Handout 5

Some general points about bandstructure

5.1 Comparison of tight-binding and nearly-free-electron bandstructure

Let us compare a band of the nearly-free-electron model with a one-dimensional tight-binding band

\[ E(k) = E_0 - 2t \cos(ka), \]

where \( E_0 \) is a constant. Note that

- both bands look qualitatively similar, \( i.e. \)
- both bands have minima and maxima \( i.e. \) points where \( dE/dk = 0 \) at the Brillouin-zone centres and boundaries respectively;
- both bands have the same \( k \)-space periodicity;
- the tops and bottoms of both bands are approximately parabolic \( i.e. \) \( E \) is proportional to \( (k-k_0)^2 \) plus a constant, where \( k_0 \) is the point in \( k \)-space at which the band extremum occurs).

The last point is obvious for the bottom of the lowest nearly-free-electron band. To see that the same thing happens for the tight-binding approach, we use the approximation

\[ \cos(ka) \approx 1 - \frac{(ka)^2}{2} \]

for small \( ka \) in Equation 5.1 to give

\[ E(k) \approx E_0 - 2t + ta^2k^2. \]

The equivalent proof for the top of the band \( close to \pi/a \) is left to the reader.

The above discussion shows that both very weak and very strong periodic potentials give rise to qualitatively similar bands. We therefore expect that our ideas about bands derived from these simple models will apply to the real bands in solids, where the potential strengths will fall between the two extremes. The more complex arrangements of atoms and/or molecules often found in real solids will give rise to more complex bandshapes, but qualitatively the properties of the bands will be the same as those of our simple models.
5.2 The importance of \( k \)

5.2.1 \( \hbar k \) is not the momentum

Bloch’s theorem has introduced wavevectors which we have labelled \( k \) and \( q \) (see e.g. Equation 2.25). Although at first sight \( k \) and \( q \) look similar to the straightforward electron momentum \( p = \hbar k \) in the Sommerfeld model, it is easy to show that the Bloch functions are not eigenstates of the momentum operator;

\[
\frac{\hbar}{i} \nabla \psi(r) = \frac{\hbar}{i} \nabla e^{iq \cdot r} u_{j,q} = \hbar q \psi(r) + e^{iq \cdot r} \frac{\hbar}{i} \nabla u_{j,q} \neq p \psi(r) \tag{5.4}
\]

(where the Bloch wavefunction used is defined in Equation 2.25).

The quantity \( \hbar k \) is instead a crystal momentum, the momentum of the system as a whole; it is better to think of \( k \) as a quantum number which describes a Bloch state.

5.2.2 Group velocity.

In the original formulation of the Bloch states (see Equation 2.16), the electron wavefunction was defined to be the superposition of a set of plane waves (a wavepacket). It is therefore possible to use the idea of a group velocity \( v \)

\[
v = \frac{1}{\hbar} \nabla_k E, \tag{5.5}
\]

where \( \nabla_k \) is the gradient operator in \( k \)-space, to describe the real-space motion of the electron (c.f. \( v = (d\omega/dk) \) for the wavepackets encountered in Optics). Bearing this in mind, we are now going to derive the effective mass, which is very useful in parameterising the dynamics of band electrons when they are subjected to external forces. The derivation also illustrates a very important point about \( k \). I shall follow the derivation through in one dimension; one of the problems involves doing the same thing in three dimensions.

5.2.3 The effective mass

Let an external force \( f \) be applied to a band electron. The force will do work

\[
\delta E = fv\delta t \tag{5.6}
\]

in time \( \delta t \). In addition,

\[
\delta E = \frac{dE}{dk} \delta k = \hbar v \delta k. \tag{5.7}
\]

Equating Equations 5.6 and 5.7, dividing through by \( \delta t \) and considering the limit \( \delta t \rightarrow 0 \) gives

\[
\hbar \frac{dk}{dt} = f. \tag{5.8}
\]

The equivalent three dimensional formula in the derivation of one of the problems is

\[
\hbar \frac{d\mathbf{k}}{dt} = \mathbf{f}, \tag{5.9}
\]

where \( \mathbf{k} \) and \( \mathbf{f} \) are now vectors. Equation 5.9 is enormously important; it shows that in a crystal \( \hbar \frac{d\mathbf{k}}{dt} \) is equal to the external force on the electron.

After this amazing fact, the rest of the effective mass derivation is almost an anticlimax. The rate of change of velocity with time is

\[
\frac{dv}{dt} = \frac{1}{\hbar} \frac{d^2 E}{dk \, dt} = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt}. \tag{5.10}
\]

Substituting for \( \frac{dk}{dt} \) from Equation 5.8 and rearranging gives

\[
\frac{\hbar^2}{m^*} \frac{dv}{dk^2} = m^* \frac{dv}{dt} = f, \tag{5.11}
\]
5.2. THE IMPORTANCE OF $K$

where the effective mass $m^*$ is defined by

$$m^* = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k^2}}.$$  \hspace{1cm} (5.12)

(The equivalent tensor quantities for an anisotropic band are given in one of the problems.)

Equation 5.11 shows that the effective mass gives a convenient way of describing the motion of band electrons subjected to an external force; the identity “force=(mass x acceleration)” can be used with the effective mass substituted for the inertial mass.

In general, the effective mass will be energy-dependent. However, one often has to deal with almost empty or almost full bands, i.e. the states close to the minima and maxima of the $E_j(k)$ dispersion relationships. As we have already seen in Section 5.1, these regions are often approximately parabolic (this is actually a general property of any maximum or minimum – try expanding any function possessing such an extremum close to that point using a Taylor series). Close to these points, the electrons can therefore be treated as if they were free, but with an effective mass; i.e. their dispersion relationship is

$$E(k) \approx E_0 + \frac{\hbar^2}{2m^*}(k - k_0)^2,$$  \hspace{1cm} (5.13)

where energy $E_0$ and wavevector $k_0$ define the band extremum. Note that $m^*$ can be either positive or negative. This approximation often simplifies calculations; $m^*$ in effect contains all of the necessary information about the way in which the electron’s motion is modified by the crystal potential through which it moves. The equivalent model for anisotropic band extrema is explored in the problem about the effective mass tensor.

5.2.4 The effective mass and the density of states

In the previous lectures, we have seen that it is most natural to count electron states by evaluating the volume of $k$-space occupied (e.g. the Brillouin-zone volume determines the number of electrons that a band can accommodate). The counting of states is easy, because the states are spread through phase-space uniformly. However, when one comes to consider the evaluation of quantities such as the electronic heat capacity, where thermal population of states is a significant factor, it is often convenient to work in terms of energy (see e.g. the derivation of the electronic heat capacity within the Sommerfeld model), requiring a knowledge of the number of states per unit energy range per unit volume, $g(E)$.

If one substitutes a general value of $k$ in Equation 1.22 instead of $k_F$, one obtains $n(k)$, the number of states per unit volume of $r$-space with wavevectors less than $|k|$. If the band in question is assumed to obey Equation 5.13 close to the region of interest (i.e. it is parabolic and isotropic), then

$$g(E) \equiv \frac{dn}{dE} = \frac{dn}{dk} \frac{dk}{dE} = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}}(E - E_0)^{\frac{1}{2}}.$$  \hspace{1cm} (5.14)

This shows that the effective mass is a very convenient way of parameterising the curvature of a band at a certain energy, and hence the density of states $g(E)$ at that energy. We shall use this technique in a number of subsequent derivations.

Finally, note that Equation 5.14 shows that a heavy effective mass results in a large density of states. The reason for this can be seen in Figure 5.1, which shows a parabolic band with a light effective mass (steep curve) compared to a band with a heavy effective mass (shallow curve). A fixed region of $k$-space will always contain a fixed number of states. In the case of the heavy-mass band, the $k$-space interval $\Delta k$ corresponds to a small interval of energy $\delta E_1$; the same interval of $k$ corresponds to a much larger energy interval $\delta E_2$ for the light-mass band. As the same number of states is accommodated in each energy region, the density of states $g(E)$ is much higher for the heavy-mass band.

5.2.5 Summary of the properties of $k$

The properties of the $k$ used in the Bloch wavefunction (see Equations 2.16 and 2.25) may be summarised as follows.
Figure 5.1: Comparison of a parabolic band with a light effective mass (steep curve) with a band with a heavy effective mass (shallow curve). In the case of the heavy-mass band, the $\Delta k$ corresponds to a small interval of energy $\delta E_1$; the same interval of $k$ corresponds to a much larger energy interval $\delta E_2$ for the light-mass band.
5.3. GENERAL (NON-ISOTOPIC) DENSITY OF STATES

1. \( \mathbf{k} \) is not the (physical momentum/\( \hbar \)) of the electron; it is a quantum number describing the electron’s state within a band. Each band is labelled using the index \( j \).

2. For each \( j \), \( \mathbf{k} \) takes all values consistent with the Born–von Karman boundary conditions within the first Brillouin zone; in our notation \( \mathbf{k} \) runs though all \( \mathbf{q} \). \( j \) can run through an infinite number of discrete values.

3. For a given \( j \), the electronic dispersion relationship \( E_j(\mathbf{k}) \) has no explicit form; the only constraint is that it must be periodic, i.e. \( E_j(\mathbf{k}) = E_j(\mathbf{k} + \mathbf{G}) \).

4. The velocity of an electron with energy \( E_j(\mathbf{k}) \) is given by \( \mathbf{v} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E_j(\mathbf{k}) \).

5. The rate of change of \( \mathbf{k} \) under the action of an external force \( \mathbf{f} \) is given by \( \hbar \frac{d \mathbf{k}}{dt} = \mathbf{f} \).

6. The electronic wavefunction is \( \psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{j,k,} \), where \( u_{j,k}(\mathbf{r}) = u_{j,k}(\mathbf{r} + \mathbf{T}) \). Here \( u_{j,k}(\mathbf{r}) \) has no simple explicit form.

The above list tells us all we need to know about the dynamics of electrons in solids. Let us imagine for a line or two that we know nothing about bands; a calculation of the motion of an electron in a solid due to an external force seems intractable, as the electron is also subject to a complex array of forces from the ionic cores/molecules in the crystal. Band theory gets round this problem very effectively. The external force results in a time-dependent quantum number \( \mathbf{k}(t) \). The resulting electronic velocity is obtained from the bandstructure using \( \mathbf{v} = (1/\hbar) \nabla_{\mathbf{k}} E_j(\mathbf{k}) \) and substituting \( \mathbf{k} = \mathbf{k}(t) \). The bandstructure thus tells us all that we need to know about the interaction between the electrons and the relatively static components of the crystal (ions, molecules etc.).

5.2.6 Scattering in the Bloch approach

The Bloch wavefunctions describe states which are stationary solutions to the Schrödinger equation of a periodic potential. Thus these states persist for ever and ever in a perfectly periodic infinite crystal; there will be no scattering of electrons in the absence of disorder (which disturbs the perfect periodicity) or boundaries (which destroy the periodicity/infiniteness of the crystal). This is a manifestation of the wave-like nature of electrons; in a periodic array of scatterers a wave can propagate without attenuation because of the coherent constructive interference of the scattered waves. Scattering only takes place because of lack of periodicity in \( r \)-space.

This observation is in great contrast with the Drude model (where electrons were pictured crashing into virtually every ion) and the Sommerfeld approach (where scattering was acknowledged but its cause was a mystery). In addition

- it encompasses all possible causes of scattering (phonons, other electrons, impurities and boundaries, all of which disturb the local periodicity);
- it explains the enormous low-temperature scattering lengths observed in very pure single crystals of metals (often \( \sim \) mm or even cm);
- it removes the need for the hand-waving explanations as to why the electrons in a metal “might not see the ionic cores very much” used to justify the Drude and Sommerfeld approaches.

5.3 General (non-isotopic) density of states

In Section 5.2.4 we considered the density of states \( g(E) \) where \( E(\vert \mathbf{k} \vert) \), i.e. in the special case of isotropic systems. However in non-isotropic materials we may still need to know the density of states at a particular point in \( k \)-space. In this section we will treat the more general case of non-isotropic materials, where the density of states at is expressed as \( g(E(\mathbf{k})) \).

\[
g(E(\mathbf{k})) = \sum \nu g_{\nu}(E_{\nu}(\mathbf{k})) \quad (5.15)
\]
where

\[ g_\nu(E_\nu(k)) = \begin{cases} 
\frac{1}{\pi} \frac{1}{|v_\nu E|} & \text{1D} \\
\frac{1}{2\pi} \int \frac{dl}{|v_\nu E|} & \text{2D} \\
\frac{1}{4\pi} \int \int_S \frac{dS}{|v_\nu E|} & \text{3D}
\end{cases} \]

Discussion of and a method showing how to obtain these results will presented in the lecture.

5.3.1 Van Hove singularities

This section will also be presented in lectures on the board.

5.4 Holes

It is going to be useful to be able to describe a few empty states close to the top of an almost full band using the concept of holes. Consider a band, containing electrons with quantum numbers \( k_j \), velocities \( v_j \) and energies \( E(k_j) \), where \( E = 0 \) is at the top of the band. For a full band, the values of \( k \) should all sum to zero, \( \text{i.e.} \)

\[ \sum_j k_j = 0. \]  

We consider removing one electron to create an excitation which we label a hole. Suppose that the \( l \)th electron is removed; the band then acquires a net \( k \) which we attribute to the presence of the hole. The hole has \( k = k_h \), with

\[ k_h = \sum_{j \neq l} k_j = -k_l. \]  

It is obvious that the lower down the band the empty state, the more excited the system. The hole’s energy \( E_h \) must therefore take the form

\[ E_h = -E(k_l). \]  

The full band will carry no current, \( \text{i.e.} \)

\[ \sum_j (-e)v_j = 0; \]  

the removal of the \( p \)th electron produces a current

\[ \sum_{j \neq l} (-e)v_j = -(e)v_l = (+e)v_h, \]  

\( \text{i.e.} \) the hole appears to have an associated positive charge. Finally, substitution of Equations 5.18 and 5.19 into Equation 5.12 shows that the effective mass \( m^*_h \) (or effective mass tensor components in a more complex band) associated with the hole is given by

\[ m^*_h = -m^*_l. \]  

The importance of holes stems from the fact that bands are often well-characterised only close to the band extrema. Our knowledge of the dispersion relationships away from a particular extremum is often rather nebulous; such regions are not easily studied experimentally. It is therefore easier to deal with a small number of empty states close to the well-characterised maximum of an almost full band rather than attempt to treat the huge number of poorly-characterised states lower down in the band.
The fact that holes behave as though they have positive charge and positive effective mass explains why many di- and trivalent metals have positive Hall coefficients (see Section 1.3.3 and Table 1.1). A simple instance in which this could happen is shown in Figure 3.2. The section of Fermi surface in the corner of the Brillouin zone (Figure 3.2(d)) corresponds to a small number of empty states at the top of a band; the states are therefore hole-like. By contrast, the sections of Fermi surface straddling the zone boundaries (Figure 3.2(e)) represent a few filled states at the bottom of the upper band; these states are therefore electron-like. The observed Hall coefficient would depend on the relative contributions that the various Fermi-surface sections make to the electrical conductivity.

5.5 Postscript.

We have now derived all of the ideas needed for a reasonable understanding of the bandstructures of real solids. We shall take these ideas and use them to study the properties of semiconductors and insulators in the following lecture.

5.6 Reading.
