B6: Condensed Matter Physics



Without loss of generality, we can consider the magnetic field to be orientated along \mathbf{e}_z . Then, using the method of cofactors, we can invert the matrix ρ to find the conductivity matrix $\sigma = \rho^{-1}$ as

$$\sigma = \frac{\sigma_0}{1 + (\omega_c \tau)^2} \begin{pmatrix} 1 & -\omega_c \tau & 0\\ \omega_c \tau & 1 & 0\\ 0 & 0 & 1 + (\omega_c \tau)^2 \end{pmatrix}, \quad \omega_c = \frac{e|\mathbf{B}|}{m}$$
(1.58)

where σ_0 is defined as above, and ω_c is the familiar cyclotron frequency.

The Hall Effect

The *Hall effect* is the production of a voltage or potential difference across a conductor when a magnetic field is applied in a direction perpendicular to the flow of current. An experimental set-up used to investigate this is shown in figure 1.2.



Figure 1.2: A schematic diagram of the experimental set-up used to investigate the Hall effect

We define the Hall coefficient R_H and Hall voltage V_H as

$$R_H = \frac{\rho_{yx}}{|\mathbf{B}|} = -\frac{1}{ne}, \quad V_H = R_H \frac{I |\mathbf{B}|}{t}$$
(1.59)

where t is the thickness of the sample in the direction parallel to the magnetic field. This means that by measuring the E_y that results from the application of j_x and B_z , the charge carrier density n can unlikely be determined from the Hall coefficient. However, this can often prove experimentally difficult for a number of reasons:

- Thermal fluctuations within the material may generate small EMF's, creating currents that effect the reading of the Hall voltage as its magnitude is comparable with the scale of these fluctuations
- The magnetic field needs to be calibrated properly to ensure that it is uniform throughout the sample
- The contact pins used to connect the voltmeter circuit to the conductor have a finite resistance, which provides an offset error in the data that needs to be accounted for

• The contact pins must be properly aligned, such that they are indeed measuring $E_y \ell$, instead of some perpendicular component of the voltage. This can be done through multiple measurements of moving one contact, which will cause the measured voltage to fluctuate around some value

Often, the Hall coefficient is measured experimentally to have the opposite sign to that expected from the above analysis. This indicates the presence of positive charge carriers that are not included in Drude theory. The nature of these charge carries will be revealed in section 3.3.

Thermal Transport

Recall the expression for the thermal conductivity of a kinetic gas:

$$\kappa = \frac{1}{3} n c_v \left\langle v \right\rangle \lambda \tag{1.60}$$

where c_v is the heat capacity per particle, $\langle v \rangle$ is some mean velocity, and $\lambda = \langle v \rangle \tau$ the mean-free path. Assuming that

$$c_v = \frac{3}{2}k_B, \quad \langle v \rangle = \frac{2}{\sqrt{\pi}}v_{th} = \left(\frac{8k_BT}{\pi m}\right)^{1/2} \tag{1.61}$$

the thermal conductivity can be written as

$$\kappa = \frac{4}{\pi} \frac{n\tau k_B^2 T}{m} \tag{1.62}$$

While this quantity still has the unknown scattering concerne τ in it, it also occurs in the electrical conductivity σ_0 in (1.57). Then we obtain consider the ratio of the thermal conductivity to electrical conductivity, known as the *Lotenz number*:

DIEVIE
$$\frac{\kappa}{\sigma \overleftarrow{\sigma}} = \frac{4k_B^2}{3}$$
 O.94 k 10⁻⁸ Watt Ohm K⁻² (1.63)

This result appears to differ from experiment by only a factor of order unity. This is quite astounding that this theory should predict the correct order of magnitude considering that it is a purely kinetic theory. It turns out that this is due to the fact that we have hugely overestimated the heat capacity per electron, but hugely underestimated the typical velocities of electrons (see (1.73)); these two errors roughly cancel one another out.

1.3.2 Sommerfeld Theory

Sommerfeld theory treats the electrons within metals as a degenerate fermionic gas, such that the mean occupation numbers will behave according to

$$\bar{n}_i = \frac{1}{e^{\beta(E-\mu)} + 1} \to \begin{cases} 1 & \text{for } E < \mu(T=0) \\ 0 & \text{for } E > \mu(T=0) \end{cases}$$
(1.64)

This is shown in figure 1.3. This means that electrons will begin to 'stack up' and occupy all the available single particle states from the lowest to some maximum energy at T = 0. We thus define the *Fermi energy* as

$$E_F = \mu(T = 0) \tag{1.65}$$

That is, the value of the chemical potential at T = 0, corresponding to the maximum energy per particle at this temperature. Let us find an expression for the Fermi energy.

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3.1 Atomic Chains

In this section, we consider a detailed model of vibration in a solid by examining onedimensional atomic chains. In particular, we shall examine the behaviour of this system in terms of *normal modes* (collective oscillations of the system in which all parts move with the same frequency and fixed phase relation) and *phonons* (a discrete quantum of vibration that can be described by Bose-Einstien statistics). We met the latter of these when studying the Debye Model of heat capacity 1.2.3.

3.1.1 Monatomic Chain

Consider the case of a one-dimensional chain of N atoms of mass m, each connected by classical springs of spring constant κ , as in figure 3.1 below. Suppose that the atoms are separated by an equilibrium distance a. This can be thought of as our lattice constant, and the dotted box one possible unit cell for the system.



where a dot denotes a derivative with respect to time. Our system is clearly periodic in a in real space, meaning that our wave-like solution must also be periodic in $2\pi/a$ in k-space. We thus consider a solution of the form

$$\delta x_n = A e^{i(\omega t - kna)} \tag{3.3}$$

It is easy to verify that this is indeed invariant under the transformation $k \mapsto k + 2\pi/a$.

Dispersion Relation

Substituting the solution into (3.2), it follows quickly that the dispersion relation for the monatomic chain is given by

$$\left| \omega = 2\omega_0 \left| \sin \frac{ka}{2} \right|, \quad \omega_0 = \sqrt{\frac{\kappa}{m}}$$

$$(3.4)$$

Once again, we observe that this is $2\pi/a$ periodic in k-space, meaning that the first Brillouin zone has boundaries $[-\pi/a, \pi/a]$. By definition, all physically distinct states of the system must be contained within this range, and so the dispersion relation and any quantities derived from it must have this periodicity.

We now assume that the classical vibrations of our monatomic chain can be modelled as lattice phonons that obey Bose-Einstein statistics. Then, we can write the energy as

$$U = \int d\omega \,\bar{n}_i g(\omega) \hbar \omega = \frac{2N}{\pi} \int_0^{\omega_m} d\omega \,\frac{1}{\sqrt{\omega_m^2 - \omega^2}} \,\frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \tag{3.16}$$

The heat capacity is given by

$$C_V = \frac{\partial U}{\partial T} = -\frac{\beta}{T} \frac{\partial U}{\partial \beta} = \frac{\beta}{T} \frac{2N}{\pi} \int_0^{\omega_m} d\omega \, \frac{(\hbar\omega)^2}{\sqrt{\omega_m^2 - \omega^2}} \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$
(3.17)

We can non-dimensionalise this integral using the usual substitution $x = \beta \hbar \omega$, such that

$$C_V = \frac{2Nk_B}{\pi} \int_0^{x_m} dx \, \frac{1}{\sqrt{x_m^2 - x^2}} \, \frac{x^2 e^x}{(e^x - 1)^2} \tag{3.18}$$

In the high temperature limit, $x, x_m \ll 1$ meaning that the second fraction in the integrand becomes approximately unity. This means that the heat capacity becomes $C_V = Nk_B = R$, which is the law of Dulong-Petit in one dimension.

3.1.2**Diatomic Chain**

Let us now generalise the previous discussion above to systems containing more than one type of atom. We shall consider the case where have a one-dimensional chain of N unit cells of length a, containing two atoms of masses m_1 and m_2 , connected by a classical spring of spring constant κ . We shall label the atoms of mass m_1 by the positions q_{μ} and the atoms of mass m_2 by y_n , as shown in figure 3.4 below.



As before, we can use NII to find the equations of motion for both species of masses:

$$m_1 \,\delta \ddot{x}_n = \kappa (\delta y_{n-1} - \delta x_n) - \kappa (\delta x_n - \delta y_n) = \kappa (\delta y_{n-1} + \delta y_n - 2\delta x_n) \tag{3.19}$$

$$m_2 \,\delta\ddot{y}_n = \kappa(\delta x_{n+1} - \delta y_n) - \kappa(\delta y_n - \delta x_n) = \kappa(\delta x_{n+1} + \delta x_n - \delta 2y_n) \tag{3.20}$$

As before, we suppose that we have wave-like solutions of the form

$$\delta x_n = A_r e^{i(\omega t - kna)} \tag{3.21}$$

$$\delta y_n = A_u e^{i(\omega t - kna)} \tag{3.22}$$

Note that we have not assumed that the amplitudes of oscillation for each species is the same (as it is indeed not). Substituting these solutions into the equations of motion yields a matrix equation

$$\begin{pmatrix} 2\kappa - m_1\omega^2 & -\kappa\left(1 + e^{ika}\right) \\ -\kappa\left(1 + e^{-ika}\right) & 2\kappa - m_2\omega^2 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix} = 0$$
(3.23)

For a solution to exist, we require that the determinant of the coefficient matrix is zero. Performing this calculation gives the dispersion relation

$$\omega_{\pm}^{2} = \kappa \left(\frac{1}{m_{1}} + \frac{1}{m_{2}}\right) \pm \kappa \left(\frac{1}{m_{1}^{2}} + \frac{1}{m_{2}^{2}} + \frac{2}{m_{1}m_{2}}\cos ka\right)^{1/2}$$
(3.24)

arises due to the fact that the electron has lower energy when confined to a larger area (more orbitals). We thus want to find some Hamiltonian that satisfies

$$\langle n | H | n \rangle = E_0 \tag{3.33}$$

$$\langle n \pm 1 | H | n \rangle = -t \tag{3.34}$$

We now assume that all of the states $|n\rangle$ are orthogonal, which corresponds to the electrons being very tightly bound to the atoms, such that it has a very low probability of being on any other site. With this assumption, it is clear that the correct Hamiltonian is given by

$$H = \sum_{n} \left[\left(E_0 \left| n \right\rangle \left\langle n \right| \right) - t \left(\left| n \right\rangle \left\langle n - 1 \right| + \left| n \right\rangle \left\langle n + 1 \right| \right) \right]$$
(3.35)

where the sum n runs over all of the atoms N. We can now look for solutions to the Time Independent Schrödinger equation that are a superposition of all the possible orbital states:

$$\left|\psi\right\rangle = \sum_{n} \phi_{n} \left|n\right\rangle \tag{3.36}$$

Then:

$$\sum_{n} (E_0 \phi_n - t \phi_{n-1} - t \phi_{n+1}) |n\rangle = E \sum_{n} \phi_n |n\rangle$$
(3.37)

As the states $|n\rangle$ are orthogonal, we can drop the summation notation, such that our equation becomes:

$$E_{0}\phi_{n} - t\phi_{n-1} - t\phi_{n+1} = E\phi_{n}$$
(3.38)

Motivated by Bloch's theorem, let us use the wave ansate

which upon substitution lives the dispersion relation
$$70$$
 (3.39)

$$\mathbf{P} \mathbf{e}^{\mathbf{F}} \mathbf{P} \mathbf{e}^{\mathbf{F}} \mathbf{e}_{0} - 2t \cos(ka)$$
(3.40)

Like in the case of the atomic chain model, the dispersion is periodic, and the Brillouin zone is of the same width $2\pi/a$. Furthermore, this dispersion relation gives rise to an *energy* band that comprises of the possible energy states at a given k, dictated by the amount of orbital overlap (hopping). The width of this energy band (the *bandwidth*) is 4t.



Figure 3.7: Energy dispersion for the tight-binding model with a single orbital per site

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Figure 3.8: Energy dispersion for the tight-binding model with two orbitals per site $(E_0^B < E_0^A)$

3.2.3 The Nearly-Free Electron Model

As the same suggests, we are now going to look at the other extreme in which the electrons are free to move throughout our lattice, but subject to some weak periodic potential $V(\mathbf{r})$, such that the Hamiltonian of the system becomes:

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}), \quad V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}) \mathbf{e} \mathbf{CO} \mathbf{V}$$
(3.59)

Suppose that we initially have an incident plane weile \mathbf{r} the form $\langle \mathbf{r} | \mathbf{k} \rangle = A e^{i \mathbf{k} \cdot \mathbf{x}}$ for some wavevector \mathbf{k} . This will be scattered by the weak potential to give a wave of the form $\langle \mathbf{r} | \mathbf{k}' \rangle = B e^{i \mathbf{k}' \cdot \mathbf{x}}$. We can decompose our potential as

$$\mathbf{P}(\mathbf{e}^{\mathbf{V}}, \mathbf{e}^{\mathbf{P}}) = \sum_{\mathbf{G}} e^{i\mathbf{G} \cdot (\mathbf{r} + \mathbf{R})} V_{\mathbf{G}}$$
(3.60)

In order for the terms in this sum to be non-zero, we require that the Laue condition is satisfied, meaning that $\mathbf{k'} = \mathbf{k} + \mathbf{G}$. Thus, we can write the state of the system (in the position representation) as:

$$\langle \mathbf{r} | \psi \rangle = A e^{i \mathbf{k} \cdot \mathbf{r}} + B e^{i (\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}, \quad |\psi\rangle = |\mathbf{k}\rangle + |\mathbf{k}'\rangle$$
(3.61)

By (1.6), we want to calculate the matrix elements for our Hamiltonian. We define the matrix elements

$$\langle \mathbf{k} | H | \mathbf{k} \rangle = E_0(\mathbf{k}) + V_0 \tag{3.62}$$

$$\left\langle \mathbf{k}' \right| H \left| \mathbf{k}' \right\rangle = E_0(\mathbf{k}') + V_0 \tag{3.63}$$

$$\left\langle \mathbf{k} \right| H \left| \mathbf{k}' \right\rangle = V_{\mathbf{k}-\mathbf{k}'} = V_{-\mathbf{G}} = V_{\mathbf{G}}^* \tag{3.64}$$

meaning that our effective Schrödinger equation becomes:

$$\begin{pmatrix} E_0(\mathbf{k}) + V_0 - E & V_G \\ V_G^* & E_0(\mathbf{k}') + V_0 - E \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = 0$$
(3.65)

We shall now consider two particular cases of this expression, as the general case is not particularly interesting or informative. Arguably, none of this is neither interesting nor informative; such is Condensed Matter Physics at an undergraduate level.

At the Brillouin Zone Boundary

Suppose that we are on the Brillouin zone boundary. Then, $\mathbf{k} = \mathbf{k}'$, meaning that we can solve (3.65) very simply to yield

$$E_{\pm}(\mathbf{k}) = \frac{\hbar^2 |\mathbf{k}|^2}{2m} + V_0 \pm |V_{\mathbf{G}}|$$
(3.66)

where we have used the fact that $\mathbf{E}_0(\mathbf{k})$ is the expectation value of the kinetic energy. This is graphed (in one dimension) in figure 3.9 below.



Figure 3.9: Energy dispersion for the nearly free electron Encer on the Brillouin zone boundary

Once again, the energy is frames of into bands, with a band-gap $2|V_{\mathbf{G}}|$. What is the condition for this gap tracks? In general, want dire that the highest energy in the lower band to be maller than the lowest one by in the upper band. In this case, we shall say that the potential needs to be of our order of the kinetic energy at the Brillouin zone boundary, namely that

$$V_{\mathbf{G}} \approx \frac{\hbar^2 |\mathbf{k}|^2}{2m} \tag{3.67}$$

We can also gain an understanding of how this band-gap originates. The two eigenstates of the system (in the position representation) are

$$\langle \mathbf{r} | \mathbf{k} \rangle_{\pm} = \frac{1}{\sqrt{2}} \left[\langle \mathbf{r} | \mathbf{k} \rangle \pm \langle \mathbf{r} | \mathbf{k}' \rangle \right]$$
 (3.68)

Suppose that we are in the one-dimensional potential $V(x) = V_0 + V_G \cos(2\pi x/a)$. Then, the eigenstates become

$$\langle x|k\rangle_{+} \propto \cos\frac{\pi x}{a}, \quad \langle x|k\rangle_{-} \propto \sin\frac{\pi x}{a}$$
 (3.69)

Considering the probability densities $|\langle x|k\rangle_{\pm}|^2$ of both eigenstates, it is clear that $\langle x|k\rangle_+$ has its probability density concentrated at the maxima of V(x), where as $\langle x|k\rangle_-$ has its density concentrated at the minima of V(x). This gives rise to an energy difference between the two states, as it raises the energy of one by V_G and lowers the energy of the other by V_G .

Near the Brillouin Zone Boundary

We shall treat this situation in one-dimension. Near the Brillouin zone boundary, we let the kinetic energies be

$$E_0(k+\delta k) = \frac{\hbar^2}{2m} \left[\left(\frac{n\pi}{a}\right)^2 + \frac{2n\pi}{a}\delta k + \delta k^2 \right]$$
(3.70)

$$E_0(k'+\delta k) = \frac{\hbar^2}{2m} \left[\left(\frac{n\pi}{a}\right)^2 - \frac{2n\pi}{a}\delta k + \delta k^2 \right]$$
(3.71)

where we have let $k = n\pi/a$ and $k' = -n\pi/a$ for some integer n. From (3.65), we have the eigenvalue problem

$$(E_0(k) - E) \left(E_0(k') - E \right) - |V_G|^2 = 0$$
(3.72)

Substituting the above relationships in, we find that

$$E_{\pm} = \frac{\hbar^2}{2m} \left[\left(\frac{n\pi}{a}\right)^2 + \delta k^2 \right] \pm |V_G| \left[1 + \left(\frac{\hbar^2}{2m} \frac{2n\pi}{a} \frac{\delta k}{|V_G|}\right)^2 \right]^{1/2}$$
(3.73)

We can now expand for $\delta k \ll k = n\pi/a$, $\delta k \ll |V_G|$, such that

$$E_{\pm} = E_{\pm}(\delta k = 0) + \frac{\hbar^2 \delta k^2}{2m} \left[1 \pm \frac{\hbar^2 (n\pi/a)^2}{m|V_G|} \right]$$
(3.74)

where $E_{\pm}(\delta k = 0)$ is simply the energy corresponding to being exactly on the Urhlouin zone boundary, as given by (3.66). This can also be written as

$$E_{\pm} = E_{\pm} (\delta \mathbf{N} \mathbf{L} \mathbf{O} \frac{b \sigma i^{2}}{2m_{\pm}^{*}}$$
(3.75)

where we have defined by effective masses
$$500m$$

 $prev = m$
 $\left[1 \pm \frac{\hbar^2 (n\pi/a)^2}{m|V_G|}\right]$
(3.76)

It is clear that the nearly free electron model predicts very similar behaviour to the tightbinding model in terms of the energy dispersion; they predict the formation of discrete energy bands, and the associated band gaps, when electrons are exposed to a periodic potential. As such, we are inclined to think that real lattices - that can be characterised by a periodic potential - also exhibit this behaviour.



Figure 3.12: The Fermi surface for divalent atoms in a square lattice in the presence of a moderate potential. The left- and right-hand sides correspond to the extended and reduced zone schemes respectively

a band gap of more than this value, it appears transparent, since no single visible photon can cause excitation to the conduction band. This means that there is no scattering of electrons which causes opacity. This is the case with diamond, for example.

We also have to consider the way in which the electron transitions. Direct transitions between the valence and conduction bands do not change the value of \mathbf{k} , where as indirect transitions occur between the top of the valence band and the bottom of the conduction band, changing the value of \mathbf{k} . The minimum energy transition is an indirect one, by definition. However, photons alone cannot excite indirect transition as momentum is not conserved. We still observe some electrons being and act this way, as lattice phonons can re-distribute some of the momentum bit time is not a very minimum effect due to the poor coupling between photons are phonons.

Note that base herry completely increase the Coulomb interaction between electrons, despite the fact that the associated energy can be greater than the Fermi energy. However, it turns out that it is fine to do this, for reasons that we shall not go into here. However, this does cause band theory to fail in describing Mott insulators, materials where the electron-electron repulsion is indeed a dominant effect, preventing our notional bands from filling up easily.

3.3.3 Semiconductor Physics

As they are the most physically intriguing out of insulators, conductors, and semiconductors, we shall examine further the physics of the latter. We will not be covering semiconducting devices, as these are non-examinable, and there are plenty of resources for further reading in this area if the reader so desires.

Electrons and Holes

The general picture of a semiconductor is a material with a mostly-full valence band, and a almost-empty conduction band, separated by a small band gap. As a result, it is convenient to define a *hole* as the absence of an electron in the valence band. This is a useful concept as we can characterise the motion of electrons in the conduction band as a flow of positively charged holes in the valence band, as the valence band is itself inert. This leads to the positively charged mass carriers that we mention in relation to the Hall effect. Note that we generally refer to the density of electrons as n and the density of holes as p.



Figure 4.1: Plotting the Brillouin function $B_J(x)$ for J = 1, J = 2, J = 3, J = 5 and $J \to \infty$

4.2.2 Larmor Diamagnetism

The only time we can ever observe diamagnetic is if J = 0, as otherwise it is completely overshadowed by Curie paramagnetism. This often occurs in atoms with filled otter hells, such as the noble gases. Consider the diamagnetic term in (4.7):

$$\delta H_{\text{diamagnetic}} = \frac{e^2}{200} \frac{1100}{100}$$
 (4.25)

We again assume that **B** is grief tated along \mathbf{e}_z , such that first order shift in the energy can be written as

$$\mathbf{P}(\mathbf{e}^{2} \otimes E_{\mathrm{d}} \mathbf{p}^{2} \otimes \mathbf{r}^{2}) \approx \mathbf{r}^{2} \left\langle x^{2} + y^{2} \right\rangle$$

$$(4.26)$$

As our atoms exhibit spherical symmetry, we can use spatial isotropy to write that

$$\langle x^2 + y^2 \rangle = \frac{2}{3} \langle x^2 + y^2 + z^2 \rangle = \frac{2}{3} \langle r^2 \rangle$$
 (4.27)

such that the energy shift becomes

$$\delta E_{\rm dia} = \frac{e^2 B^2}{12m_e} \left\langle r^2 \right\rangle \tag{4.28}$$

The magnetic moment m for each electron is then given by

$$m = -\frac{\partial \delta E_{\text{dia}}}{\partial B} = -\left[\frac{e^2}{6m_3}\left\langle r^2\right\rangle\right]B \tag{4.29}$$

Assuming that there is a density $\rho = Zn$ of electrons within the system, we can write the magnetic susceptibility as

$$\chi_{\text{Larmor}} = -\frac{Zne^2\mu_0 \langle r^2 \rangle}{6m_e}$$
(4.30)

This accounts for the diamagnetic of electrons in core orbitals. For the conduction of electrons in a metal, we need to consider the Landau-diamagnetism $\chi_{\text{Landau}} = -\chi_{\text{Pauli}}/3$ that combines with the Pauli paramagnetism to reduce the total magnetism of the conduction electrons by 1/3.