

## Handout 3

# The nearly-free electron model

### 3.1 Introduction

Having derived Bloch's theorem we are now at a stage where we can start introducing the concept of bandstructure. When someone refers to the bandstructure of a crystal they are generally talking about its electronic *dispersion*,  $E(\mathbf{k})$  (i.e. how the energy of an electron varies as a function of crystal wavevector). However, Bloch's theorem is very general and can be applied to any periodic interaction, not just to electrons in the periodic electric potential of ions. For example in recent years the power of band theory has been applied to photons in periodic dielectric media to study *photonic bandstructure* (i.e. dispersion relations for photons in a "photonic crystal").

In this lecture we will firstly take a look at dispersion for an electron in a periodic potential where the potential very weak (the *nearly free electron approximation*) and in the next lecture we will look at the case where the potential is very strong (*tight binding approximation*). Firstly let's take a closer look at dispersion.

### 3.2 Dispersion $E(\mathbf{k})$

You will recall from the Sommerfeld model that the dispersion of a free electron is  $E(k) = \frac{\hbar^2 k^2}{2m}$ . It is completely isotropic (hence the dispersion only depends on  $k = |\mathbf{k}|$ ) and the Sommerfeld model produces exactly this bandstructure for every material – not very exciting! Now we want to understand how this parabolic relation changes when you consider the periodicity of the lattice.

Using Bloch's theorem you can show that translational symmetry in real space (characterised by the set translation vectors  $\{\mathbf{T}\}$ ) leads to translational symmetry in k-space (characterised by the set of reciprocal lattice vectors  $\{\mathbf{G}\}$ ). Knowing this we can take another look at Schrödinger's equation for a free electron in a periodic potential  $V(\mathbf{r})$  :

$$H\psi_{\nu\mathbf{k}}(\mathbf{r}) = \left\{-\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r})\right\}\psi_{\nu\mathbf{k}}(\mathbf{r}) = E_{\nu\mathbf{k}}\psi_{\nu\mathbf{k}}(\mathbf{r}). \quad (3.1)$$

and taking the limit  $V(\mathbf{r}) \rightarrow 0$  we know that we have a plane wave solution. This implies that the Bloch function  $u(\mathbf{r}) \rightarrow 1$ . However considering the translational invariance in k-space the dispersion relation must satisfy:

$$E_{\nu\mathbf{k}} = \frac{\hbar^2|\mathbf{k}|^2}{2m} = \frac{\hbar^2|\mathbf{k} + \mathbf{G}|^2}{2m} \quad (3.2)$$

for the set of all reciprocal lattice vectors  $\{\mathbf{G}\}$ . This dispersion relation is show in Fig. 3.1

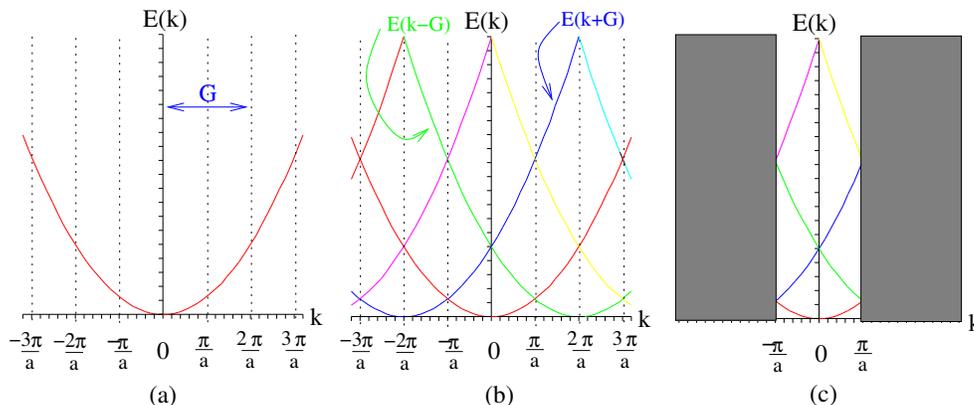


Figure 3.1: Simple bandstructure diagrams for a one dimensional periodic solid in the limit  $V(\mathbf{r}) \rightarrow 0$  expressed in the extended zone (a), repeated zone (b), and reduced zone (c) schemes.

### 3.3 Nearly free electron model

Since we are in the weak potential limit we can treat the crystal potential as a weak perturbation added to the Hamiltonian of a free electron. Let's start with the Schrödinger equation for a free electron

$$\hat{H}_0 \psi_{\nu\mathbf{k}}(\mathbf{r}) = E_{\nu\mathbf{k}} \psi_{\nu\mathbf{k}}(\mathbf{r}) \quad (3.3)$$

where

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} \quad (3.4)$$

which has plane wave eigenstates

$$\psi_{\nu\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_{r3}}} \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (3.5)$$

We now introduce a small perturbation,  $\hat{H}'$  associated with the crystal potential

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (3.6)$$

. Since the lattice is periodic we may expand the perturbation into a Fourier series where  $\{\mathbf{G}\}$  are a set of vectors and  $V_{\mathbf{G}}$  are Fourier coefficients<sup>1</sup>

$$\hat{H}' = V(\mathbf{r}) = \sum_{\{\mathbf{G}\}} V_{\mathbf{G}} \exp(-i\mathbf{G} \cdot \mathbf{r}). \quad (3.7)$$

Since the lattice is periodic we may expand the perturbation into a Fourier series where  $\mathbf{G}$  are a set of vectors and  $V_{\mathbf{G}}$  are Fourier coefficients.

⋮

**Treating the nearly free electron model using degenerate perturbation theory has been shown on the blackboard during lectures**

### 3.4 Consequences of the nearly-free-electron model.

In the lectures we have derived two simple rules, which are

- away from Brillouin-zone boundaries the electronic bands (*i.e.* dispersion relationships) are very similar to those of a free electron;

<sup>1</sup>By considering  $V(\mathbf{r} + \mathbf{T}_n) = V(\mathbf{r})$  you can show that  $\mathbf{G}$  turns out to be the reciprocal lattice vector (see Section 2.2)

- bandgaps open up whenever  $E(\mathbf{k})$  surfaces cross, which means in particular at the zone boundaries.

To see how these rules influence the properties of real metals, we must remember that each band in the Brillouin zone will contain  $2N$  electron states (see Sections 2.3 and 2.6), where  $N$  is the number of primitive unit cells in the crystal. We now discuss a few specific cases.

### 3.4.1 The alkali metals

The alkali metals Na, K *et al.* are monovalent (*i.e.* have one electron per primitive cell). As a result, their Fermi surfaces, encompassing  $N$  states, have a volume which is half that of the first Brillouin zone. Let us examine the geometry of this situation a little more closely.

The alkali metals have a body-centred cubic lattice with a basis comprising a single atom. The conventional unit cell of the body-centred cubic lattice is a cube of side  $a$  containing two lattice points (and hence 2 alkali metal atoms). The electron density is therefore  $n = 2/a^3$ . Substituting this in the equation for free-electron Fermi wavevector (Equation 1.23) we find  $k_F = 1.24\pi/a$ . The shortest distance to the Brillouin zone boundary is half the length of one of the  $\mathbf{A}_j$  for the body-centred cubic lattice, which is

$$\frac{1}{2} \frac{2\pi}{a} (1^2 + 1^2 + 0^2)^{\frac{1}{2}} = 1.41 \frac{\pi}{a}.$$

Hence the free-electron Fermi-surface reaches only  $1.24/1.41 = 0.88$  of the way to the closest Brillouin-zone boundary. The populated electron states therefore have  $k$ s which lie well clear of any of the Brillouin-zone boundaries, thus avoiding the distortions of the band due to the bandgaps; hence, the alkali metals have properties which are quite close to the predictions of the Sommerfeld model (*e.g.* a Fermi surface which is spherical to one part in  $10^3$ ).

### 3.4.2 Elements with even numbers of valence electrons

These substances contain just the right number of electrons ( $2Np$ ) to completely fill an integer number  $p$  of bands up to a band gap. The gap will energetically separate completely filled states from the next empty states; to drive a net current through such a system, one must be able to change the velocity of an electron, *i.e.* move an electron into an unoccupied state of different velocity. However, there are no easily accessible empty states so that such substances should not conduct electricity at  $T = 0$ ; at finite temperatures, electrons will be thermally excited across the gap, leaving filled and empty states in close energetic proximity both above and below the gap so that electrical conduction can occur. Diamond (an insulator), Ge and Si (semiconductors) are good examples.

However, the divalent metals Ca *et al.* plainly conduct electricity rather well. To see why this is the case, consider the Fermi surface of the two-dimensional divalent metal with a square lattice shown in Figure 3.2. Initially, the free-electron Fermi surface is a circle with an area equivalent to the first Brillouin zone (Figure 3.2(a)), which consequently straddles the Brillouin-zone boundary (Figures 3.2(b) and (c)). Figures 3.2 (d) and (e) show what happens when a weak periodic potential is “turned on” and bandgaps open up at the Brillouin-zone boundaries; the band gap raises the energy of the states close to the zone edge in Figure 3.2(c) and lowers those close to the zone edge in Figure 3.2(b) (see Figure ??). For ease of reference, we shall call the former states “the upper band” and the latter states “the lower band”. Hence some electrons will transfer back from the upper band (the states above the gap) to the lower band (the states below it), tending to distort the Fermi surface sections close to the Brillouin-zone boundaries.

In the situation shown in Figures 3.2(d) and (e), the material is obviously still an electrical conductor, as filled and empty states are adjacent in energy. Let us call the band gap at the centres of the Brillouin-zone edges  $E_g^{\text{cent}}$  and that at the corners of the Brillouin zone  $E_g^{\text{corn}}$ .<sup>2</sup> The lowest energy states in the upper band will be at points  $(\pm \frac{\pi}{a}, 0)$ ,  $(0, \pm \frac{\pi}{a})$ , where  $a$  is the lattice parameter of the square lattice, with energy

$$E_{\text{lowest}}^{\text{u}} = \frac{\hbar^2 \pi^2}{2m_e a^2} + \frac{E_g^{\text{cent}}}{2}, \quad (3.8)$$

<sup>2</sup> $E_g^{\text{cent}}$  and  $E_g^{\text{corn}}$  will in general not be the same; two plane waves contribute to the former and four to the latter. However, the gaps will be of similar magnitude.

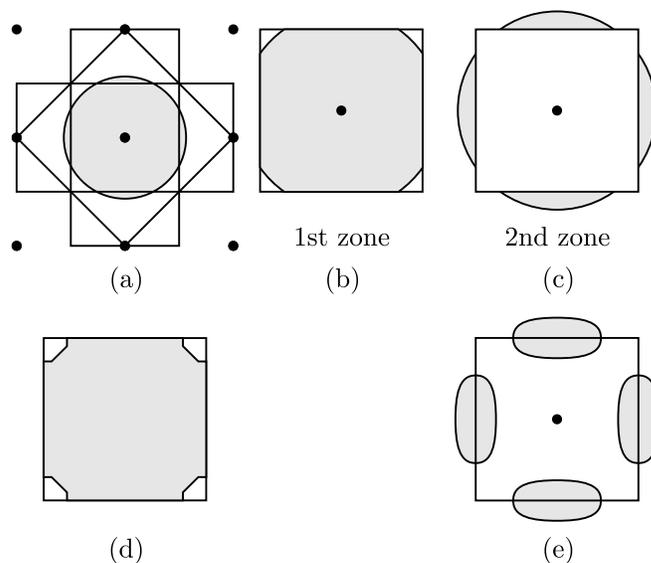


Figure 3.2: The evolution of the Fermi surface of a divalent two-dimensional metal with a square lattice as a band gap is opened at the Brillouin zone boundary: (a) free-electron Fermi surface (shaded circle), reciprocal lattice points (solid dots) and first (square) second (four isosceles triangles) and third (eight isosceles triangles) Brillouin zones; (b) the section of Fermi surface enclosed by the first Brillouin zone; (c) the sections of Fermi surface in the second Brillouin zone; (d) distortion of the Fermi-surface section shown in (b) due to formation of band gaps at the Brillouin-zone boundaries; (e) result of the distortion of the Fermi-surface section in (c) plus “folding back” of these sections due to the periodicity of  $k$ -space.

*i.e.* the free-electron energy plus half the energy gap. Similarly, the highest energy states in the lower band will be at the points  $(\pm\frac{\pi}{a}, \pm\frac{\pi}{a})$ , with energy

$$E_{\text{highest}}^l = \frac{\hbar^2}{2m_e} \frac{2\pi^2}{a^2} - \frac{E_g^{\text{corn}}}{2}, \quad (3.9)$$

*i.e.* the free-electron energy minus half the energy gap. Therefore the material will be a conductor as long as  $E_{\text{highest}}^l > E_{\text{lowest}}^u$ . Only if the band gap is big enough for  $E_{\text{highest}}^l < E_{\text{lowest}}^u$ , will all of the electrons be in the lower band at  $T = 0$ , which will then be completely filled; filled and empty states will be separated in energy by a gap and the material will be an insulator at  $T = 0$ .

Thus, in general, in two and three dimensional divalent metals, the geometrical properties of the free-electron dispersion relationships allow the highest states of the lower band (at the corners of the first Brillouin zone boundary most distant from the zone centre) to be at a higher energy than the lowest states of the upper band (at the closest points on the zone boundary to the zone centre). Therefore both bands are partly filled, ensuring that such substances conduct electricity at  $T = 0$ ; only one-dimensional divalent metals have no option but to be insulators.

We shall see later that the empty states at the top of the lowest band ( *e.g.* the unshaded states in the corners in Figure 3.2(d)) act as *holes* behaving as though they have a *positive* charge. This is the reason for the positive Hall coefficients observed in many divalent metals (see Table 1.1).

### 3.4.3 More complex Fermi surface shapes

The Fermi surfaces of many simple di- and trivalent metals can be understood adequately by the following sequence of processes.

1. Construct a free-electron Fermi sphere corresponding to the number of valence electrons.
2. Construct a sufficient number of Brillouin zones to enclose the Fermi sphere.

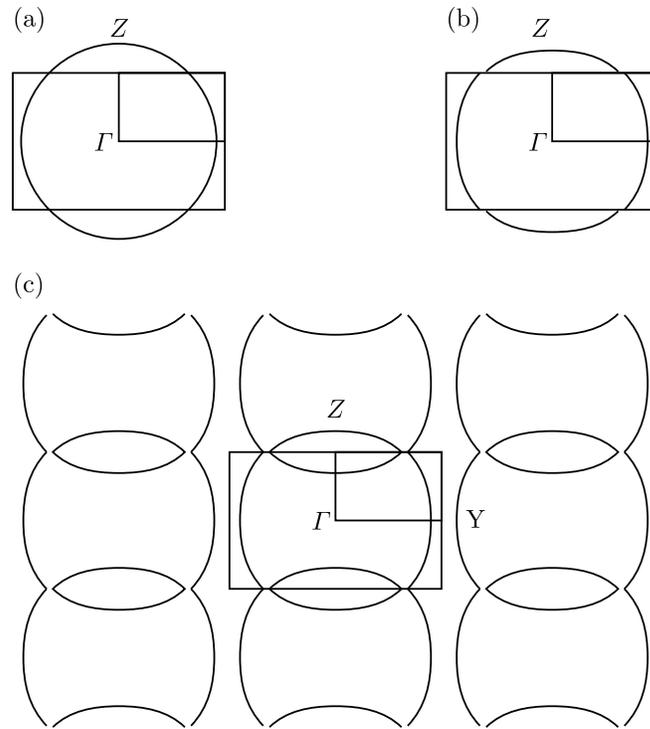


Figure 3.3: The evolution of the Fermi surface of a divalent two-dimensional metal as a band gap is opened at the Brillouin zone boundary. (a) Free-electron Fermi circle and rectangular Brillouin zone; (b) the effect of a band gap opening up at the Brillouin-zone boundary; (c) resulting Fermi surface sections in the extended-zone scheme.

3. Split and “round off” the edges of the Fermi surface wherever it cuts a Brillouin-zone boundary (*i.e.* points at which band-gaps opens up).
4. Apply the periodicity of  $k$ -space by replicating all of the Fermi-surface sections at equivalent points in the first Brillouin zone.

These steps are illustrated in great detail for a number of cases in *e.g.* *Solid State Physics*, by N.W Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976) Chapter 9.

Note that the shape of the Brillouin zone has a profound effect on the Fermi surface sections generated, as shown by the Fermi surface of Figure 3.3. As in Figure 3.2, we have a divalent metal. However, in Figure 3.3, the Brillouin zone is *rectangular*, rather than square, so that the Fermi surface only cuts two of the Brillouin zone edges. Thus, after band gaps have opened up, the Fermi surface consists of a closed ellipse plus corrugated open lines, rather than the two closed sections of Figure 3.2.

### 3.5 Reading

An expansion of this material is given in *Band theory and electronic properties of solids*, by John Singleton (Oxford University Press, 2001), Chapter 3. A more detailed treatment of traditional elemental metals is given in *Solid State Physics*, by N.W Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976) Chapters 8, 9, 10 and 12 (even if you understand nothing of the discussion, the pictures are good). Simpler discussions are available in *Electricity and Magnetism*, by B.I. Bleaney and B. Bleaney, revised third/fourth editions (Oxford University Press, Oxford) Chapter 12, *Solid State Physics*, by G. Burns (Academic Press, Boston, 1995) Sections 10.1-10.21, *Electrons in Metals and*

*Semiconductors*, by R.G. Chambers (Chapman and Hall, London 1990) Chapters 4-6, *Introduction to Solid State Physics*, by Charles Kittel, seventh edition (Wiley, New York 1996) Chapters 8 and 9.