0 \delta(x)\delta(y)\mathbf{z} \tag{14.205}$$

and because of the symmetry of the problem we have $\mathbf{H} = H(r)\mathbf{z}$ where r is the distance in the plane perpendicular to the field. Therefore, the above equation becomes

$$H(r) - \frac{\lambda^2}{r}\frac{d}{dr}\left(r\frac{dH}{dr}\right) = \frac{\Phi_0}{2\pi}\frac{\delta(r)}{r}. \tag{14.206}$$

Let us write the solution as

$$H(r) = \frac{\Phi_0}{2\pi\lambda^2} f\left(\frac{r}{\lambda}\right) \tag{14.207}$$

where

$$f(x) - \frac{1}{x}\frac{d}{dx}\left(x\frac{dH}{dx}\right) = \frac{\delta(x)}{x}. \tag{14.208}$$

One of the boundary conditions is that $f(x \to \infty) = 0$. First observe that for $x \neq 0$ the solution is a Bessel function of imaginary argument

$$f(x) = K_0(x) \tag{14.209}$$

where for $x >> 1$

$$K_0(x) \approx \sqrt{\frac{\pi}{2x}} e^{-x} \tag{14.210}$$

while for $x << 1$ we have

$$K_0(x) \approx \ln(x) \tag{14.211}$$

which is singular at $x = 0$. Actually it is easy to show that (14.209) is actually the full solution of (14.208) for all x, that is,

$$H(r) = \frac{\Phi_0}{2\pi\lambda^2} K_0\left(\frac{r}{\lambda}\right) \tag{14.212}$$

is the solution of (14.206). We can now calculate the current associated with this field configuration which is given by (14.141) and it is easy to see to rotate in the plane perpendicular to the flux and which has an amplitude

$$J = \frac{1}{4\pi}|\nabla \times \mathbf{H}| \approx \frac{\Phi_0}{8\pi^2\lambda^2}\frac{1}{r} \tag{14.213}$$

for $r << \lambda$. This configuration is called a vortex.

The energy required to create the vortex is simply

$$\begin{aligned} E &= \int d\mathbf{r}\frac{1}{8\pi}\left(\mathbf{H}^2 + \lambda^2(\nabla \times \mathbf{H})^2\right) \\ &= \frac{\lambda^2}{8\pi}\int d\mathbf{S}\cdot\mathbf{H}\times(\nabla\times\mathbf{H}) \end{aligned} \tag{14.214}$$

where the integral is taken to be over the surface of the core which has radius ξ. Thus, the energy per unit of length along the vortex filament is

$$\begin{aligned} \frac{dE}{dz} &= \frac{\lambda^2}{4}\xi H(\xi)|\nabla \times H(\xi)| \\ &= \left(\frac{\Phi_0}{4\pi\lambda}\right)^2 \ln\left(\frac{\lambda}{\xi}\right). \end{aligned} \tag{14.215}$$

We can now evaluate H_{c1} since the energy given in (14.215) has to equal the magnetic energy for the creation of the vortex which is given by $BH/(4\pi)$. But observe that $B = \Phi_0/S$ where S is the area of the vortex core. Thus, the amount of energy per unit of volume required to create a vortex is $(1/S)dE/dz$ and thus we have

$$\begin{aligned} H_{c1} &= \frac{4\pi}{\Phi_0}\frac{dE}{dz} \\ &= \frac{\Phi_0}{4\pi\lambda^2}\ln\left(\frac{\lambda}{\xi}\right) \end{aligned} \tag{14.216}$$

Notice that

$$\frac{H_{c1}}{H_c} = \frac{\pi}{\sqrt{24}}\frac{\xi}{\lambda}\ln\left(\frac{\lambda}{\xi}\right) \tag{14.217}$$

and therefore $H_{c1} << H_c$ for strong type II superconductors.

14.4 Problems

1. Generalize the Bogoliubov-De Gennes equation (1.21) for the case where the electrons in a superconductor are subject to an external potential $V(\mathbf{r})$ which couples to the electron density. Show that in this case the problem is equivalent to replace μ by $\mu - V(\mathbf{r})$ in those equations.

2. Consider the interface between a semi-infinite superconductor with gap Δ located at $x > 0$ and a normal metal located at $x < 0$. Consider the solution of the Bogoliubov-De Gennes equation (1.21) for this situation and show that the coefficients $u(\mathbf{r})$ and $v(\mathbf{r})$ can be written as

$$u(\mathbf{r}) = u(x)e^{i\mathbf{k}_{||}\cdot\mathbf{r}}$$
$$v(\mathbf{r}) = v(x)e^{i\mathbf{k}_{||}\cdot\mathbf{r}}$$

   where $k_{||}$ is the momentum of the particle parallel to the interface (that is $\mathbf{k}_{||} = (k_y, k_z)$). The problem of reflections of particles at the interface of a superconductor and a normal metal is called Andreev reflection.

   (i) Find the solution for $u_N(x)$ and $v_N(x)$ in the normal region, that is, for $x < 0$. Show that the solution is a combination of plane waves with momentum in the direction x given by

$$k_{\pm} = \sqrt{k_F^2 - k_{||}^2 \pm 2m|E|/\hbar^2}$$

   and that $u_N(x)$ depends only of k_+ and $v_N(x)$ only on k_-. Show that there are 4 unknown parameters which depend on the boundary conditions.

   (ii) Repeat the calculation of item (i) for the superconducting side and show that the solution is given is given in terms of

$$k^{\pm} = \sqrt{k_F^2 - k_{||}^2 \pm 2m\epsilon/\hbar^2}$$

   where

$$\epsilon = \sqrt{E^2 - \Delta^2}\,.$$

Show that there are 4 unknown parameters as well.

(*iii*)What are the boundary conditions at the interface?

(*iv*) Consider a particle with energy $E > \Delta$ wave-vector k_+ incident on the superconductor from the right. Show that in this case one of the unknown coefficients of item (*i*) vanish in the normal side of the interface. Assume that there are only outgoing waves in the superconductor side and calculate the calculate the transmission coefficient of the problem.

3. Using the BCS wavefunction (1.38) and the anti-commutation relations between the electron operators calculate $\langle BCS|a^{\dagger}_{\mathbf{k},\uparrow}a_{\mathbf{k}',\uparrow}|BCS\rangle$.

4. Consider the case of two superconductors S_1 and S_2 which are physically separated in space. Suppose we allow electrons to tunnel from one superconductor to another by adding to the Hamiltonian a term like

$$H_T = t\sum_{\mathbf{k},\mathbf{k}',\sigma}(a^{\dagger}_{1,\mathbf{k},\sigma}a_{2,\mathbf{k}',\sigma} + a^{\dagger}_{2,\mathbf{k}',\sigma}a_{1,\mathbf{k},\sigma})$$

where a_1 and a_2 are the destruction operators for electrons in the superconductor 1 and 2 respectively and t is the hopping energy between the superconductors.

(*i*) Show that the wavefunction of the problem in the absence of H_T for a system with fixed number of electrons $2N$ can be written as $|M\rangle = |1, 2(N-M)\rangle \otimes |2, 2M\rangle$ where $|M\rangle$ describes $2M$ electrons coupled in pairs in S_2 and $2(N-M)$ electrons coupled in pairs in S_1. Moreover, in this case the problem can be diagonalized as

$$H_0|M\rangle = E_M|M\rangle \tag{14.218}$$

where H_0 is the Hamiltonian in the absence of tunneling.

(*ii*)Show that if M increases by 1 we must have

$$E_{M+1} - E_M = 2(\mu_1 - \mu_2) \tag{14.219}$$

where $\mu_{1(2)}$ is the chemical potential of $S_{1(2)}$.

(ii)Assume that if $\mu_1 = \mu_2$ and the system is degenerate, that is, E_M is independent of M, then show that H_T removes this degeneracy. Show that in perturbation theory the first order correction to the energy has the form

$$T = t^2 \sum_{\mathbf{k},\mathbf{k}',\sigma} \sum_{\mathbf{p},\mathbf{p}'} \frac{\langle M+1|a^\dagger_{1,\mathbf{k},\sigma} a_{2,\mathbf{k}',\sigma}|M'\rangle\langle M'|a^\dagger_{1,\mathbf{p},\sigma} a_{2,\mathbf{p}',\sigma}|M\rangle}{E - E_{M'}}$$

where $|M'\rangle$ is a state with $2M+1$ electrons in S_1 and $2(N-M)-1$ electrons in S_2.

(iii) Show using the results of the previous problem that in the BCS state we have

$$T = -4t^2 \sum_{\mathbf{k},\mathbf{k}'} \frac{u_{\mathbf{k}} v_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'}}{E_{\mathbf{k}} + E_{\mathbf{k}'}} .$$

(iv) The above results show that to second order in t we can write the Schrödinger equation as

$$H|M\rangle = E|M\rangle + T\left(|M+1\rangle + |M-1\rangle\right) .$$

Show that the solution of this problem can be solved by Fourier transform

$$|\phi\rangle = \sum_M e^{i\phi M}|M\rangle$$

and that the eigenvalues are given by

$$E(\phi) = E + 2T\cos(\phi) .$$

(v)Observe that the solution of two coupled superconductors can be thought of a wave-packet of states with different number of particles. Show that this wave-packet has group velocity

$$v = -2T\sin(\phi)$$

and therefore there is a current flowing from one superconductor to another which is given by

$$I = -\frac{4eT}{\hbar}\sin(\phi) .$$

Assume that a potential $U(t)$ is applied between the superconductors. Show that in this case

$$\frac{d\phi}{dt} = \frac{2e}{\hbar} U(t) \,. \tag{14.220}$$

(*vi*) Show that if a constant voltage U is applied to the system the current in the circuit oscillates with frequency $\frac{2eU}{\hbar}$. This is the so-called Josephson effect.

5. Calculate the density of states for a superconductor with gap Δ by assuming that in the normal state the density of states is $N(0)\Theta(W - |E|)$.

6. Consider the Ginzburg-Landau approach for a very thin superconducting film of thickness a carrying a current J along the x axis (notice the J is given!). Assume that $\xi, \lambda >> a$ and show that in this case $|\Psi|$ and J can be considered as constants independent of position.

   (*i*) Assume that $\Psi(\mathbf{r}) = |\Psi| e^{i\phi(\mathbf{r})}$ and show that the free energy of the problem can be written as

$$\begin{aligned} J &= 2e|\Psi|^2 v \\ \delta F &= \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4 + \frac{m|\Psi|^2 v^2}{2} + \frac{H^2}{8\pi} \end{aligned}$$

   where

$$v = \frac{1}{m}\left(\hbar\frac{\partial\phi}{\partial x} - \frac{2e}{c}A_x\right) .$$

   (*ii*) Minimize the free energy and show that

$$\begin{aligned} |\psi| &= \Psi_0 g \\ J &= 2e\psi_0^2\sqrt{\frac{-2\alpha}{m}}g^2\sqrt{1-g^2} \end{aligned}$$

   where $\Psi_0 = -\alpha/\beta$.

   (*iii*)Show that for $g < g_c = 2/3$ there is no solution for the equations above and that g_c determines a critical current J_c. Calculate J_c.

7. Show that (14.185) is indeed a solution of (14.183).

Chapter 15

Phase fluctuations

In the last chapter we have studied the problem of superconductivity and its relationship to the spontaneous breaking of the gauge symmetry. We have seen that the order parameter in a superconductor is not a gauge invariant quantity because it has an amplitude and a phase (it is a complex number) and the phase is directly related to an applied electromagnetic gauge potential. We have shown, however, that in the BCS theory the wavefunction has a well-defined phase and an ill-defined number of particles. This uncertainty in the relationship of the phase to the number of Cooper pairs is related with phase fluctuations in the system. We can say that in a BCS superconductor phase fluctuations are suppressed. But this is not generically true. In this chapter we are going to study problems which are directly related to the fluctuations of the phase and we will find that a new physics emerges from effects related to phase fluctuations. We are going to see that phase fluctuations are particularly important in lower dimensions where long range order is completely suppressed by fluctuations, in contrast with mean field theories such as the Ginzburg-Landau where long range order is independent of the dimensionality of the system.

15.1 Josephson Effect

The most famous example of the importance of phase fluctuations is given by the Josephson effect depicted in Fig.15.1. Consider two su-

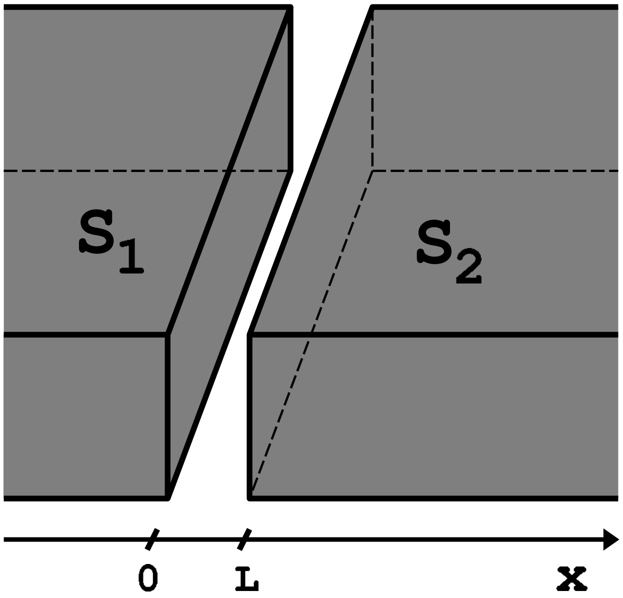

Figure 15.1: *.Josephson Junction*

perconductors S_1 and S_2 which are separated by a distance L as shown in Fig.15.1. If the superconductors are very far apart we can consider them as isolated from each other having a superconducting order parameter Δ_1 and Δ_2 given by BCS theory. If these superconductors are identical and are held at the same temperature we expect that $|\Delta_1| = |\Delta_2|$. Observe that this relationship does not imply that their phases, say, φ_1 and φ_2 are related with each other. In fact if the superconductors are infinitely apart we expect no relationship whatsoever between their phases. But consider approaching the two superconductors to such a small distance that Cooper pairs from S_1 can tunnel to S_2 and vice-versa. The situation here is very similar to the problem of the H_2 atom discussed in the first Chapter. In this case we expect that although the amplitude of the order parameter does not change, that is, $|\Delta_1| = |\Delta_2|$, some kind of relationship should occur among their phases because when $L = 0$ they become a single superconductor and therefore their phase difference, $\varphi = \varphi_1 - \varphi_2$ vanishes. Thus it is natural to expect that φ depends strongly on L.

In order to make the discussion of the problem simple we will apply the Ginzburg-Landau approach to the problem and work with the order parameter $\Psi(x)$. It is clear that for $|\Psi_1(0)| = |\Psi_2(L)| = \Psi_0$ are the order parameters in the bulk. The question is what happens in between. Here we use (14.183) which gives the variation of the of the order parameter in between the superconductors:

$$-\xi^2 \frac{d^2 f}{dx^2} - f + f^3 = 0 \tag{15.1}$$

with boundary conditions $|f| = 1$ for $x \leq 0$ and $x \geq L$. Thus, without lack of generality we impose the boundary conditions: $f(0) = 1$ and $f(L) = e^{i\varphi}$. Moreover, we will assume that the distance between superconductors is much smaller than the correlation length, $L \ll \xi$. In this case we would have $\xi^2 \frac{d^2 f}{dx^2} \approx (\xi/L)^2 f \gg f$ and the above equation simplifies to:

$$\frac{d^2 f}{dx^2} \approx 0 \tag{15.2}$$

with trivial solution (using the boundary conditions given above)

$$f(x) = 1 - \frac{x}{L} + \frac{x}{L} e^{i\varphi} . \tag{15.3}$$

This solution now allows us to calculate the current of Cooper pairs between the two superconductors which is given in (14.172):

$$\begin{aligned} J_s &= -\frac{ie^*\hbar|\Psi_0|^2}{m^*}\left(f^*\frac{df}{dx} - f\frac{df^*}{dx}\right) \\ &= \frac{2e^*\hbar|\Psi_0|^2}{m^* L}\sin(\varphi) \end{aligned} \tag{15.4}$$

and therefore the total super-current between S_1 and S_2 is:

$$I_S = I_c \sin(\varphi) \tag{15.5}$$

where

$$I_c = \frac{2e^*\hbar|\Psi_0|^2}{m^*} \frac{A}{L} \tag{15.6}$$

where A is the area of the junction. The free energy in (14.169) can be easily calculated

$$\delta F = \frac{\hbar}{2e} I_c (1 - \cos(\varphi)) . \tag{15.7}$$

Naturally the free energy is minimized for $\varphi = 0$ which is the situation in which the two superconductors reach equilibrium and no current flows between then, that is, $I_S = 0$.

Suppose a constant electric field is applied in the x direction $\mathbf{E} = E_0 \mathbf{x}$. From electromagnetic relations the vector potential is given by

$$\mathbf{A} = -c E_0 t \mathbf{x} \tag{15.8}$$

since

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} . \tag{15.9}$$

The next step would be to couple the electromagnetic field to the order parameter through the Ginzburg-Landau approach. Instead we are going to find a more straightforward way and use the gauge invariance of the problem as discussed in the previous chapter. We have seen from (14.106) that the gauge invariant vector is

$$\mathbf{g}(\mathbf{r}) = \nabla \varphi(\mathbf{r}) - \frac{e^*}{\hbar c} \mathbf{A}(\mathbf{r}) \tag{15.10}$$

and therefore to study the effect of an external electric field one just have to make the substitution

$$\begin{aligned} \varphi &\rightarrow \varphi - \frac{e^*}{\hbar c} \int d\mathbf{l} \cdot \mathbf{A}(\mathbf{r}) \\ &\rightarrow \varphi + \frac{e^* L}{\hbar} E_0 t \end{aligned} \tag{15.11}$$

where the line integral was taken in between the two superconductors. Therefore from (15.5) we see that in the presence of an electric field the super-current between S_1 and S_2 is

$$I_S(V, t) = I_c \sin\left(\varphi + \frac{e^* V}{\hbar} t\right) \tag{15.12}$$

where

$$V = LE_0 \tag{15.13}$$

is the drop of potential energy across the junction. Observe that a static (d.c.) electric field has produced an alternating (a.c.) current! The period of this current is $h/(e^*V)$ and depends only on e^* since h and V are known. Thus, it is possible to measure the effective charge of the Cooper pairs via the effect described above. This is called the Josephson effect. Notice that $I_S \leq I_c$ and therefore I_c is the maximum current supported by the junction for a given V. It is called the critical current. Also observe that the superconducting phase in between the two superconductors varies in time as

$$\frac{d\varphi}{dt} = \frac{e^*V}{\hbar} \tag{15.14}$$

which is known as the Josephson relation. It is clear that the Josephson effect is an effect purely based on the phase difference between superconductors and only happens because the order parameter in a superconductor has two components (complex variable) and therefore can be described as an amplitude and a phase. There are, however, a whole class of systems which are described by similar order parameters as we are going to see soon.

15.2 Homogeneous superconductors

Let us consider now the problem of phase fluctuations in the bulk of a homogeneous superconductor with an order parameter given by

$$\Psi(\mathbf{r}) = \Psi_0 e^{i\varphi(\mathbf{r})} \tag{15.15}$$

where $\Psi_0^2 = -\alpha/\beta$ as in (14.173) but the phase is now allowed to vary in space. Substituting (15.15) into the Ginzburg-Landau free energy (14.169) leads to

$$\delta F = -\frac{V\alpha^2}{2\beta} + \frac{\rho_S}{2}\int d\mathbf{r}\left(\nabla\varphi - \frac{e^*}{\hbar c}\mathbf{A}(\mathbf{r})\right)^2 \tag{15.16}$$

where

$$\rho_S = \frac{\hbar^2|\Psi_0|^2}{m^*} \tag{15.17}$$

is called the phase rigidity or stiffness. The first term in (15.16) gives the bulk free energy and the last term gives the increase of the free energy due to the variations in the phase: in the absence of external fields the system prefers to have an uniform phase $\varphi =$ constant. Notice that what appears in the free energy for the phase is the gauge invariant vector (15.10) as expected, since the energy of the system cannot depend on the choice of gauge. The super-current in the system is given in (14.172) and can be written as

$$\begin{aligned} \mathbf{J}_S &= \frac{e^*\hbar|\Psi_0|^2}{m^*}\nabla\varphi - \frac{(e^*)^2|\Psi_0|^2}{m^*c}\mathbf{A} \\ &= e^*|\Psi_0|^2\mathbf{v}_S \end{aligned} \tag{15.18}$$

where

$$\mathbf{v}_S = \frac{\hbar}{m^*}\nabla\varphi - \frac{e^*}{m^*c}\mathbf{A} \tag{15.19}$$

is the superfluid velocity (notice that $\mathbf{v}_S = \hbar\mathbf{g}(\mathbf{r})/m^*$).

Thus, phase fluctuations in a superconductor in the absence of external fields are determined by a free energy

$$F[\varphi] = \frac{\rho_S}{2}\int d\mathbf{r}\,(\nabla\varphi)^2 \tag{15.20}$$

notice from the definition of ρ_S in (15.17) that $\rho_S(T) \propto T_c - T$ according to (14.162) and (14.173) (which is the mean field solution). This implies that ρ_S is finite in the superconducting phase ($T < T_c$) and vanishes in the disordered phase.

Long range order requires the order parameter to be finite, that is,

$$\langle\Psi\rangle = \Psi_0\langle e^{i\varphi}\rangle \neq 0 \tag{15.21}$$

so besides the amplitude to be finite (which is true for $T < T_c$) we must also require that $\langle e^{i\varphi}\rangle \neq 0$. In order to calculate the average in the equation above we have to know the partition function of the problem. Like the Ising model studied in (10.96) it is given by

$$Z = \int \prod_{\mathbf{r}} d\varphi(\mathbf{r}) e^{-\beta F[\varphi]} \tag{15.22}$$

where the free energy is given in (15.20). It is convenient to rewrite the partition function in terms of the Fourier transform of φ:

$$\varphi(\mathbf{r}) = \int \frac{d\mathbf{k}}{(2\pi)^d} e^{i\mathbf{k}\cdot\mathbf{r}} \varphi(\mathbf{k}) \tag{15.23}$$

where $\varphi^*(\mathbf{k}) = \varphi(-\mathbf{k})$. In this case the partition function is simply

$$Z = \int \prod_{\mathbf{k}} d\varphi(\mathbf{k}) \exp\left\{-\frac{\beta\rho_S}{2} \int \frac{d\mathbf{k}}{(2\pi)^d} k^2 |\varphi(\mathbf{k})|^2\right\} . \tag{15.24}$$

Moreover,

$$\begin{aligned}
\langle e^{i\varphi(\mathbf{r})} \rangle &= \langle e^{i\int \frac{d\mathbf{k}}{(2\pi)^d} e^{i\mathbf{k}\cdot\mathbf{r}} \varphi(\mathbf{k})} \rangle \\
&= \frac{1}{Z} \int \prod_{\mathbf{k}} d\varphi(\mathbf{k}) \exp\left\{-\int \frac{d\mathbf{k}}{(2\pi)^d} \left[\frac{\beta\rho_S k^2}{2} |\varphi(\mathbf{k})|^2 - i e^{i\mathbf{k}\cdot\mathbf{r}} \varphi(\mathbf{k})\right]\right\} \\
&= \exp\left\{-\frac{1}{\beta\rho_S} \int \frac{d\mathbf{k}}{(2\pi)^d} \frac{1}{k^2}\right\} \\
&= \exp\left\{-\frac{S_d}{(2\pi)^d \beta\rho_S} \int dk k^{d-3}\right\}
\end{aligned} \tag{15.25}$$

where S_d is the area of the hyper-sphere in d dimensions ($S_1 = 2$, $S_2 = 2\pi$ and $S_3 = 4\pi$). Observe that we have not introduced the limits of integration in the integral above. On the one hand we have to remember that the Ginzburg-Landau theory was obtained in the continuum. Therefore when the correlation length becomes of the order of the lattice spacing it breaks down. Thus, there is a natural upper limit for the integral say, Λ, which is of order of $1/a$. This is the so-called ultraviolet cut-off. On the other hand we are working on the thermodynamic limit so that the size of the system, L, is divergent. As we have seen many times when we work with a finite system the momenta become quantized in units of $1/L$ which is the smallest momentum possible. Thus, $1/L$ acts a lower bound in the integral above and it is called a infrared cut-off. If we use these two cut-offs in the expression above we find

$$\langle e^{i\varphi(\mathbf{r})}\rangle = \exp\left\{-\frac{S_d}{(2\pi)^d \beta\rho_S}\frac{1}{d-2}\left(\Lambda^{d-2}-\frac{1}{L^{d-2}}\right)\right\}. \qquad (15.26)$$

The above correlations become finite in the thermodynamic limit ($L \to \infty$) only for $d > 2$ implying that there is long range order in the system. Notice, however, that the above expression vanishes in the thermodynamic limit when $d \leq 2$. Indeed, for $d = 1$ we would find

$$\langle e^{i\varphi(\mathbf{r})}\rangle = e^{-\frac{L}{(\pi\beta\rho_S)}} \to 0 \qquad (15.27)$$

while for $d = 2$ we expand $\Lambda^{d-2} \approx 1 + (d-2)\ln(\Lambda)$ and find

$$\langle e^{i\varphi(\mathbf{r})}\rangle \approx e^{-\frac{\ln(\Lambda L)}{2\pi\beta\rho_S}} \to 0 \qquad (15.28)$$

as $L \to \infty$. The vanishing of these correlations imply from (15.21) that

$$\langle \Psi(\mathbf{r})\rangle = 0 \qquad (15.29)$$

for $d \leq 2$ even when the amplitude of the order parameter is different from zero. Therefore, phase fluctuations destroy long range order for $d \leq 2$. This is also known as the Mermim-Wagner theorem which you have worked on in Chapter 4, namely, when a system has a continuous symmetry breaking (of translational invariance as in the case of phonons, or symmetry of rotation in the spin space as in the case of magnons, or gauge symmetry as in the case of superconductivity) there is a *lower critical dimension*, d_c, below which order is not possible. In the case of superconductor this dimension is $d_c = 2$.

This fluctuations of the phase not only affect the order parameter but also the way correlations decay with distance. Consider the order parameter correlation function

$$\begin{aligned}\langle \Psi^\dagger(\mathbf{r})\Psi(0)\rangle &= |\Psi_0|^2\left\langle e^{-i(\varphi(\mathbf{r})-\varphi(0))}\right\rangle \\ &= |\Psi_0|^2 \exp\{-G_d(\mathbf{r})\} \qquad (15.30)\end{aligned}$$

where

$$G_d(\mathbf{r}) = \frac{1}{\beta\rho_S}\int \frac{d\mathbf{k}}{(2\pi)^d}\frac{1-e^{i\mathbf{k}\cdot\mathbf{r}}}{k^2} \tag{15.31}$$

can be calculated in a way completely analogous to the one leading to (15.25). As in the previous case the integral in (15.31) depends on the dimensionality of the system but contrary to the integral in (15.25) it is convergent because of the extra power of k brought by the exponential term. Let us calculate this function for the three different cases.

In $d = 3$ we can write

$$\begin{aligned} G_3(r) &= \frac{1}{8\pi^3\beta\rho_S}\int_0^\Lambda dk\int_{-1}^{+1} du(1-e^{ikru}) \\ &= \frac{1}{4\pi^3\beta\rho_S}\int_0^\Lambda dk\left(1+\frac{\sin(kr)}{kr}\right) \\ &\approx \frac{\Lambda}{4\pi^3\beta\rho_S} \end{aligned} \tag{15.32}$$

which in the last line we have taken the limit of $r \gg \Lambda^{-1} \approx a$ and disregarded the second term in the second line. Notice that $G_3(r)$ is independent of r. Thus, we conclude that in $d = 3$ the correlations are such that

$$\langle\Psi^\dagger(\mathbf{r})\Psi(0)\rangle \approx |\Psi_0|^2 e^{-\frac{\Lambda}{4\pi^3\beta\rho_S}} \tag{15.33}$$

which is finite in the limit of $r \to \infty$. This result implies that the order parameter in all parts of the sample are correlated. This means that the system shows *long range order*. The exponential factor is essentially a thermal correction to the order parameter. This is the analogue of the Debye-Waller factor for phonons discussed in Chapter 4.

For $d = 2$ we have

$$\begin{aligned} G_2(r) &= \frac{1}{4\pi^2\beta\rho_S}\int_0^\Lambda \frac{dk}{k}\int_0^{2\pi} d\theta(1-e^{ikr\cos(\theta)}) \\ &= \frac{1}{2\pi\beta\rho_S}\int_0^\Lambda \frac{dk}{k}(1-J_0(kr)) \\ &= \frac{1}{2\pi\beta\rho_S}\int_0^{\Lambda r} \frac{dx}{x}(1-J_0(x)) \end{aligned} \tag{15.34}$$

where $J_0(x)$ is a Bessel function. The integral above cannot be done exactly and we have to approximate. Since we are mainly interested in the limit of $\Lambda r \gg 1$ we can extract the dominating behavior of the integral. First one has to recall that $J_0(x) \approx 1 - x^2/4$ when $x \ll 1$ and $J_0(x) \approx \sqrt{2/(\pi x)} \cos(\pi/4 - x)$ for $x \gg 1$. We can therefore separate the integral as

$$\begin{aligned} \int_0^{\Lambda r} \frac{dx}{x}(1 - J_0(x)) &= \int_0^1 \frac{dx}{x}(1 - J_0(x)) + \int_1^{\Lambda r} \frac{dx}{x} - \int_1^{\Lambda r} dx \frac{J_0(x)}{x} \\ &\approx C + \ln(\Lambda r) \end{aligned} \tag{15.35}$$

where $C = \int_0^1 \frac{dx}{x}(1 - J_0(x)) - \int_1^\infty dx \frac{J_0(x)}{x}$ where we have replaced the upper limit in the last integral above by ∞ since the integral is convergent in this limit. Thus, substituting this solution into (15.30) we find that in $d = 2$:

$$\langle \Psi^\dagger(\mathbf{r}) \Psi(0) \rangle \approx |\Psi_0|^2 \frac{e^{-\frac{C}{2\pi\beta\rho_S}}}{(\Lambda r)^\eta} \tag{15.36}$$

where the exponential factor is the analogue of the Debye-Waller factor found in the 3D case and

$$\eta = \frac{1}{2\pi\beta\rho_S} \tag{15.37}$$

is the exponent which determines the decay of the correlation functions. Notice that when $\Lambda r \to \infty$ the correlation function goes to zero showing that long range order is not possible in $d = 2$. It turns out, however, that it goes to zero algebraically and not exponentially leading to a very slow decay of the correlations. Thus, even at reasonable distances some correlation is possible. This situation is called quasi-long range order. The importance of this result is quite clear: at large temperatures the correlations decay exponentially because the system is disordered. Thus there must be a temperature T_{KT} above which the correlations change from exponential to algebraic. This transition is the so-called Kosterlitz-Thouless transition. Observe that in $d = 2$ we must have $0 < T < T_{KT} < T_c$ where T_c is the temperature at which ρ_S vanishes. This transition is very specific to the 2D case and will be discussed in detail below.

In the $d = 1$ case we have:

$$\begin{aligned} G_1(x) &= \frac{1}{2\pi\beta\rho_S}\int_{-\Lambda}^{+\Lambda} dk \frac{1-e^{ikx}}{k^2} \\ &= \frac{|x|}{\pi\beta\rho_S}\int_0^{+\Lambda|x|} dz \frac{1-\cos(z)}{z^2} \\ &\approx \frac{|x|}{2\beta\rho_S} \end{aligned} \tag{15.38}$$

where in the last line we have taken $\Lambda|x| \to \infty$ and used that $\int_0^{+\infty} dz(1-\cos(z))z^{-2} = \pi/2$. Notice, therefore, that

$$\langle \Psi^\dagger(x)\Psi(0)\rangle \approx |\Psi_0|^2 e^{-|x|/(2\beta\rho_S)} \tag{15.39}$$

which shows that the correlations decay exponentially at any finite temperature and therefore $\langle \Psi^\dagger(x)\Psi(0)\rangle \to 0$ when $|x| \to \infty$ indicating complete absence of long range order at any finite temperature in $d = 1$. This conclusion agrees perfectly well with the discussion of the magnitude of the order parameter.

15.3 Connection to Magnetism

The model described by the free energy (15.20) is called the XY model as we have discussed in magnetism. It is worth understanding the connection with magnetism since it gives a way to visualize the physics of the phase of a superconductor. Consider a classical magnetic XY model which is described by a Hamiltonian

$$H = -J\sum_{<i,j>}\left(S_i^x S_j^x + S_i^y S_j^y\right) \tag{15.40}$$

where J is the magnetic exchange and S_i^x (S_i^y) is the X (Y) component of the spin on a given lattice. Here the spins are treated as functions and not operators. These are classical variables in a plane. Moreover, observe that $(S_i^x)^2 + (S_i^y)^2 = S^2$ and therefore we can parameterize

$$\begin{aligned} S_i^x &= S\cos(\theta_i) \\ S_i^y &= S\sin(\theta_i) \end{aligned} \tag{15.41}$$

in which case the energy of the system behaves as

$$\begin{aligned} E &= -JS^2 \sum_{<i,j>} (\cos(\theta_i)\cos(\theta_j) + \sin(\theta_i)\sin(\theta_j)) \\ &= -JS^2 \sum_{<i,j>} \cos(\theta_i - \theta_j) \end{aligned} \tag{15.42}$$

and therefore the energy of system depends on the relative angle between the spins. For a ferromagnetic coupling $J > 0$ we would expect that the ground state has all the spins pointing in the same direction, that is, $\theta_i = \theta$ for all sites. In this case the total energy is $E_F = -JS^2 ZN$ where Z is the number of nearest neighbor sites. Observe, that the energy does not depend on θ which reflects the symmetry of the model with respect to rotations along the Z axis. A similar situation happens for antiferromagnetic interactions $J < 0$ in which case the system breaks into two sublattices where in one sublattice we have $\theta_i = \theta$ and in the other sublattice $\theta_i = \pi + \theta$ so that the classical energy is the same as in the ferromagnetic case. Observe that at the classical level there is no difference between ferromagnetic and antiferromagnetic lattices. This is very different from what we have seen in Chapter 11 where the quantum version of these tow models are very different from each other.

Let us study now the fluctuations around the ordered state by assuming small fluctuations around the ordering position say with $\theta = 0$. in this case $\theta_i \ll 1$ and we can expand the cosine term in (15.42) as

$$E \approx -JS^2 ZN + \frac{JS^2}{2} \sum_{<i,j>} (\theta_i - \theta_j)^2 \tag{15.43}$$

where the first term is the energy of the classical vacuum and the second represent the fluctuations around it. Moreover, we will be interested in length scales much larger than the lattice spacing a in which case the variables θ_i can be seen as smooth functions of the position. Moreover, since i and j are nearest neighbors we can write

$$\theta(\mathbf{r} + a\mathbf{n}) - \theta(\mathbf{r}) \approx a\mathbf{n} \cdot \nabla\theta(\mathbf{r}) \tag{15.44}$$

where $\mathbf{n}$ is the unit vector between nearest neighbor sites. This expansion is called a gradient expansion and it allows us to look at the continuum limit of the theory. Now we replace the sum over sites by a integral such that

$$\sum_j \to \int \frac{d\mathbf{r}}{a^d} \tag{15.45}$$

and the sum over nearest neighbors is replaced by $Za^2/(2d)$. In this case the total energy becomes

$$E \approx -JS^2ZN + \frac{\rho_M}{2}\int d\mathbf{r}(\nabla\theta)^2 \tag{15.46}$$

where

$$\rho_M = \frac{JS^2Z}{2da^{d-2}} \tag{15.47}$$

is the so-called the magnetic or spin stiffness of the model. Comparison of (15.20) and (15.46) shows the superconducting model and the magnetic model are in the same universality class since they have the same free energy. The main difference here rests on the form of the rigidity which is different in the two models. Indeed, we can immediately predict that the magnetic XY model cannot have long range order in $d \leq 2$ at any finite temperature.

Furthermore, the value for the rigidity found in (15.47) is only really valid at zero temperature. Like in the case of the superconductor we expect the spin stiffness to be temperature dependent and vanish at T_c (for $d > 2$) since in the disordered case the magnetic system cannot sustain long range fluctuations. To see that this is the case dimensional analysis shows immediately that ρ_M has dimensions of energy/length^{d-2} as one can see directly from (15.47). Since close to the phase transition all length scales are set by ξ_M, the magnetic correlation length, we expect that $\rho_M \propto T_c\xi_M^{2-d}$. Remember, however, that at the phase transition we must have a divergent correlation length and therefore

$$\xi_M(T) \propto \frac{1}{(T_c - T)^\nu} \tag{15.48}$$

where ν is the correlation length exponent ($\nu = 1/2$ in the case of a BCS superconductor - see (14.184)). Therefore, we conclude that close to the transition we must have

$$\xi_M(T) \propto (T_c - T)^{\nu(d-2)}\,. \tag{15.49}$$

Observe that for the BCS (or Ginzburg-Landau) which are mean-field theories this would lead for $d = 3$ to a correlation length vanishing like $(T_c - T)^{1/2}$ in disagreement with the result in the previous section, eq. (15.17), where the rigidity vanishes linearly with temperature. In fact the two results would only agree in $d = 4$! What is the reason for the disagreement? The reason is the failure of the mean field theory in describing the phase transition close to T_c where one has strong fluctuations of the order parameter.

Let us minimize the free energy (15.46) with respect to θ. It is very simple to see that it leads to

$$\nabla^2\theta(\mathbf{r}) = 0 \tag{15.50}$$

which is the Laplace equation. Naturally, this equation has a trivial solution $\theta(\mathbf{r}) = 0$ which is the homogeneous state. But let us assume that the system has a boundary condition such that $\theta(\mathbf{r})$ is zero along the plane $x = 0$ and $\theta(\mathbf{r}) = \alpha$ at $x = L$. Then the solution of the Laplace equation is

$$\theta(x, y, z) = \alpha\frac{x}{L} \tag{15.51}$$

that is, the angle made by the spins changes continuously along the X axis until it reaches the angle α as shown in Fig.15.2.

The free energy in this case is simply

$$F(\alpha, L) = \frac{\rho}{2}L^d\left(\frac{\alpha}{L}\right)^2 = \frac{\rho L^{d-2}\alpha^2}{2} \tag{15.52}$$

which can be interpreted as a *definition* of ρ, namely,

$$\rho = Lim_{L\to\infty} 2L^{d-2}\frac{F(\alpha, L) - F(0, L)}{\alpha^2} \tag{15.53}$$

that is, the rigidity is the amount of energy required to produce a twist in the order parameter. Notice that in $d = 2$ the free energy does not depend on the length and the rigidity has dimensions of energy. As we have seen, $d = 2$ is quite special because it is the upper critical dimension and one has the Kosterlitz-Thouless transition.

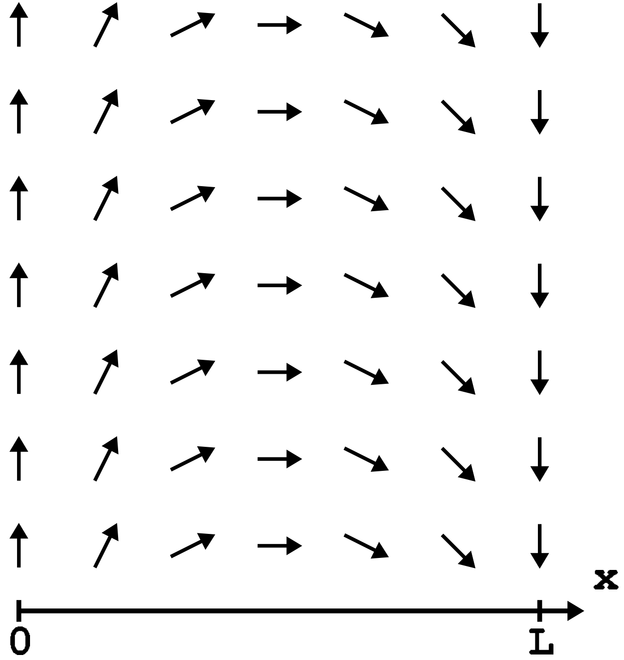

Figure 15.2: *.Twist of a spin texture along X axis by $\alpha = \pi$.*

15.4 Topological Defects

In the previous section we have seen that the homogeneous phase is a solution of the Laplace equation. There are, however, an infinite number of solutions of the Laplace equations depending on the boundary conditions. There are also singular solutions of the Laplace equation such as in the case of a fluxoid in a superconductor as discussed in the previous chapter. We are however interested in solutions in the absence of a magnetic field. These solutions are called vortices. From now on we consider only the $d = 2$ case.

Due to the cylindrical symmetry of the problem we rewrite the Laplace equation in polar coordinates:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \theta}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 \theta}{\partial \phi^2} = 0 \tag{15.54}$$

where r is the radial coordinate and ϕ the polar angle. Because θ in the spin problem is the angle the spin makes with a given axis the homogeneity of the problem implies that θ cannot depend on r. In this case the solution of the problem reduces to

$$\frac{\partial^2\theta}{\partial\phi^2} = 0 \tag{15.55}$$

which has a trivial solution

$$\theta(\mathbf{r}) = \theta_0 + n\phi \tag{15.56}$$

where θ_0 and n are, for the moment being, arbitrary constants. In Figs.15.3 and 15.4 we display the distribution of the spins for such configurations. The interesting aspect of such solutions is that they are singular at the origin. Indeed, consider the gradient of the solution given above

$$\nabla\theta(\mathbf{r}) = \frac{n}{r}\mathbf{u}_\phi \tag{15.57}$$

where $\mathbf{u}_\phi$ is the unit vector along the angle. Therefore, the gradient of θ diverges at $r = 0$. This implies that this particular solution costs energy. The singularity at the origin of the vortex has an striking property. Consider a closed line integral along a path C around the singularity

$$\int_C d\mathbf{l} \cdot \nabla\theta(\mathbf{r}) = n\int_C \frac{d\mathbf{l}\cdot\mathbf{u}_\phi}{r} = n\int_0^{2\pi} d\phi = 2\pi n \tag{15.58}$$

but observe that the quantity in the left hand side is just the total change in θ along the loop and therefore it has to be a multiple of 2π since the order parameter is periodic. This proves that n has to be an integer (positive or negative). This integer is called the *winding number* of the vortex. The energy required to create such defects can be obtained immediately from the substitution of (15.57) into (15.46):

$$\begin{aligned}\delta E &= \frac{\rho}{2}\int d\mathbf{r}\frac{n^2}{r^2} = \frac{2\pi\rho_S n^2}{2}\int_\ell^L \frac{dr}{r} \\ &= \pi n^2 \rho_S \ln(L/\ell)\end{aligned} \tag{15.59}$$

where ℓ is the size of the vortex core and L is the linear dimension of the system. We had to cut-off at very short distances because our theory was written in the continuum and therefore it is blind to length scales of the order of the lattice spacing. Quite generally we expect that there will be an extra amount of energy required in order to create the core. This energy is equivalent to the amount of energy required to suppress the order parameter in that particular region in space. In the case of the superconductor we have seen that deformations of the order parameter happen in a length scale determined by the correlation length ξ and thus we should suspect that indeed $\ell \sim \xi$. Let us estimate the size of the core using the previous results for the Ginzburg-Landau theory. From (15.16) we see that the amount of energy per unit of area (since we are in 2D) required to destroy the order parameter is given by

$$\delta f = -\frac{\delta F}{V} \approx \frac{\alpha^2}{2\beta} = \frac{\hbar^4}{8\beta(m^*)^2\xi^4} \tag{15.60}$$

where we used (14.184) (namely, $-\alpha = \hbar^2/(2m^*\xi^2)$). Thus, the total amount of energy required to destroy the order parameter in a circular region of size ℓ is

$$\delta E_c(\ell) \approx \frac{\pi\hbar^4\ell^2}{8(m^*)^2\beta\xi^4} \tag{15.61}$$

and the total energy required to create a vortex is given by the sum of the bulk energy (15.59) and the core energy (15.61)

$$\delta E(\ell) = \frac{\hbar^4\pi n^2}{2\beta(m^*)^2\xi^2}\ln(R/\ell) + \frac{\pi\hbar^4\ell^2}{8(m^*)^2\beta\xi^4} \tag{15.62}$$

where we used (15.17) and (14.173), that is,

$$\rho_S = \frac{\hbar^4}{2\beta(m^*)^2\xi^2}\,. \tag{15.63}$$

In order to calculate ℓ we minimize the total energy to create a vortex in respect to ℓ. We find

$$-\frac{\hbar^4\pi n^2}{2\beta(m^*)^2\xi^2\ell} + \frac{\pi\hbar^4\ell}{4(m^*)^2\beta\xi^4} = 0 \tag{15.64}$$

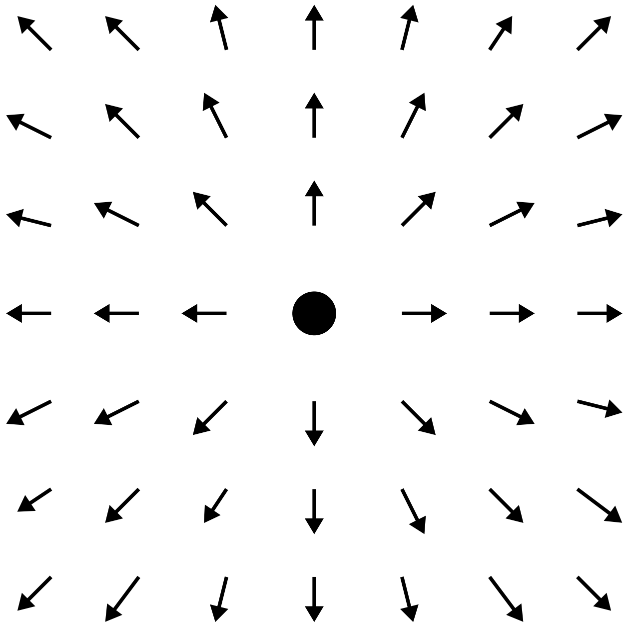

Figure 15.3: $\theta_0 = 0$, $n = 1$

and therefore

$$\ell \approx \sqrt{2} n \xi \tag{15.65}$$

and we confirm what our intuition had told us before. Observe, however, that this result also shows that the core increases with the winding number. If we replace this on (15.61) we see that

$$\delta E_c = \frac{\pi \rho_S}{2} n^2 \tag{15.66}$$

implying that the core energy of a vortex increases quadratically with the winding number. Therefore, vortices with large winding number will energetically unfavorable.

In any event we see that to create a vortex in the system requires an infinite amount of energy since, according to (15.59), this energy scales like $\ln(L)$, that is, with the size of the system. This is in fact very unlikely and therefore single, isolated, vortices are impossible to observe (unless you apply a magnetic field as we have seen in the previous

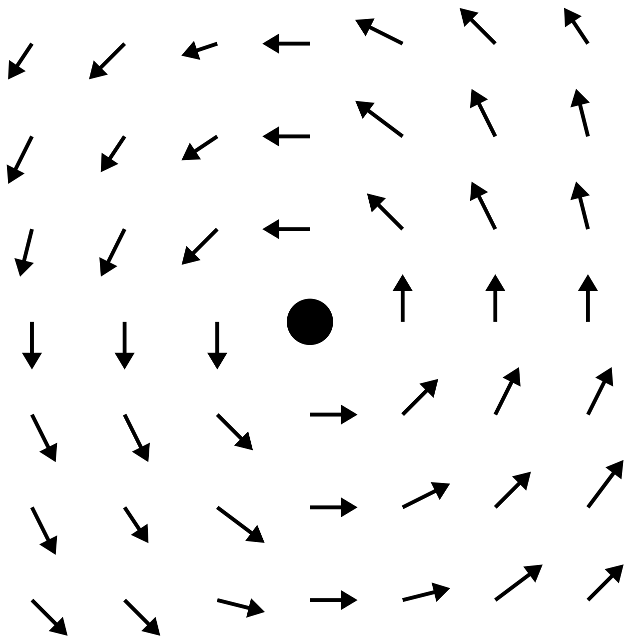

Figure 15.4: $\theta_0 = \pi/2$, $n = 1$

Chapter). Consider, however, the problem of creation of two vortices, say, θ_1 and θ_2, separated by a distance R. Your intuition would say that you need twice the energy, right? This is a situation where intuition fails miserably because the solution of the problem is a linear combination $\theta = \theta_1 + \theta_2$ and therefore the vortices have to interact. Suppose one of the vortices has winding number n_1 and the other has winding number n_2 and both of them are solution of the Laplace equation given in (15.56). The energy required to create a pair of vortices is therefore:

$$\begin{aligned} \delta E &= \frac{\rho_S}{2}\int d\mathbf{r}\,(\nabla(\theta_1(\mathbf{r}) + \theta_2(\mathbf{r}))^2 \\ &= \delta E_1 + \delta E_2 + \rho_S \int d\mathbf{r}\nabla\theta_1(\mathbf{r})\cdot\nabla\theta_2(\mathbf{r}) \\ &= \delta E_1 + \delta E_2 + 2\pi\rho_S n_1 n_2 \ln(L/R) \end{aligned} \tag{15.67}$$

where $\delta E_{1,2}$ are the energy required to create the isolated vortices. Substituting (15.59) into (15.67) we easily find

$$\delta E(n_1, n_2) = \pi(n_1 + n_2)^2\rho_S \ln(L/\ell) - 2\pi\rho_S n_1 n_2 \ln(R/\ell) \tag{15.68}$$

and therefore the dependence of the energy vanishes if $n_1 = -n_2$, that is, if the vortices have opposite winding numbers! This is a purely topological effect and it means that if you have a vortex and antivortex pair and evaluate the line integral (15.58) around the pair you will get zero. This statement can be generalized for any number of vortices in the system: if $N = \sum_i n_i$ vanishes then the total energy is independent of the size of the system. We see, however, that we still have to pay an energy

$$\delta E_{pair} = 2\pi\rho_S \ln(R/\ell) \tag{15.69}$$

in order to create a vortex-antivortex pair. But now this energy only depends on the relative distance between the pair (notice that our expression only makes sense when $R > \ell$).

A simple argument can now be used to argue that a new phase transition is possible in the presence of vortices. Consider the total free energy for the creation of a single vortex: $F = E - TS$ where S is the entropy of the system. Here E is given in (15.59). Notice that the vortex can be anywhere in the plane and since the minimum distance to create a vortex is ℓ then the number of possible positions for the vortex is of order $(L/\ell)^2$. Thus, S is given by $S = \ln[(L/\ell)^2] = 2\ln(L/\ell)$. Therefore the free energy is given by

$$F = (\pi\rho_S - 2T)\ln(L/\ell)\,. \tag{15.70}$$

Now we notice that the energy of the system is minimized by the creation of vortices when $L \to \infty$ if

$$T < T_{KT} = \frac{\pi\rho_S}{2} \tag{15.71}$$

which determines the Kosterlitz-Thouless temperature for a transition between a phase which is disordered to a phase with algebraic order.

15.5 The KT transition

In this section we are going to discuss the Kosterlitz-Thouless transition in more detail. Using (15.16) and (15.19) we can write

$$H = \frac{\rho_S}{2}\int d\mathbf{r}\ \mathbf{v}_S^2(\mathbf{r}) \tag{15.72}$$

and therefore depends on the velocity. In the presence of vortices $\mathbf{v}_S$ has an analytic part and a non-analytic part coming from vortices. The analytic part contributes only to the longitudinal component of the velocity while the vortex contribution is transverse. We write

$$\mathbf{v}_S(\mathbf{r}) = \mathbf{v}_{S||}(\mathbf{r}) + \mathbf{v}_{S\perp}(\mathbf{r}) + \mathbf{v} \tag{15.73}$$

where $\mathbf{v}$ is a uniform velocity induced by external sources. Observe that by definition:

$$\begin{aligned} \nabla \cdot \mathbf{v}_{S\perp} &= 0 \\ \nabla \times \mathbf{v}_{S||} &= 0\,. \end{aligned} \tag{15.74}$$

Let us now define a vector $\mathbf{m}$ such that

$$\begin{aligned} \mathbf{m}(\mathbf{r}) &= \nabla \times \mathbf{v}_S(\mathbf{r}) \\ &= \nabla \times \mathbf{v}_{S\perp}(\mathbf{r}) \end{aligned} \tag{15.75}$$

where we used the second equation in (15.74). Observe that $\nabla \cdot \mathbf{m} = 0$ by construction. The physical meaning of $\mathbf{m}$ becomes obvious when we consider a system with N_V vortices at positions $\mathbf{r}_\alpha$ with winding numbers n_α with $\alpha = 1, ..., N_V$ and take the integral of $\mathbf{v}_S$ along the contour C which wraps all the vortices:

$$\begin{aligned} \int_C \mathbf{v}_S \cdot d\mathbf{l} &= 2\pi \sum_\alpha n_\alpha \\ &= \int d\mathbf{S} \cdot \nabla \times \mathbf{v}_S = \int d\mathbf{S} \cdot \mathbf{m} \end{aligned} \tag{15.76}$$

where $\mathbf{S}$ is the vector oriented along the $\mathbf{z}$ direction and the first line comes from the the quantization condition (15.58) and in the second line we used Stokes theorem. Observe therefore that we must have

$$\begin{aligned} m(\mathbf{r}) &= \sum_\alpha 2\pi n_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha)\mathbf{z} \\ &= 2\pi n_V(\mathbf{r})\mathbf{z} \end{aligned} \tag{15.77}$$

where

$$n_V(\mathbf{r}) = \sum_\alpha n_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha) \tag{15.78}$$

is the vortex density in the system.

We can also invert the relationship between $\mathbf{m}$ and v_S if we consider that

$$\begin{aligned} \nabla\times\mathbf{m} &= \nabla\times(\nabla\times\mathbf{v}_{S\perp}) \\ &= \nabla(\nabla\cdot\mathbf{v}_{S\perp})-\nabla^2\mathbf{v}_{S\perp} = -\nabla^2\mathbf{v}_{S\perp} \end{aligned} \tag{15.79}$$

since the first equation of (15.74) should be valid. The general solution of this equation is

$$\mathbf{v}_{S\perp} = \nabla\times\int d\mathbf{r}' G(\mathbf{r}-\mathbf{r}')\mathbf{m}(\mathbf{r}') \tag{15.80}$$

where

$$\nabla^2 G(\mathbf{r}-\mathbf{r}') = -\delta(\mathbf{r}-\mathbf{r}') \tag{15.81}$$

which can be solved directly by Fourier transform:

$$G(\mathbf{r}) = \frac{1}{L^2}\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}G(\mathbf{q}) = -\int\frac{d^2q}{(2\pi)^2}\frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{q^2}\,. \tag{15.82}$$

The main issue is how the energy of the system is affected by the presence of a finite number of vortices. Again, by definition:

$$F(\mathbf{v}) = -\frac{1}{\beta}\ln\left(Tre^{-\beta H(\mathbf{v})}\right) \tag{15.83}$$

where, from (15.72) and (15.73), we see that

$$\begin{aligned} H(\mathbf{v}) &= \frac{\rho_S L^2 v^2}{2} + \frac{\rho_S}{2}\int d\mathbf{r}\left(\mathbf{v}_{S||}(\mathbf{r})+\mathbf{v}_{S\perp}(\mathbf{r})\right)^2 \\ &+ \rho_S\int d\mathbf{r}\mathbf{v}\cdot\left(\mathbf{v}_{S||}(\mathbf{r})+\mathbf{v}_{S\perp}(\mathbf{r})\right) \end{aligned} \tag{15.84}$$

and therefore it allows us to write the free energy in powers of $\mathbf{v}$:

$$\begin{aligned} F(\mathbf{v}) &= \frac{\rho_S L^2 v^2}{2} - \frac{1}{\beta}\ln\left(Tre^{-\beta H(\mathbf{v}=0)}e^{-\beta\rho_S\int d\mathbf{r}\mathbf{v}\cdot\left(\mathbf{v}_{S||}(\mathbf{r})+\mathbf{v}_{S\perp}(\mathbf{r})\right)}\right) \\ &\approx \frac{\rho_S L^2 v^2}{2} + F(0) - \frac{\beta\rho_S^2}{2}\int d\mathbf{r}\int d\mathbf{r}'\sum_{i,j}\langle\mathbf{v}_{Si}(\mathbf{r})\mathbf{v}_{Sj}(\mathbf{r}')\rangle v_i v_j \end{aligned} \tag{15.85}$$

where we have disregarded terms of order v^4. Observe that the average value of the velocity that appears in the above expression is calculated in the absence of external fields. In this case the longitudinal component of the velocity averages to zero and does not contribute. Thus, we just need to compute the average over the transverse component. Moreover, since the system is homogeneous the integrand above only depends on the relative distance $\mathbf{r} - \mathbf{r}'$ and therefore,

$$\frac{F(v) - F(0)}{L^2 v_s^2/2} = \rho_S - \beta \rho_S^2 \int d\mathbf{r} \langle \mathbf{v}_{S\perp}(\mathbf{r}) \mathbf{v}_{S\perp}(0) \rangle \tag{15.86}$$

which is exactly the definition of the stiffness given in (15.53). We call this the renormalized stiffness which can be written as

$$\begin{aligned} \rho_S^R &= \rho_S - \beta \rho_S^2 lim_{q\to 0} \langle \mathbf{v}_{S\perp}(\mathbf{q}) \cdot \mathbf{v}_{S\perp}(-\mathbf{q}) \rangle \\ &= \rho_S - \beta \rho_S^2 lim_{q\to 0} \frac{1}{q^2} \langle \mathbf{m}(\mathbf{q}) \cdot \mathbf{m}(-\mathbf{q}) \rangle \\ &= \rho_S - (2\pi)^2 \beta \rho_S^2 lim_{q\to 0} \frac{1}{q^2} \langle n_V(\mathbf{q}) n_V(-\mathbf{q}) \rangle \end{aligned} \tag{15.87}$$

where we used (15.80) and (15.82). Observe that in order to calculate the renormalized stiffness we need to know the correlation function for the vortex density which depends directly on the way the vortices interact. The renormalization of the stiffness is due to the presence of vortices in the system. Indeed, consider the situation of a vortex anti-vortex pair as in Fig.15.5. Because the vortices twist the background the energy required to twist each spin individually has to depend on the spatial scale of the twist, for instance, spins which are one lattice spacing apart will essentially require the same energy for the twist as in the case without vortices. Therefore, nearest neighbor spins will have a rigidity $\rho_S^R(\ell) = \rho_S$. However, spins which are far apart, say 10ℓ, from each other will be less correlated and therefore the rigidity has to decrease with distance, that is, $\rho_S(10\ell) < \rho_S$. This is the physical meaning of (15.87).

In order to calculate the change in the system due to the presence of the vortices we have to calculate their statistical properties. As we have seen in the last section (see equation (15.68) and (15.66)) the energy

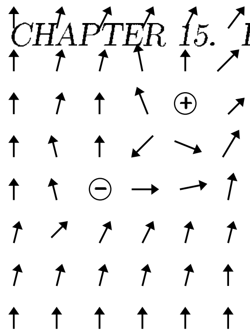

Figure 15.5: *Vortex anti-vortex pair*

for the interaction of the vortices can be written as

$$E[n_\alpha] = E_c \sum_\alpha n_\alpha^2 - \pi \rho_S \sum_{\alpha,\beta} n_\alpha n_\beta \ln(|R_\alpha - R_\beta|/\ell) \tag{15.88}$$

where the first term is just the core energy and the second term is the interaction between vortices. Moreover, we always have the constraint that

$$\sum_\alpha n_\alpha = 0 \tag{15.89}$$

which is the condition of having the same number of vortices and anti-vortices in the system. If one uses the definition of vortex density in (15.78) this expression can be written as

$$E[n_V] = E_c \sum_\alpha n_\alpha^2 - \pi \rho_S \int d\mathbf{r} \int d\mathbf{r}' n_V(\mathbf{r}) n_V(\mathbf{r}') \ln(|\mathbf{r} - \mathbf{r}'|/\ell) \tag{15.90}$$

where one must always remember that the energy given above is valid for $|\mathbf{r} - \mathbf{r}'|/\ell > 1$. Equation (15.90) has the form of the energy for a gas of charges n_α interacting with a logarithmic potential and overall neutral due to condition (15.89). This is the so-called Coulomb gas in two dimensions. Another way to rewrite the above energy is to assume that the vortices occupy sites on a lattice with lattice parameter ℓ and rewrite the energy as

$$E_V = E_c \sum_{\mathbf{R}} n_{\mathbf{R}}^2 - \pi \rho_S \sum_{\mathbf{R},\mathbf{R}'} n_{\mathbf{R}} n_{\mathbf{R}'} \ln(|\mathbf{R} - \mathbf{R}'|/\ell) \tag{15.91}$$

where $\mathbf{R}$ is the lattice vector. The whole problem now is to evaluate how the stiffness of the system renormalizes in the presence of vortices.

The problem can be simplified greatly by realizing that we are only interested in the limit of $q \to 0$ in (15.87). In fact we can write

$$\begin{aligned}
\langle n_V(\mathbf{q}) n_V(-\mathbf{q})\rangle &= \frac{1}{2L^2}\int d\mathbf{r}\int d\mathbf{r}' e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}\langle n_V(\mathbf{r}) n_V(\mathbf{r}')\rangle \\
&\approx \frac{1}{2L^2}\int d\mathbf{r}\int d\mathbf{r}' \left[1 + i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}') - (\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}'))^2\right]\langle n_V(\mathbf{r}) n_V(\mathbf{r}')\rangle \\
&\approx \kappa q^2 \qquad (15.92)
\end{aligned}$$

where the first term in (15.92) vanishes because of the charge neutrality, (15.89):

$$\int d\mathbf{r}\; n_V(\mathbf{r}) = \sum_\alpha n_\alpha = 0 \qquad (15.93)$$

and the second term vanishes by symmetry. Here we have defined

$$\begin{aligned}
\kappa &= -\frac{1}{4L^2}\int d\mathbf{r}\int d\mathbf{r}'(\mathbf{r}-\mathbf{r}')^2\langle n_V(\mathbf{r}) n_V(\mathbf{r}')\rangle \\
&= -\frac{1}{4L^2}\sum_{\mathbf{R},\mathbf{R}'}(\mathbf{R}-\mathbf{R}')^2\langle n_{\mathbf{R}} n_{\mathbf{R}'}\rangle\,. \qquad (15.94)
\end{aligned}$$

Substituting (15.92) into (15.87) we find

$$\rho_S^R = \rho_S - (2\pi)^2\beta\rho_S^2\kappa \qquad (15.95)$$

which reduces the problem to the calculation of κ in (15.94). Using (15.91) we see that the relevant function is

$$\begin{aligned}
\langle n_{\mathbf{R}} n_{\mathbf{R}'}\rangle &= \frac{1}{Z}\sum_{\{n_{\mathbf{T}}\}}\left[n_{\mathbf{R}} n_{\mathbf{R}'} e^{-\beta E_c \sum_{\mathbf{T}} n_{\mathbf{T}}^2 + \pi\beta\rho_S\sum_{\mathbf{T},\mathbf{T}'} n_{\mathbf{T}} n_{\mathbf{T}'}\ln(|\mathbf{T}-\mathbf{T}'|/\ell)}\right] \\
&= \frac{1}{Z}\sum_{\{n_{\mathbf{T}}\}}\left[n_{\mathbf{R}} n_{\mathbf{R}'} y^{\sum_{\mathbf{T}} n_{\mathbf{T}}^2} e^{\pi K\sum_{\mathbf{T},\mathbf{T}'} n_{\mathbf{T}} n_{\mathbf{T}'}\ln(|\mathbf{T}-\mathbf{T}'|/\ell)}\right] \qquad (15.96)
\end{aligned}$$

where $Z = \sum_{\{n_{\mathbf{T}}\}} e^{-\beta E_V[n_{\mathbf{T}}]}$ and we have defined

$$\begin{aligned}
y &= e^{-\beta E_c} \\
K &= \beta\rho_S\,. \qquad (15.97)
\end{aligned}$$

Notice that at low temperatures the fugacity, y, is very small and therefore it can be used as an expansion parameter. Moreover, in using the expression above one has to remember that the correlation function has to be calculated with the constraint (15.89) of charge neutrality. The first trivial term is $n_{\mathbf{T}} = 0$ for all $\mathbf{T}$ which is equivalent to the total absence of vortices. Then $\rho_S^R = \rho_S$, as expected. The first non-trivial term happens with a single vortex anti-vortex pair in the system, that is, $n_{\mathbf{T}} = \pm 1$ and $n_{\mathbf{T}} = \mp 1$. In this case $\sum_{\mathbf{T}} n_{\mathbf{T}}^2 = 2$ and we find

$$\begin{aligned} \langle n_{\mathbf{R}} n_{\mathbf{R}'} \rangle &\approx -2y^2 e^{-2\pi K \ln(|\mathbf{R}-\mathbf{R}'|/\ell)} \\ &\approx -2y^2 (|\mathbf{R}-\mathbf{R}'|/\ell)^{-2\pi K} \end{aligned} \tag{15.98}$$

implying that the correlations between vortex anti-vortex pairs decays algebraically. Inserting this expression into the definition of κ we find

$$\begin{aligned} \kappa &\approx \frac{y^2}{2L^2} \sum_{\mathbf{R},\mathbf{R}'} (|\mathbf{R}-\mathbf{R}'|/\ell)^{2-2\pi K} \\ &\approx \frac{y^2}{2} \int \frac{d\mathbf{r}}{\ell} (r/\ell)^{2-2\pi K} \\ &\approx \pi y^2 \int_\ell^\infty \frac{dr}{\ell} (r/\ell)^{3-2\pi K} \end{aligned} \tag{15.99}$$

where we have introduced the lattice cut-off ℓ. Replacing the above expression into (15.95) using the definition (15.97) we find

$$K_R \approx K - 4\pi^3 K^2 y^2 \int_\ell^\infty \frac{dr}{\ell} (r/\ell)^{3-2\pi K} \tag{15.100}$$

but remembering that we are at low temperatures so that $K \gg 1$ and using the fact that $y \ll 1$ it is convenient to rewrite the above equation as

$$K_R^{-1} \approx K^{-1} + 4\pi^3 y^2 \int_\ell^\infty \frac{dr}{\ell} (r/\ell)^{3-2\pi K} \tag{15.101}$$

which gives the renormalization of the rigidity in terms of the fugacity y and the minimum distance between vortices ℓ. Observe that if $3 - 2\pi K \leq -1$, that is, $K \geq 2/\pi$ the above integral converges in the upper limit and one finds the correction to the rigidity in the presence of vortices. However, if $K < 2/\pi$ then the integral is divergent showing that our fugacity expansion was actually wrong. We observe that the critical value of $K = 2/\pi$ is equivalent to have $k_B T = \pi \rho_S / 2$ that is, $T = T_{KT}$ as we can readily see from (15.71). Thus, the divergence is signaling the instability of the system to quasi-long range order. In the ordered phase we expect the vortices to disappear completely at zero temperature because vortices and anti-vortices attract each other through the logarithmic potential and eventually annihilate. In the disordered phase, however, the vortices are free to move and behave like independent particles. It is clear that the problem at hand has two different distance scales associated with the long range interaction and the short range core size.

Let us separate the short from the long distance part by breaking the integral in (15.101) as

$$\int_{\ell}^{\infty} \frac{dr}{\ell} (r/\ell)^{3-2\pi K} = \int_{\ell}^{\ell b} \frac{dr}{\ell} (r/\ell)^{3-2\pi K} + \int_{\ell b}^{\infty} \frac{dr}{\ell} (r/\ell)^{3-2\pi K} \tag{15.102}$$

where $b > 1$ is an arbitrary number. In this case we can rewrite (15.101) as

$$K_R^{-1}(b) = (K')^{-1}(b) + 4\pi^3 y^2 \int_{\ell b}^{\infty} \frac{dr}{\ell} (r/\ell)^{3-2\pi K} \tag{15.103}$$

where

$$(K')^{-1}(b) = K^{-1} + 4\pi^3 y^2 \int_{\ell}^{\ell b} \frac{dr}{\ell} (r/\ell)^{3-2\pi K} . \tag{15.104}$$

We now interpret (15.103) as the change in the stiffness when the lattice spacing changes from ℓ to ℓb. If we change $r \to r/b$ in (15.103) we immediately find

$$K_R^{-1}(b) = (K')^{-1}(b) + 4\pi^3 (y'(b))^2 \int_{\ell}^{\infty} \frac{dr}{\ell} (r/\ell)^{3-2\pi K} \tag{15.105}$$

where

$$y'(b) = b^{2-\pi K} y \tag{15.106}$$

which is interpreted as the change in the fugacity of the system due to rescale of the lattice spacing. In other words, we have defined a new length scale, ℓ', such that,

$$\ell' = \ell b = \ell e^{\epsilon} \tag{15.107}$$

which now becomes our new unit of length. Naturally, this change can made arbitrarily small, that is, we can write $b = e^{d\epsilon} \approx 1 + d\epsilon$ in which case we can rewrite (15.104) and (15.106) as

$$\begin{aligned} K^{-1}(1+d\epsilon) &\approx K^{-1}(1) + 4\pi^3 y^2(1) d\epsilon \\ y(1+d\epsilon) &= y(1) + (2-\pi K) y(1) d\epsilon \end{aligned} \tag{15.108}$$

where we have re-interpreted $K' = K(1 + d\epsilon)$. These equations can now be written in differential form

$$\begin{aligned} \frac{dK^{-1}}{d\epsilon} &= 4\pi^3 y^2 \\ \frac{dy}{d\epsilon} &= (2-\pi K) y \end{aligned} \tag{15.109}$$

which tell us how the rigidity of the system and its fugacity change or *renormalize* as we change the scale of distance in the system. Since ϵ can be changed arbitrarily these equations describe a continuous *flow* of the K^{-1} and y parametrically in y. This is called a *renormalization group* flow.

To understand the meaning of these equations consider the stationary points of the flow, that is, points which not change under l. It is clear that all points on the line $y = 0$ are invariant under the flow. Moreover, there is a special point at $y = 0$ and $K = 2/\pi$ which separates regions where the fugacity decreases under the flow $(dy/d\epsilon < 0)$ for $K^{-1} < \pi/2$ and therefore perturbation theory is valid, and regions where the fugacity grows $(dy/d\epsilon > 0)$ for $K^{-1} > \pi/2$ and perturbation theory breaks down indicating that the system becomes unstable. The flow of the parameters is shown on Fig.15.6.

Notice that there is a separatrix in the RG flow at $y = 0$ and $K = 2/\pi$. For points on the left hand side of the separatrix we see that $y \to 0$ while $K_R^{-1} \to K$ that is, the system flows for the case without vortices. For points on the right hand side of the separatrix we see that

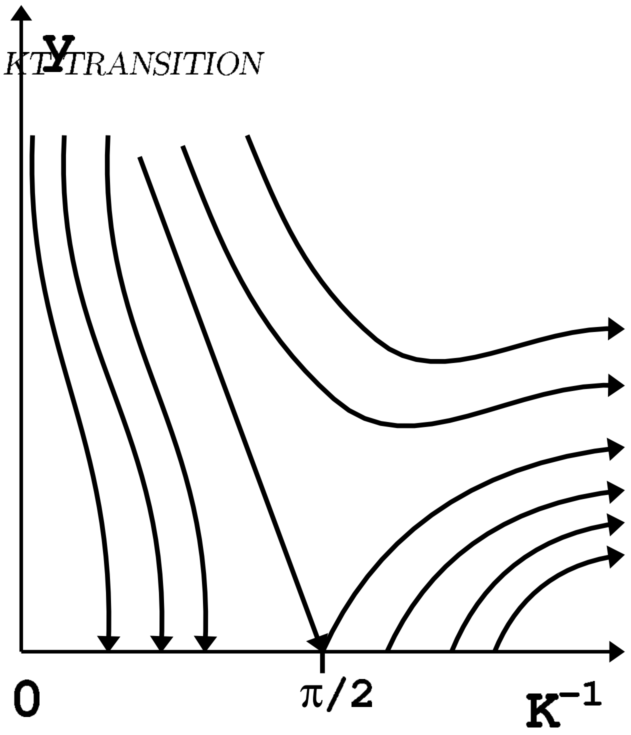

Figure 15.6: *Renormalization Group Flow*

$y \to \infty$ and $K_R^{-1} \to \infty$ indicating that the rigidity goes to zero implying a disordered phase. Exactly at the separatrix we have $y \to 0$ and $K_R^{-1} \to \pi/2$. Since K is inversely proportional to the temperature the interpretation is obvious in terms of the phase transition: at $T \to T_{KT}^-$ we have an universal value $K_R \to 2/\pi$ that is,

$$\frac{\rho_S^R}{k_B T_{KT}} = \frac{2}{\pi} \tag{15.110}$$

is independent of the details which determine ρ_S^R and T_{KT}. Looking back at equation (15.36) we see that the order parameter correlations decay like

$$\langle \Psi^\dagger(r)\Psi(0)\rangle \propto \frac{1}{r^\eta} \tag{15.111}$$

where, accordingly to (15.37) and (15.97) we have

$$\eta = \frac{1}{4} \tag{15.112}$$

at the transition. This gives the universal value of the correlations at the transition.

In order to gather more information from the RG equations given above we are going to study the RG flow close to the critical point $y = 0$ and $K = 2/\pi$ in more detail. Let us first rewrite

$$K = \frac{2}{\pi}(1 - x) \tag{15.113}$$

where $x \ll 1$ so that $K^{-1} \approx (\pi/2)(1+x)$. In this case the RG equations (15.109) are given by

$$\begin{aligned} \frac{dx}{d\epsilon} &= 8\pi^2 y^2 \\ \frac{dy}{d\epsilon} &= 2xy \end{aligned} \tag{15.114}$$

which can also be rewritten in a different form

$$\begin{aligned} \frac{dx^2}{d\epsilon} &= 16\pi^2 x y^2 \\ \frac{dy}{d\epsilon} &= 4xy^2 \end{aligned} \tag{15.115}$$

and dividing the first by the second equation we get

$$\frac{dx^2}{dy^2} = 4\pi^2 \tag{15.116}$$

which can be solved at once

$$y^2(\epsilon) = \frac{1}{4\pi^2}(x^2(\epsilon) + \delta) \tag{15.117}$$

where δ is a constant independent of ϵ. Notice that (15.117) is a parametric equation of y as a function of x which describes a set of hyperbola as shown in Fig.15.7. If $\delta > 0$ the hyperbola do not touch the horizontal axis but when $\delta < 0$ they touch the axis at $x^* = \pm\sqrt{|\delta|}$. Notice that $\delta = 0$ is the separatrix between the two different behaviors and all systems which have their parameters on the separatrix flow to the fixed point at the origin. Thus, δ measures the deviation from criticality.

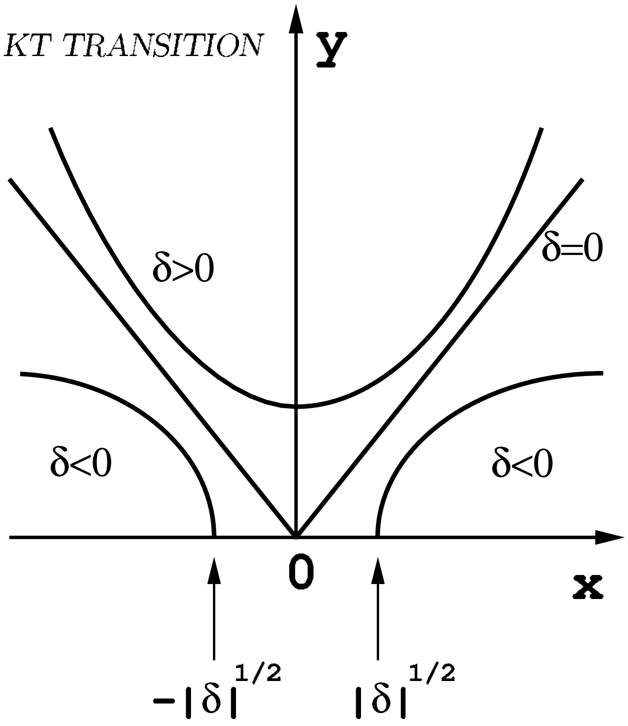

Figure 15.7: *Plot of solution (15.117).*

Close to criticality we can always expand δ is powers of the deviation from the temperature and keep the leading term:

$$\delta(T) = b^2(T - T_{KT})\,. \tag{15.118}$$

Having (15.117) at hand we can replace it back into (15.114) in order to find

$$\frac{dx}{d\epsilon} = 2(x^2 + \delta) \tag{15.119}$$

which can be integrated immediately

$$\begin{aligned} \int_{x_0}^{x(\epsilon)} \frac{dx}{x^2+\delta} &= 2\int_0^{\epsilon} d\epsilon' \\ \int_{u_0}^{u(\epsilon)} \frac{du}{u^2 + sgn(\delta)} &= 2\sqrt{|\delta|}\epsilon \end{aligned} \tag{15.120}$$

where in the second line we changed variables:

$$u(\epsilon) = \frac{x(\epsilon)}{\sqrt{|\delta|}} \tag{15.121}$$

and $sgn(x) = +1$ if $x > 0$ and -1 otherwise is the sign function.

Let us consider first the behavior of the above integral in the ordered phase ($T < T_{KT}$), that is, $\delta < 0$, and the integral is:

$$\int_{u_0}^{u(\epsilon)} \frac{du}{u^2-1} = \frac{1}{2}\ln\left(\frac{1-u}{1+u}\frac{1+u_0}{1-u_0}\right) \tag{15.122}$$

which gives

$$u(\epsilon) = -\frac{1-Ce^{-4\sqrt{|\delta|}\epsilon}}{1+Ce^{-4\sqrt{|\delta|}\epsilon}} \tag{15.123}$$

where

$$C = \frac{1+u_0}{1-u_0}. \tag{15.124}$$

Therefore we have from (15.121):

$$x(\epsilon) = -\sqrt{|\delta|}\frac{1-Ce^{-4\sqrt{|\delta|}\epsilon}}{1+Ce^{-4\sqrt{|\delta|}\epsilon}}. \tag{15.125}$$

This result has a direct physical implication. Since ϵ measures the length scales in the system it is clear that at the macroscopic level we have $\epsilon \to \infty$ in which case

$$x(\infty) = -\sqrt{|\delta|} \tag{15.126}$$

which substituted in (15.113) gives the macroscopic value of the stiffness:

$$\begin{aligned} K_R(\infty) &= \frac{2}{\pi}\left(1+\sqrt{|\delta|}\right) \\ &\approx \frac{2}{\pi}\left(1+b\sqrt{T_{KT}-T}\right) \end{aligned} \tag{15.127}$$

which shows that the stiffness is only weakly renormalized by the vortices in the ordered phase and that at $T = T_{KT}$ it reduces to the universal value given in (15.110).

In the disordered phase ($T > T_{KT}$), that is, $\delta > 0$ the integral in (15.120) gives:

$$\int_{u_0}^{u(\epsilon)} \frac{du}{u^2+1} = arctan(u) - arctan(u_0) \tag{15.128}$$

which leads to

$$x(\epsilon) = \sqrt{\delta} tan \left[arctan(x_0/\sqrt{\delta}) + 2\epsilon\sqrt{\delta} \right] . \tag{15.129}$$

Therefore, unlike the solution in the ordered phase we see that $x(\epsilon)$ becomes divergent at

$$\epsilon^* = \frac{\pi}{4\sqrt{\delta}} - \frac{arctan(x_0/\sqrt{\delta})}{2\sqrt{\delta}} \tag{15.130}$$

at this scale $x(\epsilon)$ becomes so large that our approximation of small x breaks down. First notice that for $T \approx T_{KT}$ we have from (15.118) that $\delta \to 0$. Assuming that $x_0 < 0$ we see that the above scale becomes

$$\epsilon^* \approx \frac{\pi}{2\sqrt{\delta}} . \tag{15.131}$$

Looking back into the definition of x on (15.113) that when $x \approx 1$ the stiffness should vanish. Since the stiffness measures the energy required to twist infinitesimally the order parameter it means, from (15.107), that there is a length scale above which the stiffness vanishes, that is, the spins in a XY model are not coupled anymore. But this is exactly the definition of the correlation length of the model. Thus, we see from (15.107) we have

$$\begin{aligned} \xi_{KT}(T) &= \ell e^{\epsilon^*} = \ell e^{\frac{\pi}{2\sqrt{\delta}}} \\ &= \ell e^{\frac{b'}{\sqrt{T-T_{KT}}}} \end{aligned} \tag{15.132}$$

where $b'b = \pi/2$ gives the way the correlation length of the system diverges at the transition. Observe that ξ_{KT} also sets the scale for the density of unbound vortices, n_U, in the disordered phase:

$$n_U \propto \frac{1}{\xi_{KT}^2(T)} \tag{15.133}$$

showing that the vortices disappear completely in the ordered phase, as expected.

15.6 Problems

1. Using solution (15.3) show that the super-current density is given by expression (15.4) and that the variation of the free energy is given by (15.7).

2. Demonstrate that (15.31) is correct.

3. Calculate explicitly the correlation function (15.36) for the order parameter in $d = 2$.

4. In this exercise we are going to consider the validity of the mean field theory for the Ginzburg-Landau approach. Let $\delta\Psi(\mathbf{r}) = \Psi(\mathbf{r}) - \Psi_0$ be the fluctuation of the order parameter around its average value Ψ_0. In a volume of size $V = \xi^d$ the order parameter deviates from its mean value by

   $$\delta\Psi = \frac{1}{V}\int_V d\mathbf{r}\delta\Psi(\mathbf{r})$$

   and therefore fluctuations around the average value will be small if the variance of the order parameter $\sqrt{\langle|\delta\Psi|^2\rangle}$ is much smaller than the average value, that is,

   $$\begin{aligned} \langle|\delta\Psi|^2\rangle &\ll |\Psi_0|^2 \\ \frac{1}{V^2}\int_V d\mathbf{r}\int d_V d\mathbf{r}'\langle\delta\Psi^\dagger(\mathbf{r})\delta\Psi(\mathbf{r}')\rangle &\ll |\Psi_0|^2 . \end{aligned}$$

   (*i*) Using the fact that the system is homogeneous and isotropic show that the condition above can be written as

   $$\frac{1}{V}\int_V d\mathbf{r}\langle\delta\Psi^\dagger(\mathbf{r})\delta\Psi(0)\rangle \ll |\Psi_0|^2 . \tag{15.134}$$

   (*ii*) Assuming that the Fourier transform of $\langle\delta\Psi^\dagger(\mathbf{r})\delta\Psi(0)\rangle$ is a Lorentzian with width of the correlation length, ξ, show that

   $$\langle\delta\Psi^\dagger(\mathbf{r})\delta\Psi(0)\rangle = \frac{a}{r^{d-2}}f(r/\xi) \tag{15.135}$$

where a is a constant and $f(x)$ is some function of its argument. From this result derive that

$$\frac{1}{V}\int_V d\mathbf{r}\langle\delta\Psi^\dagger(\mathbf{r})\delta\Psi(0)\rangle = \frac{C}{\xi^{d-2}} \tag{15.136}$$

where C is a constant.

(*iii*) From the Ginzburg-Landau approach show that

$$\Psi_0^2 = \frac{\hbar^2}{2m^*\xi^2}$$

and from that show that the condition (15.134) can be written as

$$\xi^{d-4} \gg \frac{2m^*C}{\hbar^2} \tag{15.137}$$

which is the condition for the fluctuations of the order parameter to be small and its average value.

(*iv*) Suppose $T \to T_c$ and $d > 4$. What can you conclude from (15.137)?

(*iv*) Suppose $T \to T_c$ and $d < 4$. What can you conclude from (15.137)?

It is obvious that $d = 4$ is special dimension in this problem. It is called the upper critical dimension.

5. Show that (15.66) is correct.

6. Consider a system with N_V vortices with winding numbers n_α with $\alpha = 1, ..., N_V$ which satisfy the Laplace equation (15.55).

   (*i*) Show that $\theta(\mathbf{r}) = \sum_{\alpha=1}^{N_V} \theta_\alpha(\mathbf{r})$ is also a solution of that equation.

   (*ii*) Show that

$$\theta_\alpha(\mathbf{r}) = n_\alpha arctan\left(\frac{y - y_\alpha}{x - x_\alpha}\right)$$

   where (x_α, y_α) is the position of the core. *Hint: use complex coordinates, $z = x + iy$.*

   (*ii*) Calculate the energy required to produce such vortices and show that it does not depend on the size of the system when condition (15.89) is obeyed.

7. Prove (15.101).

8. Starting from (15.120) show that (15.123) and (15.129) are solutions in the ordered and disordered phase, respectively.