

Solid State Physics

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Chapter 1

Second Quantization

Solid state physics deals with collective behavior of many electrons against the background of periodically placed ions. The need to treat the many-particle system in a consistent and simple manner becomes imminent. In a departure with the conventional treatment of a graduate course on solid state physics we thus begin with a discussion of second quantization, which is just such a formulation of a many-particle quantum system. Non-interacting Fermi gas is introduced both as an illustration of the power and use of second quantization and as a building block upon which the complications of real solids will be founded.

1.1 Formulation

Think of a simple problem of putting a particle in a box. We already know that the eigenstates of this particle are described by harmonic functions (sin's and cos's) and that a wave function with more nodes (this is roughly speaking the number of wavelengths that fit inside the box) generally has higher energy, etc.

Figure 1.1: A particle confined to a ring of radius R .

We can simplify the problem and solve instead the quantum-mechanical problem of a particle confined to a ring of radius R as shown in Fig. 1.1. The position of the particle can be labelled by the angle θ , or by $x \equiv R\theta$. The Schrödinger equation expressed in terms of x will read¹

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x). \quad (1.1)$$

¹I typically omit the fine distinction between a total derivative dx and the partial derivative ∂x . It will be obvious from the context.

This equation can be simplified by writing $k^2 = \frac{2mE}{\hbar^2}$, then we will have

$$\left(\frac{d^2}{dx^2} + k^2\right)\psi(x) = 0. \quad (1.2)$$

The solution of this differential equation is e^{ikx} , e^{-ikx} , or some linear combination of the two, $Ae^{ikx} + Be^{-ikx}$. Because we are dealing with a particle on a ring, we must also require that eigenfunction obey the property $\psi(x + 2\pi R) = \psi(x)$. This is the uniqueness condition of the wave function. Taking $L \equiv 2\pi R$, we immediately see that only a special selection of k values will obey this constraint:

$$kL = 2\pi n, \quad n = \text{integer}. \quad (1.3)$$

As a result eigenenergies must also occur at special values

$$E_n = \frac{\hbar^2}{2m} \left(\frac{2\pi n}{L}\right)^2. \quad (1.4)$$

What we described above is actually a very general procedure in dealing with a quantum-mechanical problem. First we reduce the problem to some sort of differential equation. The solutions of this equation are the eigenfunctions of the problem at hand. Finally there are some *constraints*, such as the uniqueness of the wave function discussed above, that restrict the allowed quantum numbers. In the case of the particle on a ring the restriction was on the momentum quantum number k , which in turn implied the quantization of energy. It can be truthfully claimed that the essence of solving one-particle quantum mechanics is all in the example just described. Now let's ask what happens if we put two particles on a ring.

It should be immediately obvious that one needs more than one coordinate to describe the system, so let's introduce x_1 and x_2 to denote the position of the particles. The Schrödinger equation for the two-particle case will go something like

$$-\frac{\hbar^2}{2m} \left(\frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2}\right)\psi(x_1, x_2) = E\psi(x_1, x_2). \quad (1.5)$$

The eigenfunction $\psi(x_1, x_2)$ depends on two coordinates because there are two particles in the system. On the other hand one cannot help the notion that each particle behaves more or less like what it did before when there was only one particle on a ring. This will be particularly true provided the two particles do not interact with each other. For example if these two particles were charged, then there will be a Coulomb potential $\frac{e_1 e_2}{|x_1 - x_2|}$ between the two, and one can no longer say that the motions of the particles are independent.

For now we ignore this interaction effect and proceed to verify our intuition about the independence of two particles. Writing $\psi(x_1, x_2) = \varphi(x_1)\varphi(x_2)$ - this is just separation of variables - and substituting it into Eq. (1.5) yields

$$\begin{aligned} \left(\frac{d^2}{dx_1^2} + k_1^2\right)\varphi(x_1) &= 0, \\ \left(\frac{d^2}{dx_2^2} + k_2^2\right)\varphi(x_2) &= 0, \end{aligned} \quad (1.6)$$

and $E = \frac{\hbar^2}{2m}(k_1^2 + k_2^2)$. The energy is the sum of the energies of the individual state $\varphi(x_1)$ and $\varphi(x_2)$, as should be the case if the two particles were indeed non-interacting. Building on our experience with the one-particle problem we know that each eigenfunction is characterized by a quantum number n , where n is given by $k = 2\pi n/L$. Since there are two particles we better have two numbers, (n_1, n_2) , to completely specify the eigenstate of the system.

The associated two-particle eigenfunction can be written down as $\phi_{n_1}(x_1)\phi_{n_2}(x_2)$. This will indicate the physical state where particle number 1 resides in the eigenstate of quantum number n_1 , and the particle number 2 in the state with quantum number n_2 . One can also ask to write down the eigenstate with the two particles located in n_2 and n_1 . However, since the two particles are assumed *identical*, this is really the same state as the the first state we wrote down. Loosely speaking, we have

$$\phi_{n_1}(x_1)\phi_{n_2}(x_2) \sim \phi_{n_1}(x_2)\phi_{n_2}(x_1). \quad (1.7)$$

So which state do we choose to describe the state that is characterized by the occupation of the two quantum states (n_1, n_2) : $|n_1 n_2\rangle$? The answer is given by Pauli's exclusion principle that states that no two electrons shall occupy the same quantum state. This statement finds its mathematical incarnation in the following linear combination:

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}}[\phi_{n_1}(x_1)\phi_{n_2}(x_2) - \phi_{n_1}(x_2)\phi_{n_2}(x_1)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{n_1}(x_1) & \phi_{n_1}(x_2) \\ \phi_{n_2}(x_1) & \phi_{n_2}(x_2) \end{vmatrix}.$$

From the well-known theorem of linear algebra one finds that this wave function vanishes if $n_1 = n_2$ (two rows are equal). Vanishing of the wave function implies zero probability of its occurring, so it will never happen. Similarly one finds that the wave function vanishes if $x_1 = x_2$ (two columns are equal). This sometimes leads to the alternative version of Pauli's principle that says that no two electrons shall occupy the same place in space. The overall factor $1/\sqrt{2}$ is inserted so that the two-particle wave function $\psi(x_1, x_2)$ is once again normalized: $\int dx_1 dx_2 |\psi(x_1, x_2)|^2 = 1$. One can check this as an exercise problem.

For three particles on a ring, the same reasoning (and a little bit of mathematical ingenuity) will allow you to write down the wave function that also obeys Pauli's principle:

$$\psi(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{n_1}(x_1) & \phi_{n_1}(x_2) & \phi_{n_1}(x_3) \\ \phi_{n_2}(x_1) & \phi_{n_2}(x_2) & \phi_{n_2}(x_3) \\ \phi_{n_3}(x_1) & \phi_{n_3}(x_2) & \phi_{n_3}(x_3) \end{vmatrix}.$$

Generalization to arbitrary N -electron system should now be obvious. Professor Slater realized this is the right way to write down the wave function for N -electron problems, so this type of determinant expression for the wave function is often known as the Slater determinant. Although the Slater determinant wave function is correct, working with it is another matter: It is too cumbersome! So a more convenient method of expression will have to be invented. It is call the "second quantization". Second quantization is just a convenient way to express the wave function for a many-particle system. Before we discuss the formalism, we are reminded once again that the whole information contained in the wave function such as Eq. 1.8 can be conveniently summarized as $|\psi\rangle = |n_1, n_2, n_3\rangle$.

We generalize to N -particles confined on the same ring. Naturally the eigenstate is characterized by N integers, (n_1, n_2, \dots, n_N) , each n_i specifying the state of the particles that make up the system. Now let's discuss a different, yet completely equivalent way of describing the same state. Instead of worrying about which particle is in what state, we simply state how many particles there are in each state. For example if there are 10 particles on a ring and three of them are in $n=1$ state, four in $n=2$ state, and the remaining three in $n=3$ state, then we say the state is $|3, 4, 3, 0, 0, \dots\rangle$. The numbers from left to right indicate how many particles there are in each eigenstate. Generally the state will be given the assignment $|N_1 N_2 N_3 \dots\rangle$ with N_i the number of particles in i -state.

There is an extremely nice way of writing down arbitrary many-particle states on a ring by invoking what's called creation operators a_n^\dagger for each state n . For instance $|3, 4, 3, 0, 0, \dots\rangle$ would be written $(a_3^\dagger)^3 (a_2^\dagger)^4 (a_1^\dagger)^3 |0\rangle$. This expression, when read from right to left, says the following: Out of the vacuum $|0\rangle$ (a state with no particles) insert(create) three particles into eigenstate 1 ($a_1^\dagger a_1^\dagger a_1^\dagger = (a_1^\dagger)^3$), then four particles into state $n=2$ ($(a_2^\dagger)^4$), and finally three into state $n=3$ ($(a_3^\dagger)^3$).

Suppose now we want to remove one of the particles that were previously in $n=3$ state. Since adding a particle was given the notation a_n^\dagger , we define a_n to express the act of removing a particle from state n . The desired state consisting of 3 particles in $n=1$, 4 particles in $n=2$, and 2 particles in $n=3$ is given by $a_3 (a_3^\dagger)^3 (a_2^\dagger)^4 (a_1^\dagger)^3 |0\rangle$. On the other hand, it should be no surprise that a completely equivalent state is given by $(a_3^\dagger)^2 (a_2^\dagger)^4 (a_1^\dagger)^3 |0\rangle$ because now there are two particles occupying 3-state. Thus, we must have $a_3 (a_3^\dagger)^3 \sim (a_3^\dagger)^2$, or more generally

$$a_n^\alpha (a_n^\dagger)^\beta |0\rangle \sim (a_n^\dagger)^{\beta-\alpha} |0\rangle, \quad \beta \geq \alpha. \quad (1.8)$$

There are a set of rules that these annihilation/creation operators must obey, which we list below.

$$\begin{aligned} a_m^\dagger a_n^\dagger &= a_n^\dagger a_m^\dagger \\ a_n a_m &= a_m a_n \\ a_m a_n^\dagger &= a_n^\dagger a_m \quad (n \neq m) \\ a_m a_m^\dagger &= a_m^\dagger a_m + 1. \end{aligned} \quad (1.9)$$

If you like, you may take the set of commutation rules given above as *ansatz*, just as the Schrödinger equation or the Newton's equation are *ansatz* about the laws of nature. We uphold these equations as sacred only because by doing so, we get wonderful agreement between our theoretical expectation and the experimental outcome. In the same vein the commutation rules, as they are known, shown in Eq.(1.9) are the *ansatz* that proved to be in wonderful agreement with the minute-to-minute workings of nature.

The first two lines of Eq. (1.9) say that when we remove or add particles from states m and n , it doesn't matter in which order we carry out the procedure. The end result is the same. The third line says more or less the same thing, provided m is not the same state as n . The last line is tricky because there is a difference of one between $a_m a_m^\dagger$ and $a_m^\dagger a_m$. In one instance this statement is saying something obvious. When we let both sides of the fourth line act on

the vacuum, then $a_m a_m^\dagger |0\rangle$ must return the vacuum again. But we cannot say $a_m^\dagger a_m |0\rangle$ is the vacuum because $a_m |0\rangle$ is a state that would have -1 particle. Such a statement is absurd and cannot possibly exist, so we write $a_m |0\rangle = 0$. The zero on the r.h.s. simply says this operation doesn't make physical sense. Without the +1 term in the fourth line of Eq. (1.9), we would have $|0\rangle = 0$, but thanks to the factor +1, we get $|0\rangle = +|0\rangle$! The important point is that the commutation algebra $[a_m, a_m^\dagger] = 1$ holds true regardless of the quantum state on which the operators act.

There are two types of particles in nature. One are bosons and they obey the commutation rules displayed in Eq. (1.9). The other are fermions, such as electrons and quarks, and they obey a different kind of rule, known as anti-commutation relation:

$$\begin{aligned} c_m^\dagger c_n^\dagger &= -c_n^\dagger c_m^\dagger \\ c_n c_m &= -c_m c_n \\ c_m c_n^\dagger &= -c_n^\dagger c_m \quad (n \neq m) \\ c_m c_m^\dagger &= -c_m^\dagger c_m + 1. \end{aligned} \tag{1.10}$$

Here c_m (c_m^\dagger) annihilates (creates) a particle, a fermion, in state m . Compared with the rules of bosons, one finds minus signs everywhere. This sign difference has powerful consequences. Let us just mention one here. Because $c_m^\dagger c_n^\dagger = -c_n^\dagger c_m^\dagger$ applies for $m = n$ as well, the same operation applied twice in a row gives $(c_m^\dagger)^2 = 0$. This means that by adding two particles on an existing state, call it $|\psi\rangle$, we get nothing because $(c_m^\dagger)^2 |\psi\rangle = 0$. This means adding two particles in the same state is forbidden in quantum mechanics for the fermions. In particular if $|\psi\rangle = |0\rangle$, we get $(c_m^\dagger)^2 |0\rangle = 0$. This implies that a given state m can be either empty ($|0\rangle$), or singly occupied ($|1\rangle$), but never anything else. This is the Pauli exclusion principle.

Using the annihilation/creation operators constructed above, we can describe all of the quantum-mechanical processes imaginable. For example, as described earlier, adding a particle to a particular state m is given the ‘‘code name’’ c_m^\dagger , and annihilating one that is already in state m is noted c_m . What about moving a particle from one state, say m , to another state n ? A short moment's reflection will lead to the conclusion that this can be achieved by first annihilating a particle which already existed at m , then creating the same particle in the new state n : $\sim c_n^\dagger c_m$. Of course one can do it the other way around, $c_m c_n^\dagger$, but due to the commutation relations they are essentially the same thing.

Now, we introduce an interesting quantity that is also very important in the construction of the Hamiltonian: $c_m^\dagger c_m$. At first sight it seems that this does *essentially nothing* to the state on which it acts, because a particle that has been removed is immediately put back into the original state. In quantum mechanics two states $|\psi_1\rangle$ and $|\psi_2\rangle$ are the same if they are equal up to a constant factor $|\psi_1\rangle = \eta |\psi_2\rangle$. Then $c_m^\dagger c_m |\psi\rangle$ returns $|\psi\rangle$ up to a multiplicative constant. The answer for arbitrary state $|m\rangle$ is

$$c_m^\dagger c_m |N_m\rangle = N_m |N_m\rangle. \tag{1.11}$$

If the state contains N_m particles in m -state, $c_m^\dagger c_m$ returns the same state with

the particle number N_m multiplying it. The proof is left as an exercise. $c_m^\dagger c_m$ is known as the number operator for an obvious reason.

Using the number operators it is straightforward to construct the Hamiltonian in the second-quantization form. It is

$$H = \sum_m \epsilon_m c_m^\dagger c_m = \sum_m \epsilon_m N_m. \quad (1.12)$$

ϵ_m is the eigenenergy of the single-particle state obtained from diagonalizing the Schrödinger equation. The Hamiltonian measures the total energy of the system, which is nothing but the sum of the individual eigenenergies multiplied by the number of particles that occupy the state.

1.2 Free electron sea of a metal

The qualitative picture of the behavior of electrons in a metal has been proposed a long time ago, almost immediately after the birth of quantum mechanics. Ignoring the Coulomb repulsion between two electrons for a moment, each electron in a metal is considered a free particle. The quantum-mechanical description of a free particle in three dimensions is given by the Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x, y, z) = E \psi(x, y, z) \quad (1.13)$$

with a solution $\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$ and the corresponding energy $E_{\mathbf{k}} = \hbar^2 \mathbf{k}^2 / 2m$. The volume of the box in which the electrons are enclosed is V .

The process of putting an electron in the particular \mathbf{k} -state is denoted $c_{\mathbf{k}}^\dagger |0\rangle$, where $|0\rangle$ represents an empty box, with zero electron number. Electron has a spin (one up and one down), and the same momentum state \mathbf{k} can be occupied by one spin-up electron and one spin-down electron. Let's say we are putting an electron in momentum- \mathbf{k} and spin- \uparrow state. Such process is given the expression

$$|\mathbf{k} \uparrow\rangle = c_{\mathbf{k}\uparrow}^\dagger |0\rangle.$$

We have an Avogadro's number of electrons each waiting for its place in this box, so we have to decide where to put the second electron in this box. One can only put an electron in one of the eigenstates of the Hamiltonian (1.13). That's simply what the eigenstate means. We can put the second electron, for instance, in the same \mathbf{k} state, but with a different spin, and the result would be a state given by

$$|\mathbf{k} \downarrow, \mathbf{k} \uparrow\rangle = c_{\mathbf{k}\downarrow}^\dagger c_{\mathbf{k}\uparrow}^\dagger |0\rangle.$$

A third electron inserted in momentum- \mathbf{p} , spin- \uparrow state will turn it into $c_{\mathbf{p}\uparrow}^\dagger c_{\mathbf{k}\downarrow}^\dagger c_{\mathbf{k}\uparrow}^\dagger |0\rangle$. Now the rule is almost self-evident. For N electrons occupying a set of levels defined by $\{\mathbf{k}_i, \sigma_i\}$, $i = 1, \dots, N$, the N -electronic state is given by

$$|\psi\rangle = \prod_{\{\mathbf{k}\sigma\}} c_{\mathbf{k}\sigma}^\dagger |0\rangle. \quad (1.14)$$

The product runs over N different labels of $\{\mathbf{k}\sigma\}$. The lowest energy state is obtained if we categorically place two electrons of opposite spins in the successively higher energy states, starting from the very lowest energy. Such a state is simply represented by

$$|\text{FS}\rangle = \prod_{|\mathbf{k}| < k_f} c_{\mathbf{k}\downarrow}^+ c_{\mathbf{k}\uparrow}^+ |0\rangle. \quad (1.15)$$

This is the lowest possible energy state for N non-interacting electrons, *i.e.* it is the ground state. The highest-energy state occupied by the electron has an energy E_f related to the Fermi momentum k_f by

$$E_f = \frac{\hbar^2 k_f^2}{2m}$$

and is called the Fermi energy. The contour consisting of \mathbf{k} -states having the same energy is in the shape of a sphere in three-dimensional space spanned by (k_x, k_y, k_z) . The highest-energy states form such a sphere too, which is called the Fermi surface. Some experimental techniques can directly measure the Fermi surface contour of a given metal and we will discuss the measurement techniques later.

Fermi momentum k_f has a close connection to the average electron density $\rho = N/V$. To see how to relate k_f to ρ , first think about a sphere of radius k_f in momentum space. All electrons live inside this sphere, so the total electron number is proportional to the volume of the sphere. The volume is given by $4\pi k_f^3/3$. If we divide this by the volume occupied by each electron, then we must obtain $N/2$. The extra factor 2 is due to the spin degeneracy.

So what is the volume of \mathbf{k} -space occupied by each electronic state? To find the answer to this, go back to the free-electron Schrödinger equation, whose solution for a box of sides (L_x, L_y, L_z) is characterized by \mathbf{k} :

$$\mathbf{k} = 2\pi \left(\frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z} \right).$$

Using this result it is easy to see that the volume associated with each state is just $(2\pi)^3/L_x L_y L_z = (2\pi)^3/V$. So we have

$$\frac{N}{2} = \frac{(4\pi k_f^3/3)}{(2\pi)^3/V} = \frac{V k_f^3}{6\pi^2}.$$

Since $N/V = \rho$, the density is indeed related to k_f through

$$\rho = \frac{k_f^3}{3\pi^2}, \quad k_f^3 = 3\pi^2 \rho. \quad (1.16)$$

Due to this relation the Fermi energy is also related to the electron density via

$$E_f = \frac{\hbar^2}{2m} (2\pi^2 \rho)^{2/3}. \quad (1.17)$$

In typical metals the Fermi momentum is roughly the inverse of the lattice spacing, $k_f \sim 1/a$. The Fermi energy is typically of order $\hbar^2/2ma^2$. Recall that the ground state level of the hydrogen atom also has an energy of order e^2/a . Due to the virial relation this is also the amount of the kinetic energy $\hbar^2/2ma^2$,

so we infer that the Fermi energy is roughly 10 eV for a typical metal. To make this argument more precise, we write

$$E_f = \frac{\hbar^2}{2ma_B^2}(k_f a_B)^2 = \frac{e^2}{2a_B}(k_f a_B)^2 \quad (1.18)$$

using the Bohr radius of hydrogen atom a_B and the known relation between potential and kinetic energies $\hbar^2/2ma_B^2 = e^2/2a_B$. The energy unit $e^2/2a_B$ is known as the Rydberg (Ry), equal to 13.6 eV. As I said, $k_f a_B \sim 1$, and $E_f \sim 1$ Ry.

There's also the concept known as the Fermi temperature that's related to the Fermi energy by $E_f = k_B T_f$, k_B being a Boltzmann's constant. The typical conversion factor is 10^4 Kelvin for 1 electron volt, so the Fermi energy of 10 eV corresponds to 10^5 degrees. An extensive list of Fermi energies and Fermi wavevector for an assortment of metals is given in p. 139, Kittel (8th Ed.), or on p. 38, Ashcroft & Mermin.

Some of the modifications brought about in a real crystal are ionic potentials, various imperfections of both magnetic and non-magnetic characters, and multiple band structures, to name a few. We will cover as much of these as time allows.

1.3 Exercise

[1][20pts]² (a) Prove that the normalized eigenstate consisting of N_m particles occupying the state m is given by

$$|N_m\rangle = \frac{(a_m^+)^{N_m}}{\sqrt{N_m!}}|0\rangle. \quad (1.19)$$

(b) Prove that for any eigenstate N_m , $a_m^+|N_m\rangle = \sqrt{N_m+1}|N_m+1\rangle$, and $a_m|N_m\rangle = \sqrt{N_m}|N_m-1\rangle$. Prove $a_m^+a_m|N_m\rangle = N_m|N_m\rangle$, as a corollary.

[2][20pts] Work out k_f and E_f as a function of electron density ρ in one- and two-dimensional electron gas.

[3][10pt] What is the Hamiltonian of a free Fermi gas?

[4][10pt] Show that the two-particle wave function $\psi(x_1, x_2)$ given in Eq. (1.8) is normalized to unity as long as the individual wave functions $\phi_{n_1}(x_1)$ and $\phi_{n_2}(x_2)$ are orthonormal: $\int \phi_m^*(x)\phi_n(x)dx = \delta_{mn}$.

²Homework problems will be graded in multiples of 5, e.g. 5 pts, 10 pts, etc.

Chapter 2

Tight-binding Model

One aspect of the electron motion in a solid which markedly departs from that in free space is that the motion is subject to a periodic potential created by the ions. The tight-binding method offers a simplistic view of the modification in the electronic motion and the energy levels caused by the potential which is both easy to grasp and still of much practical value. We begin with a discussion of Bloch's theorem, a general statement about the wave functions of Schrödinger's equation with periodically modulated potential, and the Kronig-Penny model which is the simplest exactly solvable model with the periodic potential. Tight-binding Hamiltonian is introduced using the language of second quantization we learned in the previous chapter and it is applied to a number of lattice structures.

2.1 Bloch's theorem

By a periodic potential we mean the type of potential obeying $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$ for any vector \mathbf{R} connecting two ionic sites. The Hamiltonian of electronic motion in a solid is governed by the Schrödinger's equation

$$H = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}). \quad (2.1)$$

How are we going to proceed to find the solution of this Hamiltonian? The question has been answered by F. Bloch in an elegant fashion using no more than Fourier analysis.

We present a heuristic derivation of Bloch's approach in one dimension. Since $V(x)$ is periodic over the lattice spacing a , $V(x + a) = V(x)$, its Fourier expansion must be of the form

$$V(x) = \sum_{m=-\infty}^{\infty} V_m e^{imGx} \quad (2.2)$$

where G refers to $G = 2\pi/a$. The vector¹ G and all its integer multiples are collectively known as reciprocal lattice vectors. V_m are some coefficients whose exact value depends on the exact form of $V(x)$ and obeys the relation $V_{-m} = V_m^*$.

¹It will be a vector in two and three dimensions.

On the other hand, there is no *a priori* reason why the wave function $\psi(x)$ should also have the same periodicity. Instead we impose the periodic boundary condition $\psi(x + L) = \psi(x)$, where L is the dimension of the lattice. Then $\psi(x)$ has the Fourier expansion

$$\psi(x) = \sum_{n=-\infty}^{\infty} \psi_n e^{i(2\pi n/L)x}. \quad (2.3)$$

The set of allowed modes in the expansion of $\psi(x)$ is far denser than that of allowed wave vectors in the Fourier expansion of $V(x)$ by the ratio L/a .

Bloch's proof is quite general in the sense that it applies to an arbitrary periodic potential $V(x)$, but in the spirit of keeping things simple but not simpler we will maintain the simplest form of periodic potential $V(x) = V_1(e^{iGx} + e^{-iGx}) = 2V_1 \cos[Gx]$, $G = 2\pi/a$, in the derivation. Plugging in the Fourier expansion of $\psi(x)$ [(2.3)] and $V(x)$ [(2.2)] in the Schrödinger equation, one obtains

$$\sum_k e^{ikx} \left(E - \frac{\hbar^2 k^2}{2m} \right) \psi_k = V_1 (e^{iGx} + e^{-iGx}) \sum_p e^{ipx} \psi_p. \quad (2.4)$$

Each component multiplying a plane wave e^{ikx} from either side of this equation must match. That means only the components of p which equal $k + G$ or $k - G$ survives in the sum:

$$\left(E - \frac{\hbar^2 k^2}{2m} \right) \psi_k = V_1 (\psi_{k+G} + \psi_{k-G}). \quad (2.5)$$

The set of k vectors runs over all integer multiples of $2\pi/L$, whereas $G = 2\pi/a$. Only a small subset of different k vectors are connected by the periodic modulation corresponding to wave vector G . Without any loss of generality one can restrict k values within the range $[-G/2, G/2]$ which is known as the Brillouin zone. There are a total of $(2\pi/a)/(2\pi/L) = L/a$ different k states in the Brillouin zone. This number is also equal to the number of lattice sites in the lattice.

For each k in the Brillouin zone Eq. (2.5) defines a coupled linear equation that offers a set of eigenenergies E_k^α and a set of eigenfunctions, also labeled by α . Going back to the original problem given in Eq. (2.1) we conclude that the eigenstate of the Hamiltonian is characterized by two indices, k and α . Each such eigenstate is denoted $\psi_k^\alpha(x)$, and the corresponding eigenenergy, E_k^α . The eigenstate in the Fourier expansion appears as

$$\psi_k^\alpha(x) = \sum_{n=-\infty}^{\infty} \psi_{k+nG}^\alpha e^{i(k+nG)x} \quad (2.6)$$

where ψ_{k+nG}^α are the coefficients which satisfy Eq. (2.1). Using a more general $V(x)$ will complicate the r.h.s. of Eq. (2.5), but the fact remains that there are a set of independent solutions labeled by α , for each k in the Brillouin zone. The expression (2.6) is the most general form imaginable for the solution of the periodic potential problem.

The solution thus found has a peculiar property. Since only a set of k 's differing by $G = 2\pi/a$ are connected, the real-space function has the property

$$\psi_k^\alpha(x+a) = \sum_{n=-\infty}^{\infty} \psi_{k+nG}^\alpha e^{i(k+nG)(x+a)} = e^{ika} \psi_k^\alpha(x). \quad (2.7)$$

The wave function ψ_k^α picks up a phase factor e^{ika} every time it is translated by one lattice spacing a . This is a property that must be obeyed by all eigenfunctions of the problem, and the phase factor depends only on k , not on α .

The whole argument is easily generalized to higher dimensions.

2.2 Kronig-Penney Model

In this section we consider an exactly solvable case of electronic motion in one dimension. The potential experienced by the electron has to be periodic over lattice spacing a , and we choose a series of delta functions as the potential: $V(x) = V_0\delta(x - na)$.

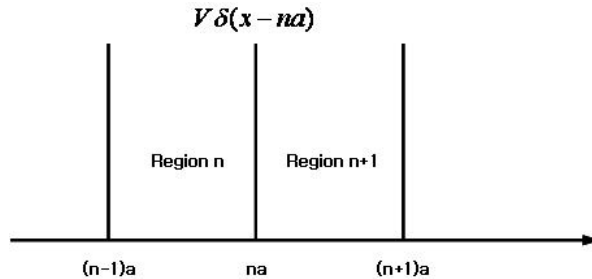


Figure 2.1: The Kronig-Penney Model

Schrödinger's equation for a particle constrained to this type of potential is

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi(x) = E\psi(x). \quad (2.8)$$

The solution to this equation is given by the form

$$\psi_n(x) = A_n e^{ik(x-na)} + B_n e^{-ik(x-na)} \quad (2.9)$$

where $(n-1)a < x < na$, because in this region the potential vanishes. Although the wave function has this form in any region the coefficients, A_n and B_n , differ for every region. The goal is to find these coefficients constrained by some boundary conditions.

The first boundary condition is that the wavefunction must be continuous when we go from one region(say n) to an adjacent region(say $n+1$). This gives

$$\psi_n(na) = \psi_{n+1}(na). \quad (2.10)$$

The next boundary condition can be obtained by integrating Schrödinger's equation from 0^- to 0^+ of $x = na$ and noting the continuity of the wave function,

$$\psi'_{n+1}(na) - \psi'_n(na) = \frac{2mV_0}{\hbar^2} \psi_n(na). \quad (2.11)$$

The third boundary condition is Bloch's theorem, which is discussed in the previous section, states that in a periodic potential the wavefunction can be chosen to satisfy

$$\psi(x+a) = e^{i\varphi} \psi(x) \quad (2.12)$$

for some suitable φ .

In summary, we have the following boundary conditions,

- $\psi_n(na) = \psi_{n+1}(na)$
- $\psi'_{n+1}(na) - \psi'_n(na) = \frac{2mV_0}{\hbar^2} \psi_n(na)$
- $\psi(x+a) = e^{i\varphi} \psi(x)$

From the last of the above boundary conditions we have

$$A_{n+1} = A_n e^{i\varphi} \quad (2.13a)$$

$$B_{n+1} = B_n e^{i\varphi} \quad (2.13b)$$

From the rest of the boundary conditions we have

$$\begin{aligned} A_n + B_n &= A_n e^{i\varphi - ika} + B_n e^{i\varphi + ika} \\ ik(A_n - B_n) - ik(A_n e^{i\varphi - ika} - B_n e^{i\varphi + ika}) + \frac{2mV_0}{\hbar^2}(A_n + B_n) &= 0. \end{aligned} \quad (2.14)$$

These two equations may be rewritten as

$$\begin{aligned} (1 - e^{i\varphi - ika})A_n + (1 - e^{i\varphi + ika})B_n &= 0 \\ \left(1 - e^{i\varphi - ika} - \frac{2imV_0}{k\hbar^2}\right)A_n - \left(1 - e^{i\varphi + ika} + \frac{2imV_0}{k\hbar^2}\right)B_n &= 0 \end{aligned} \quad (2.15)$$

or written in matrix form,

$$\begin{pmatrix} 1 - e^{i\varphi - ika} & 1 - e^{i\varphi + ika} \\ 1 - e^{i\varphi - ika} - \frac{2imV_0}{k\hbar^2} & -(1 - e^{i\varphi + ika} + \frac{2imV_0}{k\hbar^2}) \end{pmatrix} \begin{pmatrix} A_n \\ B_n \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \quad (2.16)$$

In order for A_n and B_n to have nontrivial solutions the determinant of the square matrix above must equal zero,

$$\left(1 - e^{i\varphi - ika}\right)\left(1 - e^{i\varphi + ika} + \frac{2imV_0}{k\hbar^2}\right) + \left(1 - e^{i\varphi + ika}\right)\left(1 - e^{i\varphi - ika} - \frac{2imV_0}{k\hbar^2}\right) = 0. \quad (2.17)$$

Some algebraic manipulation leads to

$$\cos \varphi = \cos(ka) + \frac{mV_0}{k\hbar^2} \sin(ka). \quad (2.18)$$

Since $\cos \varphi$ can only have values between -1 and 1 (the area between the blue lines in figure 2.2), only the k -regions marked by the red lines in Fig. 2.2 give possible values of k . For other k -values one cannot find ϕ which satisfies Eq. (2.18). The eigenenergy for the state given in Eq. (2.9) is $\hbar^2 k^2 / 2m$, but not all k -values correspond to the eigenstate. This leads to gaps in the energy spectrum as shown in Fig 2.2.

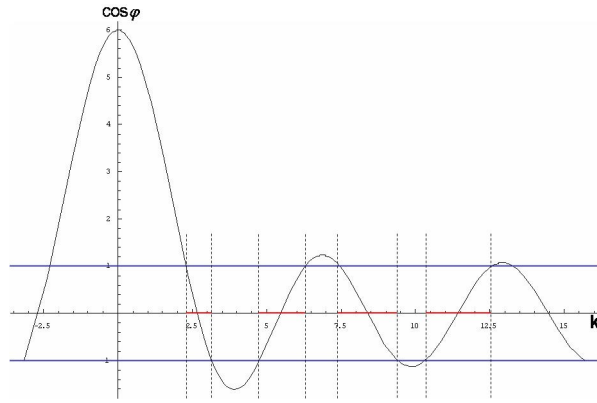


Figure 2.2: Plot of $\cos(ka) + \frac{mV_0}{k\hbar^2} \sin(ka)$. The regions where this function lies within the interval $[-1, 1]$ are indicated as red lines.

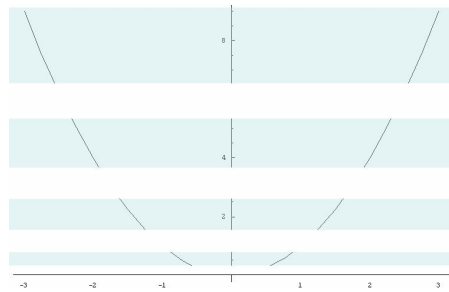


Figure 2.3: Gaps in the energy spectrum induced by the periodic potential

The Kronig-Penney model demonstrates a marked feature of the electronic motion in a periodic solid, namely the appearance of an energy gap separating different energy bands.

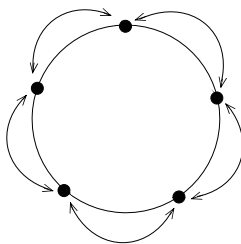


Figure 2.4: Electron hopping on a periodic lattice

2.3 Tight-binding Hamiltonian

To a first approximation electrons get strongly attracted to the ionic centers with the Coulomb force. The atomic picture of an electron orbiting a single ion is modified by coupling which enables the electron to hop from one ionic site to the next one. The origin of the coupling is that the electronic wave functions for each ion have a finite overlap with those of the neighboring one. Tight-binding model offers a simplistic yet very useful way to model these two competing tendencies which occur in any solid.

Consider the motion of electrons on a ring similar to our consideration in the previous chapter, but this time, electrons can only occupy a selection of N discrete states evenly spaced along the circumference of the ring. Figure 2.4 illustrates $N=5$ case.

Let's first think about what it means for an electron to occupy a given site i . We can for example think of each site as a potential well with its own set of energy spectra. For simplicity we assume that each well has only one energy level, with energy $-\epsilon_0$, although a real atom should possess many such levels. If an electron occupies that level, the system acquires an energy $-\epsilon_0$. If there is no electron in that state the system's energy is zero.

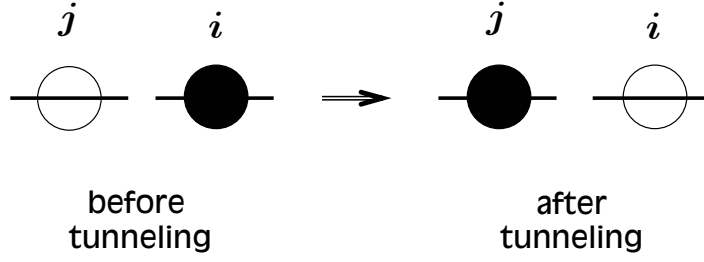
This statement can be translated in the second-quantized language using the Hamiltonian $H = -\epsilon_0 c^\dagger c$. We know that Hamiltonian is an operator whose expectation value returns the energy and we also know $c^\dagger c$ measures the number of electrons in that state. So our previous statement translates into $\langle H \rangle = -\epsilon_0 \langle c^\dagger c \rangle$, or (energy) = $(-\epsilon_0) \times$ (number of electrons present in that state) and indeed this is the correct statement.

The case in question has N identical potential wells, each characterized by the same binding energy $-\epsilon_0$. The Hamiltonian in this case is $H = \sum_i (-\epsilon_0) c_i^\dagger c_i$, where $c_i^\dagger c_i$ measures electron occupation in the i -th site. Now the statement about the energy becomes

$$(\text{total energy}) = \sum_i (-\epsilon_0) \times (\text{number of electrons at site } i).$$

This is intuitively clear. However we know that this is not the most general circumstance that can occur quantum-mechanically. The potential wells are not completely disjoint. Instead, wave functions localized at adjacent sites i and j have some non-zero overlap causing tunneling between localized levels. How do we add tunneling effect in our Hamiltonian?

What the tunneling does is, pictorially speaking, remove a particle from position i and put it at position j , across a tunneling barrier (Fig. 2.5). In the

Figure 2.5: Electron hopping from site i to j

second-quantized language this phenomenon is expressed by the term $-t(c_j^\dagger c_i + c_i^\dagger c_j)$. For example, $c_j^\dagger c_i$ acting on a state $|1\rangle_i |0\rangle_j$ (i = occupied, j = empty) returns $|0\rangle_i |1\rangle_j$. This is the quantum-mechanical expression for a particle that “hops” from i to j . Since this occurs for every adjacent pair of sites, the new Hamiltonian with the tunneling effect should read

$$H = -\epsilon_0 \sum_i c_i^\dagger c_i - t \sum_i (c_{i+1}^\dagger c_i + c_i^\dagger c_{i+1}). \quad (2.19)$$

t is some number characteristic of how strong the tunneling effect is. Real electrons also carry spin, so the above Hamiltonian must be replaced by the following one:

$$H = -\epsilon_0 \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} - t \sum_i (c_{i+1\sigma}^\dagger c_{i\sigma} + c_{i\sigma}^\dagger c_{i+1\sigma}). \quad (2.20)$$

If t is nonzero, an electron can hop from i to $i+1$. Since there is nothing to prevent the same electron to hop from $i+1$ to $i+2$, and so forth, it should be possible for an electron to make a complete tour of the ring and come back to its original position. In effect, an electron gets “delocalized”. We will now prove this statement.

As stated in the previous section, Felix Bloch first showed how to write down the eigenstate of the Hamiltonian such as (2.19). The trick is to re-write

$$c_i = \sum_k \left(\frac{1}{\sqrt{N}} e^{ikr_i} \right) c_k, \quad c_i^\dagger = \sum_k \left(\frac{1}{\sqrt{N}} e^{-ikr_i} \right) c_k^\dagger. \quad (2.21)$$

Let me first explain the terms appearing on the right. r_i is a for site label 1, $2a$ for 2, etc, $r_i = ia$. The lattice constant a measures the distance between neighboring sites. c_k is an operator that removes a particle from a state k , just like c_i is an operator that removes a particle from site i .

Because of the ring structure we have started with, we must have $c_{i+Na} = c_i$, because site $i+Na$ is nothing but site i itself. Then the r.h.s. of Eq. (2.21) must have this property, too. Since

$$c_{i+Na} = \sum_k \frac{1}{\sqrt{N}} e^{ik(r_i+Na)} c_k = \sum_k \frac{1}{\sqrt{N}} e^{ikr_i} \times e^{iNka} c_k. \quad (2.22)$$

the desired property will be fulfilled if $e^{iNka} = 1$. To ensure this, we must have $k = (2\pi/Na) \times \text{integer}$. Let's label different integer values by m , and write

$k = 2\pi m/Na$. Now the meaning of \sum_k is clear. In fact it is a sum over different m values. So we write

$$c_i = \frac{1}{\sqrt{N}} \sum_m \exp \left[2\pi i \frac{m}{N} \cdot \frac{r_i}{a} \right] c_m. \quad (2.23)$$

We will use c_m and c_k interchangeably because they mean the same thing. Notice the structure of the terms that enter in the exponent. r_i/a is always an integer, therefore one has

$$\exp \left[2\pi i \left(\frac{r_i}{a} \right) \times \frac{m}{N} \right] = \exp \left[2\pi i (\text{some integer}) \times \frac{m}{N} \right]. \quad (2.24)$$

In the above expression m values that differ by some multiple of N always gives the same value of the exponential. This means that not all m 's are independent. For example, $m = 0, 1, \dots, N-1$ give different values of the exponential. Any other values of m will give rise to an exponential identical to what one gets from the choice $m \in [0, \dots, N-1]$, and hence not independent. To conclude, we must restrict the sum in Eq. (2.23) such that

$$c_i = \frac{1}{\sqrt{N}} \sum_{m=0}^{N-1} \exp \left[2\pi i \frac{m}{N} \cdot \frac{r_i}{a} \right] c_m. \quad (2.25)$$

Now it is left as an easy exercise to prove that if c_i 's were to satisfy the commutation algebra $\{c_i, c_j^\dagger\} = 1$ and other relation discussed in the previous chapter, we must require that c_m 's obey a similar algebra,

$$\begin{aligned} c_m c_m^\dagger + c_m^\dagger c_m &= 1 \\ c_m c_{m'}^\dagger + c_{m'}^\dagger c_m &= 0 \quad (m \neq m'), \quad \text{etc.} \end{aligned} \quad (2.26)$$

After these exercises we can begin to recognize c_m, c_m^\dagger as annihilation and creation operators associated with the state labelled by m , or by $k = 2\pi m/Na$. k is a momentum eigenvalue, and our new operators c_m^\dagger, c_m add/remove a particle at the momentum eigenstate labelled k . Armed with these formalities, we directly substitute Eq. (2.25) into the Hamiltonian (2.19) and find some magical thing happen! In fact H has been turned into

$$H = \sum_k (-\epsilon_0 - 2t \cos ka) c_k^\dagger c_k = \sum_k \epsilon_k c_k^\dagger c_k. \quad (2.27)$$

Based on our previous training we should interpret the last term as

$$(\text{total energy}) = \sum_k (\text{energy of } k\text{-state}) \times (\text{number of electrons in } k\text{-state}). \quad (2.28)$$

When such interpretation is possible, we should think of ϵ_k as eigenenergy, and c_k^\dagger and c_k as operators adding/removing electrons to/from an eigenstate k .

Previously when we had $t = 0$, each eigenstate was labelled by the site i in which the particle is localized. When $t \neq 0$, site i is no longer the proper way to characterize eigenstates. Instead the correct eigenstate is the one having a definite momentum k . How many different eigenstates there are is determined by the different values allowed for $k = (2\pi/Na)m$. There are N different m

values leading to N independent eigenstates. Each eigenstate has an energy given by $-\epsilon_0 - 2t \cos(2\pi m/N)$. Previously when $t = 0$, there were also N different eigenstates, having to do with different localized sites. Now with $t \neq 0$ there are still the same number of states, but they are all extended. It was an important statement at the time Bloch first produced his eigenstates because it says electrons are spread out even though there are potential barrier. This is also why electrons can move easily through dense array of positive ions in solids.

2.4 Application to realistic lattice structures

The tight-binding method gives a rough idea of the band structure depending on the geometry of the lattice. Although quite naive and much less accurate than the full-blown LDA calculations, the method is easily adapted to any type of lattice in any dimensions. It is also a very efficient way to identify the Brillouin zone for a given lattice geometry.

Square lattice: For two-dimensional square lattice an electron at site i can hop to any one of its four neighbors at $i \pm \hat{x}$, and $i \pm \hat{y}$. Hence the tight-binding Hamiltonian reads

$$\begin{aligned} H &= -t \sum_i (c_{i+\hat{x}}^+ + c_{i-\hat{x}}^+ + c_{i+\hat{y}}^+ + c_{i-\hat{y}}^+) c_i - \mu \sum_i c_i^+ c_i \\ &= -t \sum_{\langle ij \rangle} (c_j^+ c_i + c_i^+ c_j) - \mu \sum_i c_i^+ c_i \end{aligned} \quad (2.29)$$

where $\langle ij \rangle$ indicates all nearest-neighbor pairs of the lattice. We have suppressed the spin index because it does not affect the energy spectrum at all. Using the expansion

$$c_i = \frac{1}{\sqrt{N_x N_y}} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}_i} c_{\mathbf{k}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}_i} c_{\mathbf{k}} \quad (2.30)$$

the Hamiltonian is brought into the diagonalized form

$$\begin{aligned} H &= \sum_{\mathbf{k}} (\epsilon_{\mathbf{k}} - \mu) c_{\mathbf{k}}^+ c_{\mathbf{k}} \\ \mathbf{k} &= (k_x, k_y), \quad \mathbf{r}_i = (x_i, y_i) \end{aligned} \quad (2.31)$$

where $\epsilon_{\mathbf{k}} = -2t[\cos k_x + \cos k_y]$ when the lattice constant a is taken to unity. Here we observe that the energy $\epsilon_{\mathbf{k}}$ is periodic in both k_x and k_y with the period of 2π . Only those \mathbf{k} vectors not connected by multiples of 2π are to be regarded as independent. This leads to the concept of the first Brillouin zone, or 1BZ for short, which for the square lattice is given by $[-\pi, \pi] \times [-\pi, \pi]$. The total number of independent states (independent \mathbf{k} vectors) that fit inside the 1BZ is $N_x \times N_y = N$, exactly matching the total number of allowed states on the square lattice consisting of N sites.

Triangular lattice: The same approach applied to the triangular lattice with nearest-neighbor hopping gives the diagonalized Hamiltonian of the form (2.31) with $\epsilon_{\mathbf{k}} = -2t[\cos k_x + \cos(k_x/2 + \sqrt{3}k_y/2) + \cos(k_x/2 - \sqrt{3}k_y/2)]$. In general, for a Bravais lattice, the tight-binding energy spectrum is of the form

$$\epsilon_{\mathbf{k}} = -t \sum_{j \in i} e^{i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i)} \quad (2.32)$$

encompassing all nearest-neighbor sites j for i .

Hexagonal lattice: The square and triangular lattices belong to the type of lattice structure known as the Bravais lattice, which refers to the cases having one atomic site per unit cell. In other words, every site looks exactly the same as every other site in the whole lattice. The same cannot be said of the hexagonal lattice, which is an example of a non-Bravais lattice. There are two inequivalent sites in a lattice rather than one. Calling them A -sites and B -sites, for instance, one can formally divide the fermion operators as those belonging to A and B sublattices respectively.

$$\begin{aligned} c_i^A &= \frac{1}{\sqrt{N_A}} \sum_{\mathbf{k}} c_{\mathbf{k}}^A e^{i\mathbf{k} \cdot \mathbf{r}_i} \\ c_i^B &= \frac{1}{\sqrt{N_B}} \sum_{\mathbf{k}} c_{\mathbf{k}}^B e^{i\mathbf{k} \cdot \mathbf{r}_i} \end{aligned} \quad (2.33)$$

where \mathbf{r}_i refers to the coordinate of each lattice site. The tight-binding Hamiltonian for the hexagonal lattice is written out as

$$H = -t \sum_{i \in A} c_{Bj}^+ c_{Ai} - t \sum_{i \in B} c_{Aj}^+ c_{Bi} - \mu \sum_{i \in A} c_{Ai}^+ c_{Ai} - \mu \sum_{i \in B} c_{Bi}^+ c_{Bi}. \quad (2.34)$$

On writing down the Hamiltonian in momentum space using Eq. (2.33),

$$H = \begin{pmatrix} c_{A\mathbf{k}}^+ & c_{B\mathbf{k}}^+ \end{pmatrix} \begin{pmatrix} -\mu & -t \sum_{j \in i} e^{i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i)} \\ -t \sum_{j \in i} e^{-i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i)} & -\mu \end{pmatrix} \begin{pmatrix} c_{A\mathbf{k}} \\ c_{B\mathbf{k}} \end{pmatrix}. \quad (2.35)$$

Diagonalizing the matrix finally gives the energy spectrum of the hexagonal lattice

$$\begin{aligned} \epsilon_{\mathbf{k}} &= -\mu \pm \left| \sum_{j \in i} e^{i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i)} \right| \\ &= -\mu \pm \left| e^{ik_x} + e^{ik_x/2 + i\sqrt{3}k_y/2} + e^{ik_x/2 - i\sqrt{3}k_y/2} \right| \\ &= \mu \pm \left| 3 + 2 \left(\cos \left(\frac{k_x}{2} + \frac{\sqrt{3}}{2} k_y \right) + \cos \left(\frac{k_x}{2} - \frac{\sqrt{3}}{2} k_y \right) + \cos \sqrt{3} k_y \right) \right| \end{aligned} \quad (2.36)$$

The \pm sign refers to two different energy values allowed for a given k . There are two bands, which touch each other at certain isolated points in \mathbf{k} -space.

Contrast this with the situation obtained for the Bravais lattice which had only one band corresponding to each \mathbf{k} . The appearance of multiple bands is closely tied to the existence of multiple lattice sites in a unit cell. In the hexagonal lattice, the unit cell having two inequivalent sites is the reason for having two band energies for a given \mathbf{k} .

The Hamiltonian around each localized \mathbf{k} -point is similar to the Dirac Hamiltonian of the relativistic particles in two dimensions. In the next chapter we will construct a Hamiltonian with multiple bands with a clear energy gap separating the upper and lower bands. This type of band structure gives rise to an insulator. The graphite is interesting because it lies in the middle between a metal (having a finite DOS at the Fermi level) and an insulator (having zero DOS at the Fermi level).

2.5 Exercise

[1][20pts] Generalize Bloch's argument to two dimensions using the periodic potential $V(x, y) = 2V_1(\cos k_x x + \cos k_y y)$ for a square lattice with spacing a . Identify the Brillouin zone.

[2][30pts] Solve Eq. (2.5) assuming only $\psi_{\mathbf{k}}$, $\psi_{\mathbf{k}+G}$ and $\psi_{\mathbf{k}-G}$ were non-zero. You will have derived an equation which is cubic in E . Find the solution of the cubic equation numerically and plot $E_{\mathbf{k}}$ for three different branches.

[3][10pts] Prove Eqs. (2.26).

[4][10pts] Prove Eq. (2.27).

[5][20pts] Diagonalize the tight-binding Hamiltonian for the two-dimensional triangular lattice. Identify the Brillouin zone. Show that it is in the shape of a hexagon.

[6][20pts] Identify the first Brillouin zone for the tight-binding energy band of hexagonal lattice. Identify the \mathbf{k} -points where the upper and lower energy dispersion in the hexagonal lattice meet each other.

Chapter 3

Description of metals and insulators

A metal conducts electricity; an insulator does not. That's the common way to distinguish metals and insulators. But is this also the fundamentally right way to distinguish the two states of matter? Come to think of it, because a metal is also a good conductor of heat one can equally well characterize a metal by its thermal, not electrical, properties. And yet both high electrical and thermal conductivities are a consequence of a more fundamental property of a metal, namely the presence of arbitrarily low-energy excitations above the ground state. In this chapter we discuss how the quantum mechanics of solids allows us to characterize metal from insulator in a clean way as a system with no energy gap and arbitrarily small excitations, or a system with a well-defined energy gap in the thermodynamic limit.

3.1 Metal vs. Insulator

The free electron model ignored the effects of the lattice and obtained the single-energy spectrum as if the electrons were moving in a vacuum. The lattice potential, as we saw in the tight-binding approach, modified the energy spectrum considerably. The new spectrum had both the lower and upper bound, unlike the free electron spectrum which had the lower bound only. Going back to the one-dimensional lattice as an example, we had an energy dispersion of an electron given by

$$\epsilon_k = -2t \cos k - \mu \quad (3.1)$$

where k is constrained by the condition $e^{ikL} = 1$, or $k = 2\pi n/L$; lattice spacing is taken to unity. If you count how many distinct k 's are allowed, you find that there are as many different k 's as there are lattice sites. Including spin degrees of freedom, a given tight-binding band allows only $2L$ different electrons to be occupied. Even if you have more than $2L$ electrons, there is no way they can be accommodated in a single tight-binding band. Such a problem never arose in the free electron model because the energy spectrum had no upper bound. Then where will the excess electrons go? For real solids there are usually several

energy bands, each of which is given a dispersion similar to the one given in Eq. (3.1). The excess electron will occupy the upper band until all its available states are filled. Then one will have to go to the third band, and so forth.

Figure 3.1: Schematic energy band for a metal

Suppose the chemical potential μ is chosen to be a value between $-2t$ and $+2t$. Then ϵ_k will be negative for some values of k and positive for others. According to the rule of Fermi statistics, when the temperature is zero, the negative-energy states are occupied and the positive energy states empty. Thus, the total number of electrons occupying the ground state is given by

$$N_e = 2 \sum_k \theta(-\epsilon_k). \quad (3.2)$$

The factor 2 arises from spin degeneracy. In the second-quantized language the ground state is given by

$$|\text{GS}\rangle = \prod_{|k| < k_f} \prod_{\sigma} c_{k\sigma}^+ |0\rangle. \quad (3.3)$$

The Fermi momentum is the k -value which satisfies $-2t \cos k_f - \mu = 0$. It is the momentum value up to which electrons will be occupied in the ground state at zero temperature. Due to the chemical potential, the highest-energy state allowed for an electron is effectively zero. However, that's exactly what the chemical potential does; to effectively adjust the energy levels so that Fermi statistics will select all the negative-energy states for occupation of electrons.

Now we can address the question that arises over and over again in solid state physics:

What is the lowest-energy excited state allowed for this system?

Figure 3.2: Creating an excited state for a metallic ground state

By an excited state we mean *any states* which are orthogonal to the ground state. By definition such a state must have an energy higher than E_0 which is the energy of the ground state. For a ground state of the type (3.3) the first excited state is obtained by taking an electron from just below the Fermi level μ and placing it just above it. Taking $k_f = 2\pi n_f/L$, we can write down the excited-state wave function

$$|\text{EX}\rangle = \prod_{-n_f < n < n_f - 1} \prod_{n = n_f + 1} c_k^+ |0\rangle = c_{n_f+1}^+ c_{n_f} |\text{GS}\rangle. \quad (3.4)$$

(We momentarily ignore the fact that electrons carry spin.) The energy of the excited state is

$$E_{ex} = E_{gs} + \epsilon_{n_f+1} - \epsilon_{n_f}. \quad (3.5)$$

Remembering that the momentum difference between n_f and $n_f + 1$ states is tiny, we can Taylor-expand the energy difference

$$\epsilon_{n_f+1} - \epsilon_{n_f} \approx 2t \sin k_f \times \Delta k = 2t \sin k_f \times \frac{2\pi}{L}. \quad (3.6)$$

Regardless of the exact value of $\sin k_f$ this difference is $\sim t/L$, which means that it is going down as the system size L increases. Since L is taken to infinity at the end of the day, the energy difference between $|\text{GS}\rangle$ and the first excited state vanishes. Such a situation is known as “gapless”. A metal is an example of a gapless state. The fact that a metal is a good conductor is a consequence of the gapless nature of the ground state. It costs essentially zero energy to excite one electronic state above the ground state, and the first excited state such as the one given in Eq. (3.4) has a momentum

$$\langle \text{EX} | \hat{P} | \text{EX} \rangle = +\frac{2\pi}{L}. \quad (3.7)$$

This means that the excited state is a current-carrying state, whereas the ground state carries zero current $\langle \text{GS} | \hat{P} | \text{GS} \rangle = 0$. A metal generates current that scales with the applied voltage, no matter how small the voltage is. The number of electrons “excited” by the applied voltage scales with V , and there are always some electrons which can be excited within the energy window of V because they are in a gapless state.

On the contrary, an insulator is a state for which the energy difference between the ground state and the first excited state is a finite number that does not vanish no matter how large the system size gets. To understand where this property of the insulator arises let’s first proceed to construct one.

Consider the Hamiltonian in one dimension

$$H = -t \sum_i (c_{i+1}^+ c_i + c_i^+ c_{i+1}) + \sum_i (\Delta_i - \mu) c_i^+ c_i. \quad (3.8)$$

Without Δ_i this is the tight-binding model leading to the energy dispersion $-2t \cos k - \mu$. For Δ_i , we take the form

$$\Delta_{2i} = +\Delta, \quad \Delta_{2i+1} = -\Delta. \quad (3.9)$$

All even sites have one kind of on-site energy, whereas all odd sites have the opposite on-site energy. As a result, the translational symmetry is broken and one can no longer use the trick to replace c_i as $(1/\sqrt{L}) \sum_k e^{ikn_i} c_k$ to diagonalize H .

The symmetry, however, is not that badly broken. If we look only at the even sites, once again the lattice looks translationally invariant. The same is true of the sublattice consisting of odd sites. The trick can also be generalized to apply the Fourier representation for each sublattice as

$$\begin{aligned} c_{2i} &= \sqrt{\frac{2}{L}} \sum_k e^{ik(2an_i)} a_k \\ c_{2i+1} &= \sqrt{\frac{2}{L}} \sum_k e^{ik(2an_i+a)} b_k \end{aligned} \quad (3.10)$$

Here we temporarily re-introduce the lattice spacing a in the equation. Notice that each of the above equations taken separately is just the Fourier representation of the electron annihilation operators. Only now we have $L/2$ sites corresponding to each sublattice, and the lattice spacing is $2a$ instead of a . Since the two lattices are different, the Fourier operators are given different names, a_k and b_k . Going through the same argument as before, we conclude that k is quantized in multiples of $2\pi/L$, which remains unchanged. Also note that k has the same effect on the equation (3.10) as $k + \pi/a$. That means the Brillouin zone is $[-\pi/2a, \pi/2a]$; half of what it was for a fully translationally invariant lattice. This is of course consistent with the effective lattice spacing enlarged to $2a$ in each sublattice.

Before we proceed with the diagonalization of the Hamiltonian, we point out an important aspect of the reduction of the Brillouin zone. The spacing between adjacent states in k -space is $2\pi/L$, same as in symmetry-unbroken state, but the size of the Brillouin zone is halved. That means that number of independent states allowed in the Brillouin zone is also halved, and we can accommodate only half as many electronic states as we used to when $\Delta = 0$! The resolution of this paradox can be clearly seen once we diagonalize the Hamiltonian.

Figure 3.3: Band structure with a gap in an insulator

The Hamiltonian written in Fourier representation is

$$\begin{aligned} H &= -2t \sum_k \cos k (a_k^\dagger b_k + b_k^\dagger a_k) + (\Delta - \mu) \sum_k a_k^\dagger a_k - (\Delta + \mu) \sum_k b_k^\dagger b_k \\ &= \sum_k \begin{pmatrix} a_k^\dagger & b_k^\dagger \end{pmatrix} \begin{pmatrix} \Delta - \mu & -2t \cos k \\ -2t \cos k & -\Delta - \mu \end{pmatrix} \begin{pmatrix} a_k \\ b_k \end{pmatrix} \end{aligned} \quad (3.11)$$

Diagonalizing the 2×2 Hamiltonian leads to the eigenvalue $E_k^\pm = -\mu \pm \sqrt{\Delta^2 + (2t \cos k)^2}$. A single band $-2t \cos k - \mu$ is split up into two non-overlapping bands due to the presence of Δ . Plotting the two energy spectra E_k^\pm immediately leads to the conclusion that the two bands are separated by an energy gap equal to 2Δ . The reduction of the Brillouin zone size by half is compensated by the emergence of two bands, rather than one, after the gap opening has taken place. The two bands over the reduced Brillouin zone accommodate the same number of states as a single band over the full Brillouin zone in the ungapped situation.

An interesting thing happens when μ is situated somewhere between $-\Delta$ and $+\Delta$. Then, at zero temperature, all the states in the lower band are occupied, and all states in the upper band are empty. In second-quantized language the ground state is

$$|\text{GS}\rangle = \prod_k l_k^+ |0\rangle \quad (3.12)$$

where l_k^+ places an electron in each one of the E_k^- state. The total number of electrons in this state is $L/2$, equal to the number of distinct states in the Brillouin zone discussed earlier. Including the spins, this would correspond to one electron per site.

Now we raise the question: what is the second lowest energy state allowed for half-filling with $L/2$ electrons? Since all the states in the lower band are already occupied, the only thing one could do is to move an electron from the lower band and elevate it to the upper band. It means that the first excited state is given by

$$|\text{EX}\rangle = u_{k_0}^+ l_{k_0} |\text{GS}\rangle \quad (3.13)$$

where $k_0 = \pi/2$ minimizes the upper band energy E_k^+ and maximizes the lower band energy E_k^- . In this way one can reduce the energy penalty in creating the excited state as much as possible. Still, the energy costs remains at 2Δ , regardless of the exact size N .

Remember that when we had $\Delta = 0$, a half electron per site, ignoring the spin, led to a metallic ground state because the chemical potential fell in the middle of the energy spectra. With the same number of electrons, however, the system is turned into an insulator when Δ is non-zero. The real difference caused by Δ is that the unit cell is now enlarged to include two atomic sites; in the new unit cell, there is one electron per unit cell site. This observation can be generalized into an empirical rule:

Whenever there are integer number of electrons (ignoring the spin degeneracy) in a unit cell, one has an insulator as the ground state. In all other cases, one has a metallic ground state.

If this statement were true, one would be able to open up a gap and obtain an insulator regardless of how we destroy the translational invariance. For instance, instead of introducing the on-site energy Δ that depends on site, one can modulate the hopping amplitude t as $t_1, t_2, t_1 \dots$. This will enlarge the unit cell too. Indeed one can check that one also obtains a gap proportional to $|t_1 - t_2|$.

3.2 Interfaces

We address the question what happens when two materials of different properties are joined together at a sharply defined interface. In reality the interface is a two-dimensional sheet which separates two half-infinite bulks each possessing different gaps, or a metallic bulk adjoined by an insulating counterpart, etc. Here we consider the simplified case of two one-dimensional systems joined at a sharp interface, which is a single line separating two semi-infinite wires.

Figure 3.4: An interface separating materials of different bulk properties

For concreteness, take $i = 1, \dots, N$ sites to belong to a system with “A”-type properties and $i = N + 1, \dots, 2N$ to a system with “B”-type properties. Within each semi-infinite wire we have the Hamiltonian

$$\begin{aligned} H_A &= -t \sum_{i,i+1 \in A} (c_{i+1}^+ c_i + c_i^+ c_{i+1}) + \sum_{i \in A} (\Delta_A (-1)^i - \mu_A) c_i^+ c_i \\ H_B &= -t \sum_{i,i+1 \in B} (c_{i+1}^+ c_i + c_i^+ c_{i+1}) + \sum_{i \in B} (\Delta_B (-1)^i - \mu_B) c_i^+ c_i. \end{aligned} \quad (3.14)$$

Whether each segment is metallic or insulating depends on the exact location of the chemical potentials μ_A and μ_B . If the chemical potential lies in the gapped portion of the energy spectrum it is an insulator. If not, it is a metal.

When two such systems are joined together, one would still expect to observe the same material properties as in the bulk far, far away from the interfacial region. However, the properties at and nearby the junction may be substantially modified. To see if this is really true, first consider the case of two insulators.

Here we have a half-filled insulator coupled to another half-filled insulator. Since transferring charges from region A, at energy $-\Delta_A - \mu_A$, to region B, at energy $\Delta_B - \mu_B$, will cause the amount of energy transfer

$$\Delta E = (\Delta_B - \mu_B) - (-\Delta_A - \mu_A) = \Delta_A + \Delta_B + \mu_A - \mu_B \quad (3.15)$$

which is a positive quantity, it is energetically prohibited to transfer any charges from A to B, or for that matter, from B to A.

The situation is dramatically altered if one material is a metal, and the other an insulator. Take the case where $\mu_A > \Delta_A$, so that A is a metal. The B region is still an insulator with $\mu_B \in [-\Delta_B, \Delta_B]$. Now transferring an electron from A, at the conduction band energy E_A , to B, at $\Delta_B - \mu_B$, costs an energy

$$\Delta E = (\Delta_B - \mu_B) - E_A \quad (3.16)$$

and this expression can be of either sign. In fact when the bottom of the A conduction band (which is partially filled) lies above that of the B conduction band (which is empty), this quantity is guaranteed to be negative. Electron transfer from A to B can further lower the total energy. The B side, upon receiving electrons which fill up its own conduction band, becomes metallic. So, both sides become metals, it seems. Naively one might think that the electron flow would continue until the chemical potential on both sides were equal and transfer of electrons no longer lower the energy.

Figure 3.5: Electron transfer in the metal-insulator interface.

This is however not so when you take into account the effects of Coulomb interaction. If you transfer electrons from one side to the other, side A becomes positively charged, and side B, negatively charged. Positive and negative charges attract each other, forming bound states. That means electrons moving from A to B become confined, over a *depletion layer* of width D . The width can be calculated from elementary electrostatic considerations.

Suppose the excess charge density on either side is given by σ . The corresponding electric field is $E = \sigma$, and the potential difference at $z = \pm D$ is given by $\Delta V = 2D\sigma$. An electron on side A sitting at $z = -D$ has an energy E_A , but the electron on side B sitting at $z = +D$ has an energy $\Delta_B - \mu_B + 2D\sigma$. If these two energies were equal, one could no longer transfer charges from A to B. The condition defines the depletion width

$$D = \frac{E_A - \Delta_B + \mu_B}{2\sigma}. \quad (3.17)$$

The total charge transferred is equal to σ times the depletion width D , or $Q = (E_A - \Delta_B + \mu_B)/2$, which is only fixed by the energy level differences in the original system.

3.3 Exercise

[1][40pts] Diagonalize the Hamiltonian

$$H = - \sum_i t_i (c_{i+1}^+ c_i + c_i^+ c_{i+1}) - \mu \sum_i c_i^+ c_i \quad (3.18)$$

where we have $t_{2i} = t_0 + t_1$ and $t_{2i+1} = t_0 - t_1$. Show that there is a gap opening proportional to t_1 .

[2][30pts] Diagonalize the Hamiltonian

$$H = -t \sum_i \sum_{j \in i} c_j^+ c_i + \sum_i (\Delta_i - \mu) c_i^+ c_i. \quad (3.19)$$

for two-dimensional square lattice. Δ_i is assumed to change sign between neighboring sites. $j \in i$ represents all immediate neighbor sites with respect to i .

Chapter 4

Measurable quantities

This is an ambitious chapter with an intent to cover the theories underlying some of the most routine experimental measurements of the solid state properties. There is a wide array of different measurements available to probe a material and I will cover what seems like the most routine of them all: heat capacity, electric/thermal conductivity, Hall coefficient, and magnetic susceptibility. The beauty of doing solid state physics is a theory can be readily and directly compared with the measurement being done by your neighbors downstairs. Ultimately all of physics have this interplay between experiment and theory, but nowhere is it more routinely done than in solid state physics.

4.1 Heat capacity

Heat capacity is conceptually one of the simplest quantities one could measure in the laboratories. A given state of matter comes with its own average energy $E(T)$ that varies with the temperature. The derivative dE/dT refers to the amount of energy(heat) that's required to raise or lower the temperature by a degree, and we call this the specific heat, or heat capacity. The theory for specific heat therefore amounts to the theory for the average energy E .

4.1.1 Theory

In the free electron picture of a metal, the Fermi sea is the ground state with all the k -states with the energy ϵ_k less than the Fermi energy E_f occupied by electrons of both spin species. However, this statement is only strictly true at $T = 0$. At finite temperature, each energy eigenstate E_k has a finite probability of occupation dictated by the Fermi-Dirac factor

$$F(\epsilon_k - \mu) = \frac{1}{e^{\beta[\epsilon_k - \mu]} + 1}. \quad (4.1)$$

The total number and total energy of the electrons are given by

$$\begin{aligned}
N &= \sum_{k\sigma} F(\epsilon_k - \mu) \\
E &= \sum_{k\sigma} \epsilon_k F(\epsilon_k).
\end{aligned} \tag{4.2}$$

For simple metals, the spin degeneracy simply contributes a factor two to both quantities.

The above expressions can be re-written as integral forms

$$\begin{aligned}
N &= 2V \int \frac{d^D k}{(2\pi)^D} F(\epsilon_k - \mu) \\
E &= 2V \int \frac{d^D k}{(2\pi)^D} \epsilon_k F(\epsilon_k - \mu)
\end{aligned} \tag{4.3}$$

where D is the relevant spatial dimension. It turns out that in $D = 2$ this is particularly simple to calculate:

$$\begin{aligned}
N &= 2V \int_0^\infty \frac{k dk}{2\pi} F\left(\frac{\hbar^2 k^2}{2m} - \mu\right) = V \int_0^\infty \left(\frac{m}{\pi\hbar^2}\right) F(\epsilon - \mu) d\epsilon \\
E &= V \int_0^\infty \left(\frac{m}{\pi\hbar^2}\right) \epsilon F(\epsilon - \mu) d\epsilon
\end{aligned} \tag{4.4}$$

The reason why I kept the constant factor $(m/\pi\hbar^2)$ inside the integrand, rather than outside, is as follows. In arbitrary dimension D one can write down N and E in the form

$$\begin{aligned}
N &= V \int_0^\infty D(\epsilon) F(\epsilon - \mu) d\epsilon \\
E &= V \int_0^\infty D(\epsilon) \epsilon F(\epsilon - \mu) d\epsilon
\end{aligned} \tag{4.5}$$

where $D(\epsilon)$ is the density of states, or DOS for short. By DOS we mean the number of different states within a given energy window, or in differential form, $D(\epsilon) = dN(\epsilon)/d\epsilon$, $N(\epsilon)$ being the total electron number filled up to energy ϵ . For future reference I list the DOS in the free electron picture with $D = 1, 2, 3$.

$$\begin{aligned}
D(\epsilon) &= \frac{1}{\sqrt{\epsilon}} \quad (D = 1) \\
&= \frac{m}{\pi\hbar^2} \quad (D = 2) \\
&= \frac{m}{\pi^2\hbar^2} \sqrt{\frac{2m\epsilon}{\hbar^2}} \quad (D = 3)
\end{aligned} \tag{4.6}$$

The results for one and two dimensions are relevant because the materials we study in solid state laboratories are more and more of lower dimensionality when compared to the materials studied in the past. The exact form of DOS

will be changed as we discuss the realistic band structure and electron-electron, electron-phonon interaction effects. However, the general expressions given in Eq. (4.5) will remain unchanged, and that's why we prefer to write N and E in this form.

The heat capacity, or the specific heat, is defined as the increase in the internal energy as the temperature is increased: $C = dE/dT$. According to Eq. (4.5) it is given by

$$C = \int_0^\infty D(\epsilon) \epsilon \frac{dF(\epsilon - \mu)}{dT} d\epsilon. \quad (4.7)$$

Since the energy $\epsilon - \mu$ and the temperature T always enters as a combination $(\epsilon - \mu)/T$ in the Fermi function we can invoke the identity, applicable for arbitrary function $f((\epsilon - \mu)/T)$:

$$\left((\epsilon - \mu) \frac{d}{d\epsilon} + T \frac{d}{dT} \right) f \left(\frac{\epsilon - \mu}{T} \right) = 0$$

to re-write

$$C = \int_0^\infty D(\epsilon) \frac{\epsilon(\epsilon - \mu)}{T} \left(-\frac{\partial F(\epsilon - \mu)}{\partial \epsilon} \right) d\epsilon. \quad (4.8)$$

The quantity inside the bracket,

$$-\frac{\partial F}{\partial \epsilon} = \frac{\beta/4}{\cosh^2 [\beta(\epsilon - \mu)/2]}, \quad (4.9)$$

is a rather sharply peaked function of ϵ , and integrating it over energies from 0 to ∞ gives $-F(\infty) + F(0) = 1$. In other words, the quantity in the bracket behaves a lot like a Dirac delta function whose peak is located at $\epsilon = \mu$.

Based on this peculiar property of the derivative of the Fermi-Dirac function we can approximate Eq. (4.8) as

$$\begin{aligned} C &= \int_{-\mu}^\infty D(\epsilon) \frac{\epsilon(\epsilon + \mu)}{T} \frac{\beta/4}{\cosh^2 [\beta\epsilon/2]} d\epsilon \approx \frac{D(\mu)}{4T^2} \int_{-\infty}^\infty \frac{\epsilon^2}{\cosh^2 [\beta\epsilon/2]} d\epsilon \\ &= 2D(\mu)T \times \int_{-\infty}^\infty \frac{x^2}{\cosh^2 x} dx \propto D(\mu)T. \end{aligned} \quad (4.10)$$

The final analysis reveals that the electronic specific heat is proportional to temperature and the density of states at the Fermi level, $D(\mu)$. The exact proportionality constant depends on the way we model the electron spectrum and the level of approximations involved in calculating the density of states, but the basic relation $C \propto D(\mu)T$ remains valid for metallic systems. In research papers one sometimes see the heat capacity expressed as C/T in an attempt to extract the material's DOS at low temperature. This, and the paramagnetic susceptibility to be discussed later, are two popular ways to determine the DOS at the Fermi level for metallic systems.

In contrast, the specific heat of an insulator shows a very different behavior. For instance, consider an insulator which has a gap equal to Δ between the highest occupied energy level and the lowest unoccupied one. The fraction of the electrons sitting in the level above the energy gap is $N_c/N = F(\Delta - \mu)$.

Similarly, the fraction of the electrons that has been removed from the top of the valence band is $N_v/N = 1 - F(-\mu)$. Because of the number conservation the two quantities must match,

$$F(\Delta - \mu) = 1 - F(-\mu). \quad (4.11)$$

This will be true if $\mu = \Delta/2$, because of the identity $F(x) + F(-x) = 1$ of the Fermi-Dirac function.

Having fixed the chemical potential for arbitrary temperature T , we can calculate the energy change due to the thermal population of the conduction band:

$$\Delta E = N_c \frac{\Delta}{2} - N_v \left(-\frac{\Delta}{2} \right) = (N_c + N_v) \frac{\Delta}{2} = \Delta \times F \left(\frac{\Delta}{2} \right). \quad (4.12)$$

The specific heat is just the derivative of this quantity with respect to temperature,

$$C_e = \frac{1}{2} \left(\frac{\Delta}{T} \right)^2 \frac{1}{4 \cosh^2[\Delta/4T]}. \quad (4.13)$$

A plot of this quantity quickly reveals that its behavior is very different from that of a metal.

- It is exponentially suppressed at temperatures much less than the gap, $T \ll \Delta$.
- It reaches a maximum at $T \sim \Delta$.
- It falls off exponentially for $T \gg \Delta$.

Inversely speaking, when one measures a behavior of this type, one can conclude that it possesses a gap, and the gap value can be extracted by fitting the measured temperature dependence to a formula like (4.13).

4.1.2 How we measure

These days a simple heat capacity measurement is carried out on a routine basis in the MPMS machines made by Quantum Design, Inc. In both metals and insulators one has the phonons involved in the dynamics and making a significant contribution to the specific heat. What one has to do in reality is to measure the total value, $C = C_e + C_{ph}$ and somehow subtract off the phonon part C_{ph} in order to isolate the electronic portion of the specific heat. I leave it as a homework exercise for the students to learn how the “phonon subtraction” is done in laboratories. It will be an excellent opportunity for some of the students to go over the principles behind the measurement techniques they are accustomed to.

4.2 Electrical and thermal conductivity

When we synthesize a new material, the first question one asks is “Is it a metal, an insulator, or a superconductor?”. The question is directly answered by measuring the conductivity.

4.2.1 Theory

In this section we discuss the electrical and thermal conductivity of electrons in a metal in terms of the Drude theory¹. The full-blown quantum-mechanical theories are in the realm of the many-body theory and outside the scope of this lecture. The Drude model treats each electron as a classical particle subject to the influence of electric and magnetic fields in a solid according to Newton’s law,

$$m \frac{d\mathbf{v}}{dt} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - m \frac{\mathbf{v}}{\tau}, \quad (4.14)$$

where τ is the relaxation time. Various things contribute to the relaxation processes of the electron including electron-electron scattering, electron-phonon scattering, and scattering off impurities. Our treatment here is phenomenological. In the presence of a constant electric field \mathbf{E}_0 and zero magnetic field, the initial velocity \mathbf{v}_0 develops into

$$\mathbf{v}(t) = -\frac{e\tau}{m}\mathbf{E}_0 + \left(\mathbf{v}_0 + \frac{e\tau}{m}\mathbf{E}_0\right)e^{-t/\tau}. \quad (4.15)$$

Over the time τ the electron will have “relaxed” into a constant velocity given by

$$\mathbf{v} = -\frac{e\tau}{m}\mathbf{E}_0. \quad (4.16)$$

When the density of electrons is n , the current density \mathbf{j} in response to \mathbf{E}_0 is

$$\mathbf{j} = -nev = \frac{ne^2\tau}{m}\mathbf{E}_0. \quad (4.17)$$

The electrical conductivity is the ratio of the current density divided by the electric field, $\sigma = ne^2\tau/m$. Measurements are often reported in resistivity ρ , the inverse of conductivity. Using the reported value of ρ and density n for typical metals the relaxation time can be worked out using the formula above. It is typically in the vicinity of 10^{-14} s.

Thermal conductivity is similar to the electrical conductivity. It measures the amount of internal energy transferred from one side of the system to the other in the presence of temperature gradient ∇T across it. The electrical conductivity, in contrast, measures the amount of charge transferred in the presence of the potential gradient $\nabla\phi$. The derivation of the thermal conductivity, also due to Drude (1900), is as follows.

Consider the amount of energy current passing through x when the temperature gradient dT/dx is present along the x -direction. Roughly $n/2$ electrons

¹J.J. Thompson confirmed the existence of a negatively charged particle called the “electron” in 1896. Drude made his theory of electron conduction shortly afterward. His theory has a close resemblance to the kinetic theory of gases developed some decades earlier.

from $x + v\tau$ has travelled to the left and arrived at x in time τ , each electron carrying the energy $\epsilon(x + v_x\tau)$. Another $n/2$ electrons from $x - v\tau$ has travelled the same distance, arrived at x , over the time τ carrying the energy $\epsilon(x - v_x\tau)$. The energy current is given by

$$j_\epsilon = \frac{n}{2}v_x[\epsilon(x - v_x\tau) - \epsilon(x + v_x\tau)] \approx -nv_x^2\tau\frac{d\epsilon}{dx} = -nv_x^2\tau\frac{d\epsilon}{dT}\frac{dT}{dx}. \quad (4.18)$$

Since there are many electrons traveling inside the metal, the quantities appearing in this equation should be regarded as thermal averages. From classical statistical mechanics we know that $\langle v_x^2 \rangle = (2/m)(k_B T/2) = k_B T/m$. Moreover, $d\epsilon/dT$ is the specific heat of the electrons which in classical statistical mechanics equal $(3/2)k_B$. Putting the results together,

$$j_\epsilon = -n\tau\frac{k_B T}{m}\frac{3}{2}k_B \times \frac{dT}{dx} = -\frac{3n\tau}{2m}k_B^2 T \times \frac{dT}{dx}. \quad (4.19)$$

The thermal conductivity is the ratio $\kappa = |j_\epsilon/(dT/dx)| = (3n\tau/2m)k_B^2 T$. An interesting ratio is formed between this quantity and σT :

$$\frac{\kappa}{\sigma T} = \frac{(3n\tau/2m)k_B^2 T}{(ne^2\tau/m)T} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2. \quad (4.20)$$

The ratio, known as the Lorenz (not Lorentz) number, is a surprising combination of two fundamental constants of nature, independent of the materials being looked at. Indeed the universality of this ratio is obeyed in a large number of metals and is known as the Wiedemann-Franz law after the original discoverers of the phenomenon (1853). The Lorenz number for a wide selection of metals is quoted in Kittel, p. 168 [7th Ed.].

4.2.2 How we measure

Electrical conductivity is quite simple to measure. I need a student presentation on how a typical metal's resistivity behaves when temperature is lowered and compare it to the typical behavior of an insulator and superconductor. Real measurement data need to be presented. It will be nice to add the resistivity data on a fourth kind of material, namely the one-dimensional material such as nanotubes. Thermal conductivity data for these four classes of materials need to be presented also.

4.3 Hall effect

4.3.1 Theory

Before we discuss Hall effect, we will start with a general consideration of how an electron motion is modified when a magnetic field is turned on. The spin orientation along and against the applied field direction is responsible for the energy splitting known as the Zeeman splitting. The quantum mechanical Hamiltonian giving rise to the Zeeman effect is given by

$$H_Z = \frac{\mu_B}{\hbar} g_s \mathbf{S} \cdot \mathbf{B} \quad (4.21)$$

where $\mu_B = 5.8 \times 10^{-5} \text{eV/T}$ is the Bohr magneton, g_s is the gyromagnetic ratio which for electrons is 2. The spin quantum number S_z takes on $\pm\hbar/2$ along the \mathbf{B} direction. The amount of energy level splitting under a 10T magnetic field is $5.8 \times 10^{-5} \times 2 \times 10 \text{ eV} \approx 1 \text{ meV}$ and that's a tiny fraction of the Fermi energy of typical metals. This tiny difference shows up as the paramagnetic susceptibility which we will discuss in the next section.

The trajectory of the electron on the other hand is governed by the classical equation as

$$m \left(\frac{d}{dt} + \frac{1}{\tau} \right) \mathbf{v} = -e (\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (4.22)$$

Following Edwin Hall's original experimental setup, we apply the electric field along \hat{x} direction and the magnetic field along \hat{z} for a flat strip of metal extended in the $x - y$ directions. In a steady-state situation the time derivative is zero, and we obtain

$$\begin{aligned} \mathbf{v} + \frac{\tau e}{m} (E\hat{x} + B\mathbf{v} \times \hat{z}) &= 0 \\ v_x + \frac{\tau e}{m} (E + Bv_y) &= 0 \\ v_y + \frac{\tau e}{m} (-Bv_x) &= 0. \end{aligned} \quad (4.23)$$

Solving the last equation gives $v_y = (\tau e B/m)v_x$. Although electric field is along the \hat{x} direction, there is electron motion perpendicular to it, along the \hat{y} direction, due to the magnetic field. Working out some algebra, one finds that the current density in the electric field direction is given by

$$J_x = \frac{\sigma_0}{1 + (\omega_c \tau)^2} E_x \quad (4.24)$$

where $\omega_c = eB/m$ is the cyclotron frequency, and $\sigma_0 = ne^2\tau/m$ is the dc electrical resistivity. There is a little less current along the applied potential gradient if there is a magnetic field present. Where did the missing current go? - It went the y -way, of course. The current along the y -direction can be worked out:

$$J_y = \omega_c \tau J_x = \sigma_0 \frac{\omega_c \tau}{1 + (\omega_c \tau)^2} E_x. \quad (4.25)$$

The net current divided by the electric field is $\sqrt{J_x^2 + J_y^2}/E_x = \sigma_0/\sqrt{1 + (\omega_c \tau)^2}$, and it's less than what's possible without the magnetic field. The magnetic field thus affects the electrical resistivity. The phenomenon of the dependence of the electrical conductivity on the applied magnetic field is known as the magnetoresistance.

The angle θ which the current vector makes with the electric field is set by $\tan \theta = \omega_c \tau$. This quantity is not necessarily small; if the magnetic field is very strong and the relaxation time is very large, we can have $\omega_c \tau \gg 1$. Then most of the current actually flows orthogonal to the electric field's direction. Similar to

the longitudinal conductivity $\sigma_{xx} \equiv J_x/E_x$, we can define the Hall conductivity σ_{xy} given by

$$\sigma_{xy} = \frac{J_y}{E_x} = \frac{\sigma_0 \omega_c \tau}{1 + (\omega_c \tau)^2} \sim \frac{\sigma_0}{\omega_c \tau} = \frac{ne}{B}. \quad (4.26)$$

The Hall coefficient R_H is related to σ_{xy} by $R_H = 1/(B\sigma_{xy}) = 1/ne$ in the clean limit.

4.3.2 How we measure

Hall effect is a popular way to characterize the carrier types in semiconductors. It is used extensively in the study of metallic or semi-conducting magnets. In quantum Hall systems the transverse conductivity σ_{xy} is quantized at certain discrete multiples of e^2/h , h being the Planck's constant. It will be nice to know how the Hall coefficient R_H or transverse conductivity σ_{xy} is actually measured.

4.4 Magnetic susceptibility

4.4.1 Theory

Electron spins are responsible for the magnetism in solids. Even for non-magnetic systems for which the population of up and down spins are equal, one can tip the balance by applying a magnetic field which would tend to produce more electrons having spins along the field's direction than counter to it. A complete alignment of spin direction along the field direction is hampered by thermal fluctuation in the case of localized spins, and by Pauli principle for electrons in a metal. The degree of spin polarization is expressed by the magnetization

$$M = \mu_B(n_\uparrow - n_\downarrow) \quad (4.27)$$

which is proportional to the difference of up- and down-spin electron densities. For non-magnetic systems M rises in proportional to the applied field strength, and the ratio M/B is known as the magnetic susceptibility, χ . We will evaluate the magnetization for localized spins and derive the Curie's law of susceptibility, and for conduction spins and derive the Pauli susceptibility.

Curie's law: Consider a collection of localized spins with the spin $\mathbf{S}^2 = S(S+1)$. The spin-1/2 case is the simplest to consider and we will start with this. When subject to a magnetic field, the energy levels of the two spin states are split into $\pm\mu_B B$. The population of each spin state at temperature T is dictated by the Boltzmann's law:

$$\begin{aligned} n_\uparrow &= \frac{e^{\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} \\ n_\downarrow &= \frac{e^{-\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}}. \end{aligned} \quad (4.28)$$

The magnetic moment per spin is given by the difference,

$$M = \mu \tanh(\beta\mu B). \quad (4.29)$$

As I mentioned before, a 10T field induces the Zeeman splitting $\mu B \approx 1 \text{ meV} \approx 10 \text{ K}$. At room temperature, the argument of the tanh function is a small number and we can expand the r.h.s. to first order to get

$$M \approx \frac{\mu^2 B}{kT}, \quad \chi = \frac{\mu^2}{k_B T}. \quad (4.30)$$

The plot of $1/\chi$ vs. temperature yields a straight line with the slope dictated by μ^2 .

Due to the Hund coupling, magnetic ions in real compounds often behave as if their effective spin number was larger than $1/2$. The Hamiltonian responsible for the Zeeman splitting is $H_Z = -g\mu S_z B$ with $S_z = -S, -S+1, \dots, S-1, S$. For general S , one can derive the magnetization

$$M = \sum_{m=-S}^S mP(m), \quad P(m) = \frac{e^{-\beta g\mu m B}}{\sum_{m=-S}^S e^{-\beta g\mu m B}}. \quad (4.31)$$

The sum over $2S+1$ states can be carried out straightforwardly and the magnetization yields a function known as the Brillouin function given by

$$B(x) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S} \coth\left(\frac{x}{2S}\right), \quad (4.32)$$

where $x \equiv gS\mu B/kT$. For small x , we have the susceptibility

$$\frac{M}{B} \approx \frac{S(S+1)g^2\mu^2}{3kT}. \quad (4.33)$$

By plotting $1/\chi$ vs T we can read off the slope and the effective spin S of the compound under scrutiny.

Pauli Paramagnetism: For localized electrons Pauli principle did not play a role because different spins occupied different spatial locations anyway. That's why a small magnetic field is able to completely align all the spins in the zero temperature limit for the localized magnets. This is not the case with the itinerant electrons, where the Pauli principle forbids the complete alignment of all the spins even at $T=0$.

For simplicity we use the free electron result for the kinetic energy of the electrons. Before the magnetic field is on, both spin states of the electrons have the energy $\epsilon_k = \hbar^2 k^2/2m$. The magnetic field splits the energy according to the spin orientation, so that one gets

$$\epsilon_k^+ = \frac{\hbar^2 k^2}{2m} - \mu B, \quad \epsilon_k^- = \frac{\hbar^2 k^2}{2m} + \mu B. \quad (4.34)$$

But still both spin states are filled up to the same Fermi energy E_f . That means k_f^+ and k_f^- are also different, according to

$$\frac{(\hbar k^\pm)^2}{2m} \mp \mu B = E_f. \quad (4.35)$$

Accordingly there is more up-spin than down-spin electrons, and the difference is evaluated as

$$\begin{aligned}
 N_{\uparrow} - N_{\downarrow} &= \int_{-\mu B}^{E_f} D(\epsilon + \mu B) d\epsilon - \int_{\mu B}^{E_f} D(\epsilon - \mu B) d\epsilon \\
 &= \int_0^{E_f + \mu B} D(\epsilon) d\epsilon - \int_0^{E_f - \mu B} D(\epsilon) d\epsilon = \int_{E_f - \mu B}^{E_f + \mu B} D(\epsilon) d\epsilon \\
 &\approx 2\mu B D(E_f).
 \end{aligned} \tag{4.36}$$

The magnetization and susceptibility follow as

$$M = 2\mu^2 D(E_f) B, \quad \chi = 2\mu^2 D(E_f). \tag{4.37}$$

For non-interacting electrons the density of states at the Fermi level is $D(E_f) = 3N/4E_f$, and $\chi = 3\mu^2/2k_B E_f$. Various interaction and impurity effects modify the exact expression for the density of states but the proportionality of χ to the Fermi level DOS survives many theoretical modifications. By measuring the susceptibility of a metal, one often gets a good idea of the DOS of the particular material. Heat capacity C/T and the Pauli susceptibility χ are both used to probe the Fermi-level DOS of metals.

4.4.2 How we measure

How one measures the Pauli susceptibility of a metal is an interesting topic about which I know little. A student presentation on early measurement data will be highly welcome. Same goes for the Curie susceptibility of some typical magnets.

4.5 Diamagnetism

If the paramagnetic response in a solid is due to the electron spins, the diamagnetic response under the external B field is due to the electron's orbital motion. When an electron is orbiting around a nucleus (which is a fair assumption in some ionic crystals and noble gases) and an external magnetic field is set up, the electrons will have its motion perturbed in such a way that extra flux opposing the external one will be set up. This is just Lenz's law for the electrons in an atom.

A theorem due to Larmor states that if an electron circled around a nucleus with frequency ω_0 , the external field B will produce a change in this frequency given by

$$\omega_L = \frac{eB}{2m}. \tag{4.38}$$

Note that this is half the cyclotron frequency. For such a shift in the frequency, the extra current produced can be calculated as

$$\Delta I = (-Ze) \left(\frac{1}{2\pi} \frac{eB}{2m} \right). \tag{4.39}$$

The magnetic moment produced by the extra current loop is given by the current times the area of the loop, given by the average of $\pi(x^2+y^2)$. Thus the magnetic moment induced by the B field is

$$M = -\frac{Ze^2B}{4m}\langle r^2 \rangle. \quad (4.40)$$

The magnetic susceptibility is obtained as $\chi = M/B$. The electron distribution $\langle r^2 \rangle$ can be calculated for each atom. This kind of diamagnetic response of electronic orbitals is known as the Larmor (or Langevin) diamagnetism.

If the Larmor/Langevin diamagnetism is due to the electrons confined around a nucleus and is essentially a manifestation of Lenz' law, Landau diamagnetism comes from the free electrons which form the Fermi surface. When a magnetic field is applied along the z direction, the associated vector potential in the linear gauge reads $\mathbf{A} = B(0, x, 0)$, and the Hamiltonian of the electron is modified to

$$H = \frac{1}{2m}(\mathbf{p} - e\mathbf{A})^2. \quad (4.41)$$

The eigenstates of this Hamiltonian form the new energy levels which the electrons occupy from the lowest up. The total energy of the N electron system will be dependent on the applied field B : $E = E(B)$. Using the laws of thermodynamics one can calculate the magnetic moment and the magnetic susceptibility as the first and the second derivatives of the total energy according to

$$M = -\frac{\partial E}{\partial B}, \quad \chi = -\frac{\partial^2 E}{\partial B^2}. \quad (4.42)$$

By calculating $E(B)$ one can calculate χ for a collection of free electrons. It turns out that this response is diamagnetic, and has the magnitude one third that of Pauli paramagnetic susceptibility.

4.6 Exercise

[1][10pts] Derive the density of states $D(\epsilon)$ in one and three dimensional metals.

[2][10pts] Use the equation $m(d\mathbf{v}/dt + \mathbf{v}/\tau) = -e\mathbf{E}$ for the electron drift velocity \mathbf{v} to show that the conductivity at frequency ω (i.e. $\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t}$) is

$$\sigma(\omega) = \frac{ne^2\tau}{m} \frac{1}{1 - i\omega\tau}. \quad (4.43)$$

[3][50pts] Answer one of the following questions based on your own experience in the laboratory. If you are a theory student it will be a nice opportunity to learn about how an actual measurement is being done by your friends in the basement. There will be a student presentation on each one of the measurement techniques as well. Discuss the general measurement scheme *and* an explicit case of the type of measurement you are describing. I tend to put heavy emphasis on this type of exercise so give it your best shot! I will do the grading for this problem.

- How do we measure heat capacity in the laboratory? How do we make a phonon subtraction?
- How do we measure thermal and electrical conductivity in the laboratory?
- How is the Hall conductance/conductivity measured in various devices including semiconductors, quantum Hall devices, and diluted magnetic semiconductors?
- How do we measure the magnetic susceptibility of insulators with localized spins and metals with itinerant spins?

[3][Kittel, Chap. 14, Prob. 3][20pts] Some organic molecules have a triplet ($S=1$) excited state at an energy $k_B\Delta$ above a singlet ($S=0$) ground state. (a) Find an expression for the magnetic moment M in a field B . (b) Find an expression for the heat capacity.

[4][Kittel, Chap. 14, Prob. 4][20pts] Consider a two-level system with an energy splitting $k_B\Delta$ between upper and lower states; the splitting may arise from a magnetic field or in other ways. Show that the heat capacity per system is

$$C = \left(\frac{\partial U}{\partial T} \right)_{\Delta} = k_B \frac{(\Delta/T)^2 e^{\Delta/T}}{(1 + e^{\Delta/T})^2}. \quad (4.44)$$

Plot of this function shows a pronounced peak at $T \approx \Delta$. Peaks of this type in the heat capacity are often known as Schottky anomalies.

[5][20pts] Derive Brillouin function of the magnetization for spin- S .

Chapter 5

Landau level problem

Here we show how to solve the problem of an electron moving in a two-dimensional plane subject to a constant, perpendicular magnetic field. The relevant Hamiltonian is

$$\frac{1}{2m}(\mathbf{p} - e\mathbf{A})^2\psi = E\psi. \quad (5.1)$$

5.1 Landau gauge

In the Landau gauge we choose $\mathbf{A} = B(0, x)$.

$$\frac{1}{2m}(p_x)^2\psi + \frac{1}{2m}(p_y - eBx)^2\psi = E\psi. \quad (5.2)$$

A plane-wave solution is assumed for the y -dependence, $\psi = e^{iky}\phi$. The x -dependent ϕ obeys

$$-\frac{1}{2m}\partial_x^2\phi + \frac{1}{2m}(k - eBx)^2\phi = E\psi. \quad (5.3)$$

It is convenient to introduce the magnetic length $l_B = \sqrt{\hbar/eB}$, $x_k = x - kl_B^2$,

$$-l_B^2\partial_x^2\phi + \left(\frac{x_k}{l_B}\right)^2\phi = 2mEl_B^2\psi. \quad (5.4)$$

The whole equation can be cast in the dimensionless form by re-definition $x_k/l_B \rightarrow x_k$, $2mEl_B^2 = E$:

$$-\partial_x^2\phi + x_k^2\phi = [(x_k - \partial_x)(x_k + \partial_x) + 1]\psi = E\psi. \quad (5.5)$$

We can define $a = (x_k + \partial_x)/\sqrt{2}$ and $a^\dagger = (x_k - \partial_x)/\sqrt{2}$ as annihilation and creation operators, $[a, a^\dagger] = 1$. We arrive at the familiar form

$$[2a^\dagger a + 1]\phi = E\phi, \quad (5.6)$$

with the eigenstates $|n\rangle = (a^\dagger)^n |0\rangle / \sqrt{n!}$. $|0\rangle$ is the Gaussian function satisfying

$$(x_k + \partial_x)\phi_0 = 0 \rightarrow \phi_0 = e^{-x_k^2/2}. \quad (5.7)$$

5.2 Symmetric gauge

In the symmetric gauge we choose $\mathbf{A} = B(-y, x)/2$. Before we insert this expression into the Schrödinger equation, we first introduce a new pair of operators

$$\Pi_x = p_x - eA_x, \quad \Pi_y = p_y - eA_y, \quad (5.8)$$

and $\Pi^\pm = \Pi_x \pm i\Pi_y$. Then

$$\frac{1}{2m}(\Pi_x^2 + \Pi_y^2) = \frac{1}{2m}(\Pi^- \Pi^+ - i[\Pi_x, \Pi_y]) = \frac{1}{2m}(\Pi^- \Pi^+ + eB). \quad (5.9)$$

Employing the complex coordinates $z = x + iy$ and its conjugate $\bar{z} = x - iy$, and their derivatives $\partial_z = (\partial_x - i\partial_y)/2$, $\partial_{\bar{z}} = (\partial_x + i\partial_y)/2$,

$$\begin{aligned} \Pi^+ &= -i(\partial_x + i\partial_y) - \frac{eBi}{2}(x + iy) = -2i\partial_{\bar{z}} - \frac{eBi}{2}z \\ \Pi^- &= -i(\partial_x - i\partial_y) + \frac{eBi}{2}(x - iy) = -2i\partial_z + \frac{eBi}{2}\bar{z}. \end{aligned} \quad (5.10)$$

As in the Landau gauge problem we introduce the magnetic length $l_B = \sqrt{\hbar/eB}$ and define dimensionless variables $z/(2l_B) \rightarrow z$, etc. The Hamiltonian becomes

$$\left([\bar{z} - \partial_z][z + \partial_{\bar{z}}] + 1\right)\psi = E\psi \quad (5.11)$$

Here a and a^\dagger are defined by

$$a = \frac{1}{\sqrt{2}}(z + \partial_{\bar{z}}), \quad a^\dagger = \frac{1}{\sqrt{2}}(\bar{z} - \partial_z), \quad (5.12)$$

$[a, a^\dagger] = 1$. Once again the Hamiltonian becomes

$$[2a^\dagger a + 1]\phi = E\phi, \quad (5.13)$$

with the eigenstates $|n\rangle = (a^\dagger)^n |0\rangle / \sqrt{n!}$. $|0\rangle$ is the Gaussian function satisfying

$$(z + \partial_{\bar{z}})\phi_0 = 0 \rightarrow \phi_0 = z^m e^{-z\bar{z}}. \quad (5.14)$$

Here m is an arbitrary integer, playing the role of an angular momentum.

Chapter 6

Phonon Dynamics

A solid is a solid because the positive ions stay together despite their huge Coulomb repulsion, because the attraction with the surrounding electrons is just enough to overcome the ion-ion repulsion. The ions maintain a certain distance because that's when the total energy of the solid becomes the lowest. At $T = 0$ the solid under consideration exists as the quantum-mechanical ground state for the Hamiltonian which defines it.

When the temperature is raised to a finite value, it is not only the ground state that's realized, but a lot of other low-energy excitations which lie within the range of the thermal energy T . To understand the properties of a solid, it is essential to know the whole set of allowed low-energy excitations as well. Among these, we want to focus on the low-energy dynamics of the ions - the phonons.

At $T = 0$ the ions maintain a strict distance corresponding to the minimum of the total energy. That means that if the ionic separation were a little greater or a little less than this optimal value, one would see the increase of the total energy. Write the displacement vector of each ion from its optimal position by \mathbf{u}_i , where i indicates each ionic position in equilibrium. It is sensible to assume that the total energy depends on this displacement vector as $E(\{\mathbf{u}_i - \mathbf{u}_j\})$ for all pairs of ions at i and j . It is a function of the difference only, because moving the two ions together preserves the relative distance.

Further-neighbor ions are less tightly coupled than the nearest-neighbor pair, and the simplest model for the dependence of the total energy on the ionic sites is achieved if we assume that it depends on the relative positions of the nearest-neighbor ions only. Assuming further that the displacements are a small fraction of the average spacing, one can expand the total energy in small displacement as

$$E \approx E_0 + \frac{K}{2} \sum_{\langle ij \rangle} (\mathbf{u}_i - \mathbf{u}_j)^2. \quad (6.1)$$

A quantum theory of the lattice dynamics would start from a Hamiltonian such as

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{K}{2} \sum_{\langle ij \rangle} (\mathbf{u}_i - \mathbf{u}_j)^2, \quad (6.2)$$

with the commutation relations $[p_{i\alpha}, u_{j\beta}] = -i\hbar\delta_{ij}\delta_{\alpha\beta}$. It is possible to work out the solution of the Hamiltonian (6.2) exactly, because the interaction is *harmonic*. It helps greatly to understand the classical version of the problem first because much of the classical solution carries over to the quantum case and the classical problem is slightly simpler to treat.

6.1 Classical view of phonon dynamics

As a way to build up our technical ability, it is advisable to consider the one-dimensional problem first. That is, we consider the case of a linear chain of identical mass m , each coupled to its neighboring mass to the left and right by the spring of stiffness k . The force exerted on the i -th mass is given by $k(x_{i+1} - x_i) + k(x_{i-1} - x_i) = k(x_{i+1} + x_{i-1} - 2x_i)$. Equation of motion of the i -th mass is thus

$$m \frac{d^2 x_i}{dt^2} = k(x_{i+1} + x_{i-1} - 2x_i). \quad (6.3)$$

Adopting the solution $x_i(t) = A_i e^{-i\omega t}$, the matrix equation obtained for A_i 's is

$$-m\omega^2 A_i = k(A_{i+1} + A_{i-1} - 2A_i) \quad (i = 1, \dots, N) \quad (6.4)$$

where we make the association $A_{N+1} = A_1$ and $A_0 = A_N$ (periodic boundary condition).

This problem has an exact solution given by $A_i = A_0 e^{ikn_i}$ where n_i is an integer taking on the value i for each site i . To check that this is the correct solution, first substitute it into the equation, and one will find

$$\begin{aligned} -m\omega^2 A_i &= k(e^{ik} + e^{-ik} - 2)A_i = -2k(1 - \cos k)A_i \\ \omega^2 &= \frac{k}{m} \left(2 \cos \frac{k}{2}\right)^2. \end{aligned} \quad (6.5)$$

So we obtained that the eigenfrequency ω is equal to $2\omega_0 \cos(k/2)$. But this is not yet good, unless we know what the k value is. To learn how to determine k , go back to the assignment $A_i = e^{ikn_i}$. We assumed that $A_{N+1} = A_1$, and in order to meet this requirement we must also assume that $e^{ikN} = 1$. A discrete set of k values are obtained from this condition, and thus a discrete set of ω_n .

$$k = \frac{2\pi n}{N}, \quad \omega_n = 2\omega_0 \cos\left(\frac{\pi n}{N}\right). \quad (6.6)$$

Counting how many different eigenfrequencies are possible, one finds there are N distinct ω_n 's in the problem, the same as the number of masses on a string. And that's the right result.

The eigenfrequency spectrum we obtain through this simple exercise is in fact the exact eigenenergy spectrum of the corresponding quantum problem. The eigenenergy is the frequency ω_k multiplied by Planck's constant, $\hbar\omega_k$. With the neutron scattering one can measure the energy and momentum relation of the phonons. For realistic solids the phonon dynamics is much more complicated than the simple formula ω_k indicates. Among other reasons, this is due to the

fact that there exists more than one sort of ion per unit cell in real materials. The complications brought about by multiple ions in a unit cell is illustrated by the following simple example.

Take the one-dimensional chain of ions again, but this time a pair of adjacent ions stay closer than between the pairs. The spring constant is similarly modified. For convenience label the left portion of the pair by an odd site $2i + 1$, and the right portion by an even site, $2i$. The dynamics of an odd site is given by

$$m \frac{d^2 x_{2i+1}}{dt^2} = K(x_{2i+2} - x_{2i+1}) + k(x_{2i} - x_{2i+1}). \quad (6.7)$$

There are two spring constants K and k corresponding to a shorter bond and a longer one. The dynamics of an even site is given by

$$m \frac{d^2 x_{2i}}{dt^2} = k(x_{2i+1} - x_{2i}) + K(x_{2i-1} - x_{2i}). \quad (6.8)$$

The chain consists of N pairs of ions, and the periodic boundary condition is $x_{i+2N} = x_i$. Looking at the even sites alone, it appears that all ions are identical. The same is true of all the odd sites. Therefore, one can try out the same type of solution

$$\begin{aligned} x_{2i} &= A \exp(ik[2n_i] - i\omega t) \\ x_{2i+1} &= B \exp(ik[2n_i + 1] - i\omega t) \end{aligned} \quad (6.9)$$

In general there is no reason to expect $A = B$ because the even and odd ions are, after all, not identical. Inserting these trial solutions into the equation (6.7) and (6.8),

$$\begin{aligned} -m\omega^2 A &= k(e^{ik}B - A) + K(Be^{-ik} - A) \\ -m\omega^2 B &= K(e^{ik}A - B) + k(e^{-ik}A - B) \end{aligned} \quad (6.10)$$

After a little re-arrangement we get

$$\begin{pmatrix} k + K - m\omega^2 & -ke^{ik} - Ke^{-ik} \\ -Ke^{ik} - ke^{-ik} & k + K - m\omega^2 \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = 0 \quad (6.11)$$

The characteristic equation, $(m\omega^2 - k - K)^2 - (k^2 + K^2 + 2kK \cos 2k) = 0$ offers two solution

$$m\omega^2 = k + K \pm \sqrt{k^2 + K^2 + 2kK \cos 2k}. \quad (6.12)$$

After solving a challenging problem such as this one has to do a little sanity check. For $k = K$ one has to recover the prior solution, so let's see if this is the case. With $k = K$, Eq. (6.12) reduces to

$$m\omega^2 = 2K \pm \sqrt{2K^2(1 + \cos 2k)} = 2K(1 \pm |\cos k|). \quad (6.13)$$

In the previous case we obtain $m\omega^2 = 2K(1 - \cos k)$.

Here the separation of a single energy spectrum into two branches is artificial. But for the diatomic model the separation is real, and one can really observe two independent branches of phonons per each k known as acoustic(lower) and optical(higher) branches.

6.2 Quantum view of phonon dynamics

In the previous section, we mentioned that the quantum counterpart of the classical phonon dynamics is also exactly solvable, giving rise to the identical energy spectrum. This implies that the quantum Hamiltonian, Eq. (6.2), once properly diagonalized, will be reduced to the form

$$H = \sum_k \hbar\omega_k a_k^+ a_k \quad (6.14)$$

where a_k^+ and a_k are the creation and annihilation operators for the phonon mode of momentum k . What lies between this result and the classical result is the introduction of annihilation and creation operators ($K \equiv m\omega_0^2$)

$$\begin{aligned} a_i &= \sqrt{\frac{m\omega_0}{2\hbar}} \left(x_i + \frac{ip_i}{m\omega_0} \right) \\ a_i^+ &= \sqrt{\frac{m\omega_0}{2\hbar}} \left(x_i - \frac{ip_i}{m\omega_0} \right). \end{aligned} \quad (6.15)$$

Insert these into the 1D Hamiltonian $H = \sum_i (p_i^2/2m) + (K/2) \sum_i (x_{i+1} - x_i)^2$ and use the Fourier representation

$$a_i = \frac{1}{\sqrt{N}} \sum_k a_k e^{ikr_i}, \quad (6.16)$$

one indeed recovers Eq. (6.14). The derivation is left as an exercise.

Now that we have a diagonalized Hamiltonian (6.14) for the phonon dynamics, what are the physical implications of the energy spectrum thus worked out? In a sense, it is the specific heat which offers the most straightforward answer because it is the easiest quantity to calculate. The specific heat is just the derivative of the total energy U with respect to temperature, so it is needed to work out the average energy $U = \langle H \rangle$ at a given T .

The phonons are bosons because the operators involved in diagonalizing the phonon Hamiltonian obey bosonic commutation relations, $[a_i, a_j^+] = \delta_{ij}$. As a consequence, the boson occupation number $\langle a_k^+ a_k \rangle$ must obey the Bose-Einstein distribution ($\hbar \equiv 1$)

$$\langle a_k^+ a_k \rangle = B_k = \frac{1}{e^{\beta\omega_k} - 1}. \quad (6.17)$$

The internal energy is given by

$$U = \sum_k \frac{\omega_k}{e^{\beta\omega_k} - 1}. \quad (6.18)$$

The Bose-Einstein distribution rises rapidly for lower energy. Because of the mathematical structure of the Bose-Einstein function, the low energy phonons make much more important contributions in the specific heat than the high energy phonons. As a simplification, one can disregard the optical branch and consider only the acoustic branch, and in particular its $k \rightarrow 0$ portion which is approximated by $\omega_k \approx ck$. Then the internal energy becomes

$$U = \sum_k \frac{ck}{e^{\beta ck} - 1} = V \int \frac{d^3k}{(2\pi)^3} \frac{ck}{e^{\beta ck} - 1} = V \frac{T^4}{c^3} \int \frac{d^3x}{(2\pi)^3} \frac{x}{e^x - 1}. \quad (6.19)$$

It follows that the specific heat has a temperature dependence $C(T) \sim T^3$, which is a prediction explicitly checked by experiments.

The T^3 dependence of the specific heat, often known as the Debye T^3 law, holds in the low-temperature region where only the low-energy phonon excitations make a substantial contribution to the specific heat. It is observed in insulators where the electronic specific contribution is absent due to the energy gap. The deviation from T^3 behavior occurs at higher temperatures.

To see how the deviation from T^3 dependence occurs, first re-write the phonon internal energy in the form

$$U = \int_0^\infty g(\omega) \frac{\omega}{e^{\beta\omega} - 1} d\omega. \quad (6.20)$$

The factor $g(\omega)$ is the phonon density of states. For a linear energy spectrum $g(\omega) = 3V\omega^2/(2\pi^2c^3)$ in three dimensions. However, there can be only as many phonon modes as there are atomic sites. In 3D, the number of phonon modes are constrained to be $N_{ph} = 3N$. The density of states is thus required to obey $\int_0^\infty g(\omega)d\omega = 3N$, and Debye assumed that $g(\omega)$ behaves as ω^2 all the way to some cut-off frequency ω_D :

$$\int_0^{\omega_D} g(\omega)d\omega = 3N \rightarrow \omega_D = (6\pi^2n)^{1/3}c. \quad (6.21)$$

The heat capacity is now obtained from the formula

$$C = 9N \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2}. \quad (6.22)$$

The Debye temperature is defined by $k_B T_D = \hbar\omega_D$. At high temperature C reduces to $3N$, and at low temperature one recovers T^3 behavior. The interpolation between the low-temperature T^3 behavior to the high-temperature classical specific heat is known as the Debye interpolation scheme.

6.3 Debye-Waller Broadening

When Laue decided to shoot down an X-ray on a crystal and observe what comes out, there was an argument as to whether the thermal agitation of the ions would completely wash out any observable effects. In fact there was a diffraction pattern observed, at the locations expected for a perfect regular array. The thermal agitation of ions does have some other observable consequences, which was clarified by Debye.

The deviation of a ion at site i is denoted x_i (assuming one dimension) and the potential energy for the deviation is $(K/2)x_i^2$. Only the optical branch of the vibration is considered for simplicity. Using the relation $x_i = (\hbar/2m\omega_0)^{1/2}(a_i + a_i^+)$, the average of the squared deviation reads

$$\langle x_i^2 \rangle = \frac{\hbar}{2m\omega_0} \langle a_i a_i^\dagger + a_i^\dagger a_i \rangle = \frac{\hbar}{m\omega_0} \left(B(\omega_0) + \frac{1}{2} \right). \quad (6.23)$$

In the theory of X-ray scattering, the intensity of the diffraction pattern can be shown to be “weakened” by the factor $e^{-\alpha \langle x_i^2 \rangle}$ compared to its purely classical value, where α is a numerical factor of order unity. One has the result

$$\begin{aligned} \frac{I}{I_{cl}} &= \exp \left(-\frac{\alpha \hbar}{m\omega_0} \left(B(\omega_0) + \frac{1}{2} \right) \right) \rightarrow \exp \left(-\frac{\alpha \hbar}{2m\omega_0} \right) \\ &\rightarrow \exp \left(-\frac{\alpha T}{K} \right) \end{aligned} \quad (6.24)$$

in the extremely quantum and classical limits, respectively. The thermal and quantum effects do reduce the scattering intensity, but not catastrophically.

6.4 Exercise

[1][20pts] Discuss how the neutron scattering probe can measure the phonon dynamics.

[2][10pts] Derive Eq. (6.14) from Eq. (6.2).

[3][20pts] Derive the phonon density of states for the dispersion relation Eq. (6.6) of a monatomic chain with nearest-neighbor interaction.

[4][20pts] Calculate the specific heat of the phonons in a layered two-dimensional lattice with the spring constant K along the x -direction, but k along the y -direction with $K \gg k$. Show that in the extremely low temperature limit the phonon specific heat behaves as $\sim T$ rather than $\sim T^2$ as expected in 2D solids.

Chapter 7

Ordering in solids

7.1 Magnetism

In the previous chapters we have examined some properties of metals and insulators. Implicitly we treated both spin species to have the same energy so that the ground state is necessarily non-magnetic. On the other hand there is a wide array of compounds for which the ground state possesses macroscopic magnetic moments. While the details of the mechanism responsible for the magnetism is outside of the scope of this lecture, the Hamiltonian responsible for magnetic ordering usually takes the form

$$H = \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (7.1)$$

Each spin \mathbf{S}_i are spin $S=1/2$ operators. However it is often a good approximation to consider these as classical spins, of fixed magnitude $|\mathbf{S}_i| = S$. Often the magnitude S is absorbed in the definition of J_{ij} and the rotational degrees of freedom is expressed as a uni-modular vector, $\mathbf{S}_i \cdot \mathbf{S}_i = 1$. Furthermore, because the mechanism responsible for the spin-spin interaction is short-ranged, it is a good idea to treat the case of nearest-neighbor interaction only, so that J_{ij} is non-zero if and only if i and j are the two adjacent sites of the lattice. The sign of J can be either negative, in which case the model is ferromagnetic, or positive (antiferromagnetic). How and why long-range magnetic order occurs for models such as (7.1) is an important subject for the theory of magnetism.

7.1.1 Mean-field Theory

The simplest variant of the Heisenberg model that gives the long-range ordering of spins is given by the Ising model

$$H = J_z \sum_{\langle ij \rangle} S_{iz} S_{jz}. \quad (7.2)$$

From here on we will drop the z altogether, and treat the ferromagnetic case $J_z = -J < 0$ first. Due to the uni-modular condition, S_{iz} can only point either up ($S_{iz} = +1$), or down ($S_{iz} = -1$). It is claimed that a simple model

like the Ising model above is sufficient to capture the qualitative features of ferromagnetism and the transition from para- to ferro-magnetic phase.

Ising model is a many-body model in the sense that spin at site i interacts with its neighboring spins at j each of which interacts with its own neighbors at k , *ad infinitum*. In essence, two spins which are very very far apart manage to affect, and be affected by, each other. In this regard, solving for the Ising model is a lot like solving coupled, multi-variable equations. For the Ising model, the number of variables equals the number of spins, which is a huge number of Avogadroian scale. To get the answers you must know the values of all the variables at once. In most cases, of course, exact, analytic answers won't be available, and one must rely on approximations. However, the nature of approximation must be such that you can later make systematic improvement should you wish to get a more accurate answer. And often times, a reasonable approximation is the one based on sound physical picture. A general guiding principle for reducing a hard, interacting problem to a simple, non-interacting problem has been found a long time ago, and goes under the title of "mean-field theory"

Let's look at the energy Eq. (7.2) from the perspective of a spin at one particular site, i . Then the piece of the total energy that *it cares about* is given by

$$E_i = -S_i(J \sum_{j \in i} S_j). \quad (7.3)$$

Here we introduced $j \in i$ to indicate a sum over all nearest neighbors of i . For a moment write $h_i \equiv J \sum_{j \in i} S_j$, then E_i becomes $-h_i S_i$, which looks exactly like the energy of a single, isolated spin subject to an external magnetic field h_i . Of course h_i is not really an external field; it is a *variable*, that depends on the spin values of sites j . If S_j changes, then so does h_i . But rewritten in this suggestive form, it shows that what the neighboring spins do is basically to provide an effective magnetic field on the i -th spin.

Here comes the key logical loop:

If spins do order, then S_j are more or less a fixed number, and so is h_i . So in effect, S_i is subject to a more or less constant magnetic field which polarizes the orientation of S_i and gives rise to a finite average of S_i .

The nature of the argument, as you can see, is self-consistent, and the self-consistency is one of the defining characteristics of any mean-field theory.

So, let's do make the replacement

$$h_i = J \sum_{j \in i} S_j \rightarrow J \sum_{j \in i} m_j, \quad (7.4)$$

where $m_j \equiv \langle S_j \rangle$ is the thermodynamic average, and define the mean-field energy as

$$E_{mf} = \sum_i E_i = - \sum_i h_i S_i. \quad (7.5)$$

In this form, the spins are no longer interacting with each other. Partition

function can be readily derived,

$$\begin{aligned} Z_i &= \sum_{S_i=\pm 1} e^{-\beta E_i} = 2 \cosh[\beta h_i] \\ Z_{mf} &= \prod_i Z_i = \prod_i (2 \cosh[\beta h_i]). \end{aligned} \quad (7.6)$$

Magnetization of the spin at each site follows immediately:

$$m_i = \langle S_i \rangle = \tanh(\beta h_i). \quad (7.7)$$

We have thus managed to reduce the initial, difficult many-body problem to something that involves only one site index i at a time. But wait.... We have reduced the problem to something that looks simpler, but have we really solved it yet?

Remember that $h_i = J \sum_{j \in i} m_j$, and that $m_i = \tanh(\beta h_i)$. From these we derive

$$m_i = \tanh(\beta J \sum_{j \in i} m_j), \quad (7.8)$$

which is a set of N coupled equations in N variables $\{m_i\}$!! As I mentioned earlier, solving Ising model is really lot like solving coupled, multi-variable, *and non-linear*, equations! The many-body nature of the original problem is embedded in the above, non-linear equations.

The only way to solve equations like these is to make an *ansatz*. For a ferromagnet, fortunately, we already know that all spins are equal, $m_i = m$, and the above, coupled equations reduce to a single equation

$$m = \tanh(\beta J z m) \quad (7.9)$$

where z is the *coordination number* indicating how many neighbors there are for a given site. For a square lattice z equals 4, and for cubic, $z = 6$. For generality, we keep z in the expression. The solution of this equation can be found by graphical means, or by two short lines of programming on Mathematica. You will find a familiar curve of m as a function of T which saturates to 1 at low temperature and vanishes as $\sqrt{T_c - T}$ near $T_c \equiv Jz$.

7.1.2 Magnetic susceptibility

The lesson of the mean-field analysis is that there exists a transition temperature T_c which separates the ferromagnetically ordered phase from the paramagnetic one. The paramagnetic phase of a magnet is similar to the paramagnetic phase we discussed in the previous chapter, where we deduced the paramagnetic susceptibility

$$\chi_p = \frac{S(S+1)g^2\mu_B^2}{3k_B T}. \quad (7.10)$$

The ferromagnetic susceptibility in the paramagnetic phase is given by

$$\chi_f = \frac{S(S+1)g^2\mu_B^2}{3k_B(T - T_c)} \quad (7.11)$$

where the mean-field analysis give $T_c = zJS^2 = zJS(S+1)$.

From the paramagnetic susceptibility $1/\chi$ plotted against T yields a slope which equals the inverse of $S(S+1)g^2\mu_B^2/3k_B$. The intercept of the $(1/\chi, T)$ curve gives the transition temperature. By independently measuring T_c we can also extrapolate the exchange energy by the relation

$$J = \frac{T_c}{zS(S+1)}. \quad (7.12)$$

7.1.3 Magnons

Visualize throwing a small piece of rock into a pond in the pristine hours of the morning and watching the ripples emanate from the point of the rock's entry. Pretty much the same thing happens in the system composed of many spins. The ground state we have worked out in the previous chapter corresponds to an utterly still surface of the pond. A disturbance, such as throwing a rock, can cause ripples on the pond's surface, which in the case of spin systems we call "spin waves". A spin wave is just a collective motion of the spins in the same way that a ripple is a collective dance of all the water droplets composing the surface. Various things, or "perturbations" can excite the spin waves. For instance, a magnetic field applied locally over a small portion of the magnet will tilt the spins in that region to lie along the direction of applied field. If you suddenly turn it off, the spins will try to move back to its ground state position. In so doing, they will necessarily cause the spins outside the region to dance together with them because spins tend to interact with its neighboring spins.

How each spin will dance in coordination with the others is determined by the Hamiltonian

$$H = -J \sum_{\langle ij \rangle} S_i \cdot S_j, \quad (7.13)$$

and the equation of motion for the individual spin S_i that follows from it. We first remind ourselves of the fundamental commutation relations of spin

$$[S_i^\alpha, S_j^\beta] = i\delta_{ij}\epsilon_{\alpha\beta\gamma}S_i^\gamma \quad (\hbar \equiv 1). \quad (7.14)$$

From this one can calculate, for instance,

$$\frac{dS_i^x}{dt} = -i[S_i^x, H] = -J \sum_{j \in i} (S_j^y S_i^z - S_j^z S_i^y) = -J \sum_{j \in i} (S_j \times S_i)^x. \quad (7.15)$$

Combined with the equation of motion for the y - and z -components, we get

$$\frac{dS_i}{dt} = -J \sum_{j \in i} S_j \times S_i. \quad (7.16)$$

This equation is of a typical, nonlinear type because the quantities we must solve for, S_i , appears as a product on the r.h.s. In other words, one can never solve the above equation *exactly*. However we must remind ourselves that it is the small fluctuation away from the ground state that concerns us, and as

such we can decompose the spin operator as $S_i = \langle S_i \rangle + \delta S_i = m_i + \delta S_i$, where m_i represents the ground state spin average. For a ferromagnetic ground state, $m_i = S\hat{z}$. A small fluctuation means $|\langle S_i \rangle| \gg |\delta S_i|$. In making such a comparison of magnitudes we must be careful to remember that m_i is a number, but δS_i is not. So, it's not altogether clear what exactly we mean by the magnitude of δS_i . Nevertheless, we can at least make the substitution $S_i = m_i + \delta S_i$ as a matter of formal definition, and proceed to plug it into Eq. (7.16).

$$\begin{aligned} \frac{d}{dt} \delta S_i &= -J \sum_{j \in i} (m_j + \delta S_j) \times (m_i + \delta S_i) \\ &\approx -J \left(\sum_{j \in i} m_j \right) \times m_i - J \left(\sum_{j \in i} m_j \right) \times \delta S_i - J \left(\sum_{j \in i} \delta S_j \right) \times m_i \end{aligned} \quad (7.17)$$

ignoring terms of order $(\delta S)^2$. Once again, the justification is that δS is a small quantity, and $(\delta S)^2$, even smaller. We take the quantization axis \hat{z} and write $m_i = m\hat{z}$ everywhere. Then¹

$$\frac{d}{dt} \delta S_i = -Jzm\hat{z} \times \delta S_i - Jm \left(\sum_j \delta S_j \right) \times \hat{z}. \quad (7.18)$$

The \hat{z} -component of this equation reads $\frac{d}{dt} \delta S_i^z = 0$, hence the fluctuation in the \hat{z} -component of spin is zero, $S_i^z(t) = m$. For the \hat{x} - and \hat{y} -components we get

$$\begin{aligned} \frac{d}{dt} S_i^x &= JzmS_i^y - Jm \sum_{j \in i} S_j^y, \\ \frac{d}{dt} S_i^y &= -JzmS_i^x + Jm \sum_{j \in i} S_j^x. \end{aligned} \quad (7.19)$$

We have dropped the δ symbol in front. Introducing the complex notation $Z_i \equiv S_i^x + iS_i^y$ simplifies the equation a lot:

$$\frac{dZ_i}{dt} = iJm \left(\sum_{j \in i} Z_j - zZ_i \right). \quad (7.20)$$

We will solve this equation using the ansatz

$$Z_i = Z_0 e^{ik \cdot r_i - i\omega_k t}, \quad (7.21)$$

which yields the self-consistency condition

$$\omega_k = Jm \left(z - \sum_{j \in i} e^{ik \cdot (r_j - r_i)} \right). \quad (7.22)$$

For a 3-dimensional cubic lattice, $\sum_{j \in i} e^{ik \cdot (r_j - r_i)} = 2(\cos k_x + \cos k_y + \cos k_z)$, and with $z = 6$, $\omega_k = 2Jm(3 - \sum_{\alpha} \cos k_{\alpha})$. For 2D square lattice we will get $\omega_k = 2Jm(2 - \cos k_x - \cos k_y)$. This is the desired spin wave energy for a spin disturbance associated with a wavevector k .

¹I apologize for the multiple use of z here: z is the number of neighbors, or the coordination number, whereas \hat{z} is the unit vector along the z -axis.

7.1.4 Antiferromagnetism and Ferrimagnetism

In an antiferromagnet the spins are ordered in antiparallel arrangement with zero net moment at temperatures below the transition (Neel) temperature. Each sublattice has a macroscopic magnetic moment which is cancelled by the magnetic moment of the other sublattice. The susceptibility χ rises as

$$\chi_{af} = \frac{C}{T + \theta}. \quad (7.23)$$

From the plot of $(1/\chi, T)$ and reading off the intercept one can deduce the Curie temperature θ . It is often not the same as the Neel transition temperature T_N . When $\theta/T_N \gg 1$ we say the magnet is *frustrated*. The magnon spectrum in the antiferromagnetically ordered phase disperses linearly with k : $\omega \sim k$, not $\sim k^2$ as in the ferromagnet.

7.2 Superconductivity

Kamerlingh Onnes in 1911 discovered that mercury, a kind of metal, loses its electrical resistance when cooled below the critical temperature of 4K. An extremely pure copper may also have a very low resistance but there is a qualitative difference between a good metal and a superconductor. When the external driving force, the battery, is pulled off, even the best conductor loses conduction in a matter of 10^{-13} s. A superconducting ring on the other hand can sustain a stable current without an external driving force for over a year. Response to external magnetic field highlights the difference even more.

Typical metals are more or less transparent to the magnetic field, meaning that the fields penetrate the metal as if it was not there. For a superconductor the fields are completely repelled from it. This is the Meissner effect. The fact that Meissner effect is closely tied to the dissipationless flow of current can be seen from the following gedanken experiment.

Imagine a loop of superconducting wire with a current I flowing around it. Due to scattering with impurities and phonons the current wants to slow down. Less current means less magnetic flux penetrating through the inside of the loop, and that means some flux lines will have to go through the wire to leave the interior ring. But going through the wire is disallowed in the case of a superconductor, so the current will have to maintain its constant value. Now this qualitatively sums up the phenomena of superconductivity. The question is how one can explain it.

The efforts to answer the origin of superconductivity took up some of the best minds in the history of the 20th century physics including Pauli, Bloch, and even Feynman. Eventually it was due to Bardeen (another giant of the 20th century physics), Cooper (Bardeen's then post-doc) and Schrieffer (Bardeen's then graduate student) to figure out the correct theory of superconductivity - the BCS theory. To explain microscopic theory is one thing, but one can go a long way to understand superconductivity using only the phenomenological approaches. The phenomenological approach is still used nowadays when a new phenomenon shows up in some novel superconducting materials, and even to understand simple phenomenon using a simple language rather than the many-

body language with which the BCS theory had been written down.

7.2.1 Phenomenological Theory

Phenomenological theory is from its inception designed to understand or reproduce the known set of phenomena. The most compelling phenomenological mystery of superconductivity, as I said above, is the complete expulsion of magnetic fields from the metals' interior. This falls into the realm of how the electrons constituting the superconductor respond to the external electromagnetic field. It is assumed that electrons move in response to the electric field without damping, so that

$$m \frac{d\mathbf{v}}{dt} = -e\mathbf{E}, \quad \frac{d\mathbf{j}}{dt} = \frac{ne^2}{m} \mathbf{E}. \quad (7.24)$$

There is also a relation between the current density \mathbf{j} and the magnetic field defined by one of four Maxwell's equations (bear in mind that Maxwell's equations are absolutely true, whether the medium be a metal, an insulator, or a superconductor)

$$\nabla \times \mathbf{B} = 4\pi\mathbf{j} + \frac{d\mathbf{D}}{dt}. \quad (7.25)$$

The displacement current \mathbf{D} is small compared to the physical current and can be ignored. Hence, taking the time derivative on both sides of the above equation gives

$$\frac{d}{dt}(\nabla \times \mathbf{B}) = 4\pi \frac{d\mathbf{j}}{dt} = \frac{4\pi ne^2}{m} \mathbf{E}. \quad (7.26)$$

A second Maxwell's equation, $(d\mathbf{B}/dt) + \nabla \times \mathbf{E} = 0$, allows us to re-write the above equation in the form

$$\begin{aligned} \frac{d}{dt}(\nabla \times \nabla \times \mathbf{B}) &= \frac{4\pi ne^2}{m}(\nabla \times \mathbf{E}) = -\frac{4\pi ne^2}{m} \frac{d\mathbf{B}}{dt}, \\ \frac{d}{dt} \left(\nabla \times \nabla \times \mathbf{B} + \frac{4\pi ne^2}{m} \mathbf{B} \right) &= 0. \end{aligned} \quad (7.27)$$

Knowing that the magnetic field is always expelled from the inside of a superconductor, i.e. $\mathbf{B}(t) = 0$, London assumed that the quantity inside the parenthesis in the last of the above equation must be zero:

$$\nabla \times (\nabla \times \mathbf{B}) + \frac{4\pi ne^2}{m} \mathbf{B} = 0. \quad (7.28)$$

This is the London's equation.² Since $\nabla \times (\nabla \times \mathbf{B}) = \nabla(\nabla \cdot \mathbf{B}) - \nabla^2 \mathbf{B} = -\nabla^2 \mathbf{B}$, London's equation is reduced to

$$\mathbf{B} - \lambda_L^2 \nabla^2 \mathbf{B} = 0, \quad \frac{1}{\lambda_L^2} = \frac{4\pi ne^2}{m}. \quad (7.29)$$

²London's equation also implies $\nabla \times \mathbf{j} + (ne^2/m)\mathbf{B} = 0$, i.e. a linear relation between the current and magnetic field.

λ_L is the London penetration depth. To see why λ_L has anything to do with penetration, take the case of a superconductor which occupies all of space for $z < 0$. Looking for solutions which are independent of x and y , one gets

$$\mathbf{B} - \lambda_L^2 \frac{d^2 \mathbf{B}}{dz^2} = 0, \quad (7.30)$$

the solution of which is $\mathbf{B}(z) \sim \mathbf{B}_0 e^{z/\lambda_L}$. The magnetic field inside the superconductor decays over the characteristic length set by λ_L . Since the current is related to the penetrating field, it is also evident that the current can only reside on the surface of the thickness $\sim \lambda_L$.

Such is the approach used by London to understand the repulsion of magnetic flux in a superconductor. It is admittedly ad-hoc, and only capable of describing one aspect of superconductivity. A more general framework is provided by the Ginzburg-Landau theory advanced by (who else?) Landau and his finest disciple, V. L. Ginzburg.

At the time Landau and Ginzburg advanced their theory of course they did not know exactly what was causing superconductivity. In hindsight we know that a finite density of superconducting, or condensate electrons is responsible for superconducting phenomenon. In analogy with the way we understood magnetism, we may assume the free energy to be a functional of the superconducting electron density, $|\psi|^2$. Here ψ is sort of like the wave function of an electron, but of course it cannot be exactly that, because there are many, many electrons in a superconductor and we haven't specified which one electron we are describing with this wave function. For electrons no two electrons can be in the same quantum state, so every electron's wave function ought to be different. For bosons, on the other hand, it is possible that many particles occupy the same state. In particular the lowest energy state has a good chance of being occupied by a huge number of particles. If that happened, then it makes sense to talk about THE WAVE FUNCTION, since majority of the particles are sitting in the same quantum state anyway. But then electrons are not bosons, hence the conundrum.

A beautiful resolution of this paradox is what made Bardeen and his disciples so famous.³ They argued that electrons first pair up, so that the pair behaves as a boson. Then a large number of these bosons can sit in the same state. ψ is the wave function for the bosonic pairs of electrons, not for the individual electrons. To be slightly more concrete, a boson pair is made up of one electron having momentum k and spin \uparrow , and another electron having the opposite momentum $-k$ and spin \downarrow . The corresponding paired state is described by the operator

$$B_k^+ = c_{k\uparrow}^+ c_{-k\downarrow}^+ - c_{k\downarrow}^+ c_{-k\uparrow}^+. \quad (7.31)$$

The way we arranged the operators ensure that the spin sector remains in a singlet state.

I wish we could say that B_k^+ operator defined above obeys the boson commutation rules and a macroscopic number of particles sit in that state, etc. Unfortunately the story is not so simple. The analogy with the Bose condensation of paired electrons, in my view, is at most allegorical. Nevertheless, description of

³I read it in some article that Bardeen and his wife was hosting some guests but Bardeen was so deeply immersed in thoughts that he hardly paid attention to the invitees. When the guests were ready to leave Bardeen got up and said, "I know how to solve superconductivity."

the superconducting state in terms of the macroscopic wave function ψ proved to be a successful idea, and it continues to be a fruitful way to think about and solve superconductivity. In the spirit of Landau-Ginzburg theory we expand the free energy in powers of ψ as

$$F = F_0 + \int d^3\mathbf{r} \left(\alpha |\psi(\mathbf{r})|^2 + \frac{\beta}{2} |\psi(\mathbf{r})|^4 + \frac{1}{8\pi} \mathbf{B}(\mathbf{r})^2 + \frac{1}{2m} |(-i\hbar\nabla + 2e\mathbf{A}(\mathbf{r}))\psi(\mathbf{r})|^2 \right). \quad (7.32)$$

The vector potential \mathbf{A} , $\nabla \times \mathbf{A} = \mathbf{B}$ is introduced to describe coupling of paired electrons with the electromagnetic field. Minimizing the free energy with respect to ψ yields

$$\left[\alpha + \beta |\psi|^2 + \frac{1}{2m} (-i\hbar\nabla + 2e\mathbf{A})^2 \right] \psi = 0. \quad (7.33)$$

Minimizing the free energy with respect to \mathbf{A} yields the relation⁴

$$\begin{aligned} \nabla \times \mathbf{B} &= 4\pi \mathbf{j} \\ \mathbf{j} &= -\frac{2e\hbar}{2im} [\psi^* \nabla \psi - \psi \nabla \psi^*] - \frac{4e^2}{m} \mathbf{A} |\psi|^2. \end{aligned} \quad (7.34)$$

When the self-consistent solutions of Eqs. (7.33) and (7.34) gives non-zero ψ one say it's in a superconducting state. Otherwise $\psi = 0$ implies normal state. We will use $e_s \equiv 2e$ and $m_s \equiv m$ to represent charge and mass of superconducting pair of electrons, respectively.

Without the external field to worry about one has only one equation to solve:

$$\alpha + \beta |\psi|^2 = 0. \quad (7.35)$$

Assuming that $\alpha = \alpha_0(T - T_c)$, ψ follows $|\psi| = \sqrt{\alpha_0(T_c - T)/\beta}$ for $T < T_c$. T_c represents the temperature at which superconductivity sets in. A spectacular set of predictions can be made on the basis of the GL equations which agree very well with the phenomenology of superconductors. To name a few, I mention flux quantization, Josephson effects, existence of two types of superconductors, and Abrikosov vortex lattice in type-II superconductors.

7.2.2 Type-I and type-II superconductors

The GL theory defines two length scales, coherence length ξ and the London penetration depth λ_L , each defined by

$$\xi^2 = \frac{\hbar^2}{2m|\alpha|}, \quad \lambda_L^2 = \frac{m\beta}{4\pi|\alpha|e_s^2}. \quad (7.36)$$

Real superconductors also have these two lengths scales. They are well documented and tabulated. The coherence length has to do with the rescaling of the

⁴If you were to interpret ψ as the density of only those electrons in the superconducting state, one find the relation that $\nabla \times \mathbf{B} = 4\pi \mathbf{j}_s$, where \mathbf{j}_s is NOT the total electron current, but only the current density of the superconducting electrons. This is in clear violation of the Maxwell's equations. Landau-Ginzburg theory does not seem to say how to resolve this apparent conflict clearly.

GL equation (7.34) by the maximal allowed value of $|\psi|_M = \sqrt{-\alpha/\beta}$. If you re-define $\psi/|\psi|_M$ to be the new ψ , the GL equation reads

$$-\xi^2 \nabla^2 \psi - \psi + \psi |\psi|^2 = 0 \quad (7.37)$$

in the absence of the vector potential. The equation can be solved exactly in one dimension with the solution

$$\psi = \tanh \frac{x}{\sqrt{2}\xi}. \quad (7.38)$$

This solution extends to ± 1 as x tends to $\pm\infty$ and describes how the condensate wave function evolves between two superconductors having different phases for ψ . ξ represents a “healing length” over which the transition from one superconductor’s behavior to the other is achieved.

Penetration depth, as we saw in the London’s equation, has to do with the response of a superconductor to applied magnetic field. Looking at the relation (7.34) for the current density in the presence of the vector potential one finds that $\mathbf{j} \approx -(e_s^2/m)|\psi|^2 \mathbf{A}$ when the condensate is more or less uniform and the applied field is weak. Taking the curl on both sides and invoking the Maxwell’s equation,

$$\begin{aligned} 4\pi \nabla \times \mathbf{j} &= -\frac{4\pi e_s^2}{m} |\psi|^2 \nabla \times \mathbf{A} = -\frac{e_s^2}{m} |\psi|^2 \mathbf{B} = \nabla \times \nabla \times \mathbf{B} \rightarrow \\ \nabla^2 \mathbf{B} &= \frac{4\pi e_s^2 |\psi|^2}{m} \mathbf{B} \equiv \frac{1}{\lambda_L^2} \mathbf{B} \end{aligned} \quad (7.39)$$

Using $|\psi|_M = |\alpha|/\beta$ immediately gives λ_L as defined previously.

If one re-scaled the distance in units of ξ the LG equation (7.37) becomes dimensionless. This cannot be achieved when \mathbf{A} is also present. One can also introduce a dimensionless vector potential $\mathbf{a} \equiv (2e_s/\sqrt{2m|\alpha|})\mathbf{A}$ to renders the two LG equations as

$$\begin{aligned} \psi - \psi |\psi|^2 + (-i\nabla + \mathbf{a}/2)^2 \psi &= 0 \\ \frac{\lambda_L^2}{\xi^2} \nabla \times \nabla \times \mathbf{a} &= i(\psi^* \nabla \psi - \psi \nabla \psi^*) - |\psi|^2 \mathbf{a}. \end{aligned} \quad (7.40)$$

Hence it proves that

$$\kappa = \frac{\lambda_L}{\xi} \quad (7.41)$$

is the only free parameter in the GL theory.

Discussion of surface energy

7.2.3 Flux quantization

7.2.4 Josephson effects

7.2.5 Abrikosov vortex lattice

7.3 CDW and SDW

7.4 Exercise

[1, Kittel, Chap. 12, Prob. 2][20pts] Use the approximate magnon dispersion relation $\omega = Ak^2$ to find the leading term in the heat capacity of a three-dimensional ferromagnet at low temperatures $k_B T \ll J$. The result is $0.113k_B(k_B T/\hbar A)^{3/2}$ per unit volume.

[2, A&M, Chap. 33, Prob. 3][20pts] Show that the ground state of the four spin antiferromagnetic nearest-neighbor Heisenberg linear chain,

$$H = J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_3 \cdot \mathbf{S}_4 + \mathbf{S}_4 \cdot \mathbf{S}_1) \quad (7.42)$$

is

$$E_0 = -4JS^2 \left(1 + \frac{1}{2S} \right). \quad (7.43)$$

[3, A&M, Chap. 33, Prob. 7][30pts] Consider a magnetic structure made up of two types of spins that occupy two interpenetrating sublattices. Let spins within sublattice 1 be coupled by exchange constants J_1 , within sublattice 2, by J_2 , and between sublattices 1 and 2, by J_3 . Derive the mean-field equations for the spontaneous magnetization of the sublattices M_1 and M_2 .

[4, A&M, Chap. 34, Prob. 4] Do the Cooper problem.

Chapter 8

Special Topics

8.1 Peierls transition

8.2 Mott transition