CHAPTER W1

The band theory of solids

Explanation

This chapter is a supplement to the book:

Understanding the properties of matter

by Michael de Podesta.

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CHAPTER W1

The band theory of solids

W1.1 Introduction

This is a special section of *Understanding the Properties of Matter*. It is special because it is an almost entirely theoretical look at solids. In the rest of the book I have focussed on experimental properties, and then developed theories only to the extent that they are needed to understand the experimental data. My motivation in making this additional section available is that it addresses a question that is central to understanding of what 'really happens' inside solids. This question can be simply summarised as 'How do we describe the electronic states within solids?'

The challenge

Consider the solid form of two elements: argon and potassium. We know from §6.2 and §7.3, that argon is described as a molecular solid. However, when we describe potassium, we would naturally discount the theory for argon as irrelevant, and use the theory for a free electron gas described in §6.5. This may seem obvious: after all, one is a metal and the other an insulator. Well the essential question is: 'Why is it obvious?' Argon and potassium atoms differ by only a single electron in their outer shells. In describing the *internal* electronic structure of their atoms, we use the same 'language' to describe both argon and potassium. What we would like is a unified picture, which will describe the nature of electronic states in *all* solids. From this we should be able to *deduce* that argon is an insulator and potassium is a metal. This is the challenge.

The problem

The problem with this approach is that the electronic states in solids are not simple. Some states are like the corresponding states on the isolated atoms, and some appear to be like free-electron states i.e. plane waves. Most states, at least most of the valence states, in solids are in a state somewhere between these two extremes, and the challenge is to find a way to describe such states. The solution to this problem has been 'known' for half a century or more, but it is not at all clear to be who it is who has been doing the 'knowing'. I say this, because while physical descriptions of the nature of electronic states are extremely rare, but dense mathematical tomes are plentiful. In this exposition, It is my intention to keep the mathematical complexities to an absolute minimum. However, the level of mathematical ability required (particularly with regard to the tight-binding theory) is definitely higher than for the topics in the main text. Some familiarity with the apparatus of quantum mechanics is also assumed.

We shall proceed as follows:

§W1.2 and §W1.3 k-space, the reciprocal lattice and free electron theory of metals. These sections repeat some of the material Chapters 6 and 7 of the main text. The purpose of this repetition is to clearly establish the context in which the following discussion takes place.

§W1.4 **Nearly-free electron theory of metals and insulators.** In the free electron theory, all materials with mobile valence electrons are metals. In this section we will see that the introduction of a weak periodic potential allows us to understand how such materials can behave as metals, semi-metals, semiconductors, or insulators.

§W1.5 **Tight-binding theory.** In this section, we introduce a theory which does not ignore the fact that solids are made of atoms. The result is theory of electronic states in solids which is almost realistic.

W1.1 *k*-space

General description

As we saw in §6.5, *k*-space is a geometrical construction used for counting quantum states. Aside from its use in counting states, the use of **k**-vectors provides an extremely compact way of *describing* quantum states. Just by specifying a single point, $\mathbf{k} = (k_x, k_y, k_z)$ we describe a function $A\cos(\mathbf{k}\,.\,\mathbf{r})$ which takes up the whole of the volume of a metal

You should be familiar with the above description if you have read §6.5. There are two points about *k*-space that I would like to draw to your attention.

The first concerns the quantisation of *k*-space arising from the finite extent of the crystal. We will revisit this topic in §W1.1.2 and use a mathematical trick known as *Born-von Karmen* boundary conditions to try to justify the results summarised in Equation 6.59

$$k_x = \frac{2m_x\pi}{L_x}, k_y = \frac{2m_y\pi}{L_y}, k_z = \frac{2m_z\pi}{L_z} \qquad (6.59^*)$$

The second concerns the *extent* of *k*-space. It might seem that the mesh of allowed states would simply extend, uninterrupted, forever. This is nearly true: *k*-space does extended indefinitely, but it is not a completely barren landscape. There are certain special values of **k** that reflect the periodicity of the crystalline potential energy. These form a pattern known as the *reciprocal lattice*, and are discussed in §W1.1.3

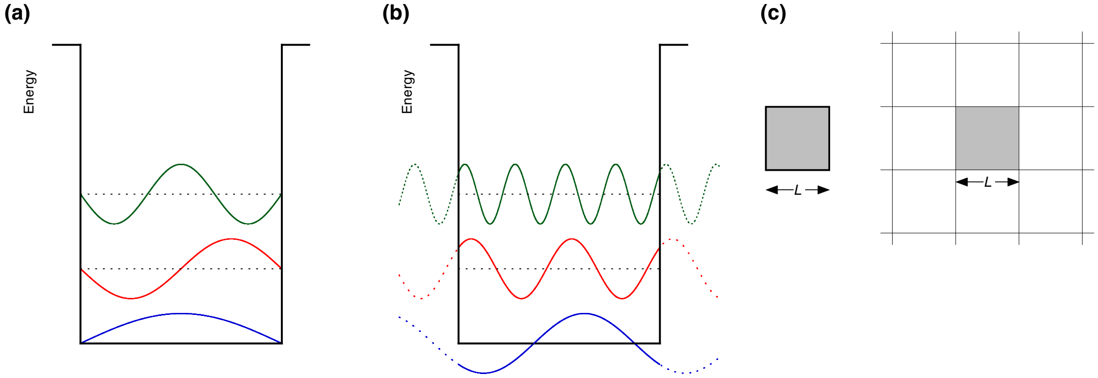
Let us look at each of these two points in turn.

W1.1.2 Quantisation

Born-von Karmen boundary conditions

Let us think back to the solutions of the particle in a box problem that we considered in §2.3. There we required the wave functions to be zero at the edge of the box. This was because we imagined the edge of the box to represent walls of some kind. For a metal, we considered the edge of the box to be the surface of the metal. Now, however, we consider a more complex situation: we imagine a volume which is *representative* of the situation within the box as a whole and we imagine it to surrounded by *identical volumes*.

Figure W1.1 Illustration of two approaches to the particle in a box problem. (a) The first approach uses the idea of an isolated box representing the entire crystal. The second approach (b) uses the idea of a box of representative material surrounded by identical copies of itself. Thus the wave functions need not go to zero but must have (i) the same value and (ii) the same slope at either side of the box. Thus one could imagine placing the boxes side by side and the wave would be identical in each box The edges of the actual crystal are imagined to be far enough away that they do not significantly affect the particles deep inside the box. (c) The same idea applied in two dimensions



The differences between this situation and the standing wave situation are illustrated in Figure W1.1. The reader may consider this change to be 'trickery', and indeed it is. It is a mathematical trick, but it will allow us to see more clearly the physics of what is happening in the metal. First of all, we expect any small region of a metal crystal to be typical of the crystal as a whole. Furthermore, we would not expect its properties to depend at all upon the state of the surface of the crystal. The motivation for using this trick is that we are able to use *travelling wave* solutions to the particle in a box problem.

The mathematical effect of this change in representation concerns the *boundary conditions* that the wave function Ψ must satisfy. Originally we required that the wave functions be zero at the edges of the box i.e.

$$\Psi(-L_x/2)=\Psi(-L_x/2)=0 \qquad \text{(W1.1)}$$

where L_x is the length of the box in the *x*-direction Now we require that the wave functions be identical in neighbouring boxes i.e.

$$\Psi(x)=\Psi(x+L_x) \qquad \text{(W1.2)}$$

If the solutions are of the form $\sin(k_x x)$ or $\cos(k_x x)$, this is equivalent to requiring that:

$$\cos(k_x x)=\cos(k_x[x+L_x]) \qquad \text{(W1.3a)}$$

or

$$\sin(k_x x)=\sin(k_x[x+L_x]) \qquad \text{(W1.3b)}$$

The requirements given by these Equations W1.3 are known as *Born-von Karmen boundary condition.* Their effect is to allow only discrete values of *k* as solutions. Let us follow one of Equations W1.3 through explicitly to find these conditions for k_x. The boundary conditions require that:

$$\begin{aligned}\cos(k_x x)&=\cos(k_x[x+L_x])\\&=\cos(k_x x+k_x L_x)\end{aligned}. \qquad \text{(W1.4)}$$

Using the trigonometric identity:

$$\cos(A+B)=\cos A\cos B-\sin A\sin B \qquad \text{(W1.5)}$$

Equation W1.4 can be rewritten as:

$$\begin{aligned}\cos(k_x x)&=\cos(k_x x+k_x L_x)\\ \cos(k_x x)&=\cos(k_x x)\cos(k_x L_x)-\sin(k_x x)\sin(k_x L_x)\end{aligned} \qquad \text{(W1.6)}$$

Clearly, this equation is not true in general! It is only true when:

- $\cos(k_x L_x)=1$, and
- $\sin(k_x x)\sin(k_x L_x)$is zero. Since x can vary, this will only be true when $\sin(k_x L_x)=0$.

Now $\cos(k_x L)=1$ when :

$$k_x L_x=0,\pm2\pi,\pm4\pi,\ldots. \qquad \text{(W1.7)}$$

and these values of $k_x L_x$ also cause $\sin(k_x L_x)=0$. So, the Born–von Karmen boundary conditions are satisfied when Equation W1.7 is true i.e. when:

$$k_x=0,\frac{\pm2\pi}{L_x},\frac{\pm4\pi}{L_x},\ldots \qquad \text{(W1.8)}$$

or in general when:

$$k_x=\frac{2m_x\pi}{L_x} \qquad \text{(W1.9)}$$

where $m_x=0,\pm1,\pm2,\ldots$ Similar equations apply in the *y* and *z* directions and, as we stated in §6.5 we find that for a three dimensional box::

$$k_x=\frac{2m_x\pi}{L_x},k_y=\frac{2m_y\pi}{L_y},k_z=\frac{2m_z\pi}{L_z} \qquad \text{(6.59*)}$$

Note for pedants

Notice that the solution where $m_x=m_y=m_z=0$ is not an allowed solution, even though it is permitted by the boundary conditions. It is not allowed because (since $p_x=\hbar k_x$ and $\lambda_x=2\pi/k_x$) it corresponds to a solution with zero momentum and infinite wavelength. This is only an allowed solution in free space, and not inside any finite container. This does not make much difference except in cases where the number of states is very small like the *Option A – Option B* counting exercise that we carried out for an eight atom metal.

'Volume' of *k*-space per quantum state

As illustrated in Figure 6.19, each allowed **k**- state can be considered to 'occupy' a small cuboid of 'volume':

$$\begin{aligned}\Delta k_{\mathrm{x}}\Delta k_{\mathrm{y}}\Delta k_{\mathrm{z}} &= \frac{2\pi}{L_{\mathrm{x}}}\times\frac{2\pi}{L_{\mathrm{y}}}\times\frac{2\pi}{L_{\mathrm{z}}} \\ &= \frac{8\pi^3}{V}\end{aligned} \qquad \text{(W1.10)}$$

where V is the total volume of the crystal. I have used the word 'volume' in quotation marks above Equation W1.10 because I am referring to 'volume' on a k-space graph. As you can see from Equation W1.10, the 'volume' on the k-space graph actually has the dimensions of inverse volume i.e. m^{-3} rather than m^3. The final point we need to make is that we need to take account of the internal spin of electrons. This allows two electrons with opposite spin to occupy each k-state. Thus, the volume of k-space required for each electron is given by:

$$\Delta\mathbf{k} = \frac{4\pi^3}{V} \qquad \text{(W1.11)}$$

Equation W1.11 tells us that the larger the volume of the crystal V, the more closely spaced are the quantum states. Thus if we imagine doubling the physical size of crystal from say 1 mm^3 to 2 mm^3, then the 'volume' of k-space per allowed quantum state decreases from 1.24×10^8 m^{-3} to 6.2×10^7 m^{-3}. At first sight you might be puzzled as to how this change occurs: how does k-space 'know' about the volume of the crystal. In fact, it highlights clearly the nature of the k-space: it is not a real place: it is a *concept* used to help us count quantum states. So the change in the density of allowed states in k-space is not a real physical change, but is simply the way in which we account for the fact that larger crystals obviously contain more particles and so must have more quantum states to accommodate them.

W1.1.3 The reciprocal lattice

Introduction

The reciprocal lattice, is, like k-space itself, a concept. It is an abstract idea. If you persist in your studies of solids, I am sure you will find it a useful concept, but it is quite possible that initially at least, you will not see the point of the reciprocal lattice. All I can say is this: *you will not be alone!*

The 'metal as a box' approach

Figure 6.16 illustrates the rationale that we chose for describing a metal as a box. We know that in a metal, the potential energy $V(\mathbf{r})$ will vary in a complex way from place to place. Importantly, we assumed that $V(\mathbf{r})$ was periodic so that:

$$V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R}) \qquad \text{(W1.12)}$$

where $\mathbf{R}$ is a vector which is some multiple of the crystalline period. We noted that since the wave functions $\Psi(\mathbf{k},\mathbf{r})$ did not have this period, then we would expect that in each unit cell of the crystal, the wave function would have a different value of potential energy. Thus, we replaced the 'corrugations' on the 'bottom of the box' with a 'flat bottom'.

The reciprocal lattice is a set of points $\mathbf{K}$ which reflects the periodicity of the crystalline potential i.e. $\mathbf{K}$ is the set of values of $\mathbf{k}$ which describe waves which have *exactly the same value* at *every* lattice site in the crystal.

Now three-dimensional geometry is hard, and I do not want to tax you too much. However, you must now face up to the realities of our three-dimensional world. I will try to make life easier for you by discussing mainly (but not exclusively) just one crystal structure, *simple cubic*. This crystal structure is illustrated in Figure 6.6 and also in Figure W1.2.

In Figure W1.2 I have also illustrated a couple of the waves which have same periodicity as the lattice. For example, if the lattice has periodicity a, the wave with $\mathbf{k} = (2\pi/a,0,0)$ clearly has the same value at every point in the lattice. You can verify this by noting that:

$$\cos\frac{2\pi x}{a} = \cos\frac{2\pi(x+ma)}{a} \qquad \text{(W1.12)}$$

To see this we need merely to separate out the terms:

$$\cos\left[\frac{2\pi x}{a}\right]=\cos\left[\frac{2\pi x}{a}+\frac{2\pi ma}{a}\right] \tag{W1.13}$$

$$\cos\left[\frac{2\pi x}{a}\right]=\cos\left[\frac{2\pi x}{a}+2m\pi\right] \tag{W1.14}$$

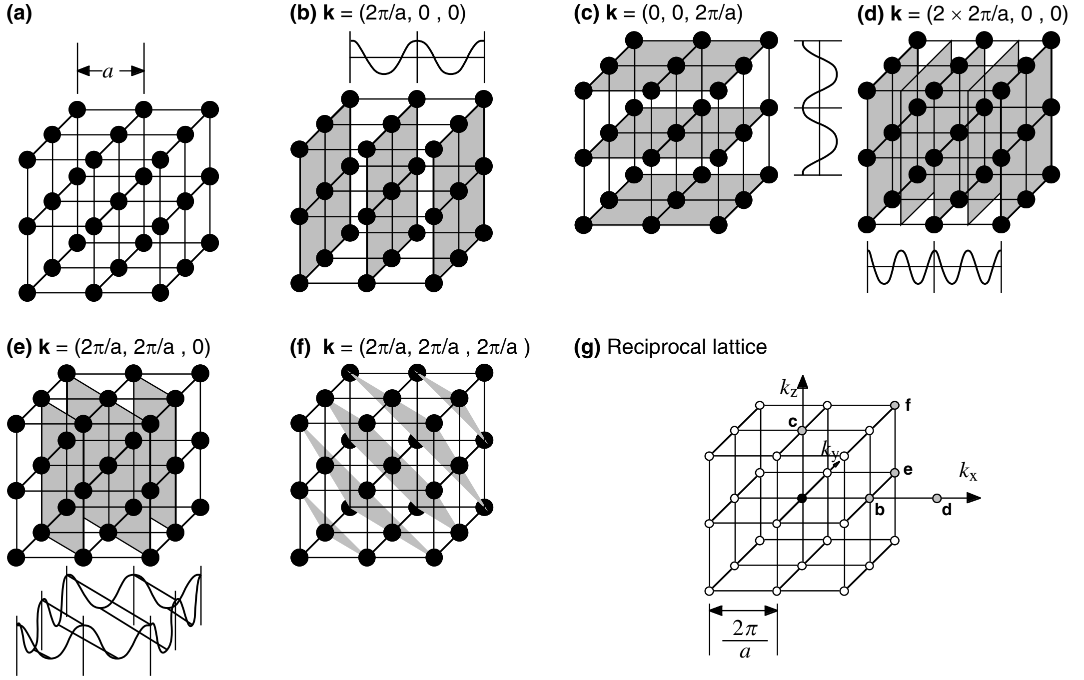
and then note that all trigonometric functions repeat after any integer number of 2π increments. We thus dignify the vector $\mathbf{k}=(2\pi/a,0,0)$ by saying it belongs to the reciprocal lattice of the simple cubic crystal structure. This point, and several other reciprocal lattice vectors, are plotted in Figure W1.2

Reciprocal lattices in general

You may have noticed that we started with a crystal with simple cubic structure with lattice constant a, and we ended up with reciprocal lattice which was also simple cubic with a lattice constant $2\pi/a$. In fact, every type of repeating lattice has a corresponding reciprocal lattice. The reciprocal lattice is the set of all the wave vectors $\mathbf{K}$ that are special to a particular lattice. By 'special' we mean that the wave has *exactly the same phase in every unit cell of the crystal*. However, most reciprocal lattices are more difficult to visualise than the simple cubic lattices that we are dealing with in this section.

It is also interesting that we can plot any kind of waves in k-space. So, for example, we can plot points representing phonons (§7.6) or points representing photons of different wavelengths such as light, or X-rays or points representing the wavelengths of electron wave functions. We will see that the relationship between the wave vectors of these various waves and particles, and the reciprocal lattice will be very important for determining the properties of crystals.

Figure W1.2 (a) A simple cubic lattice with lattice constant *a* (b) to (f) Various waves belonging to the reciprocal lattice i.e. waves which have the same value at every lattice site within the crystal. (g) A segment of the reciprocal lattice showing the points which represent the waves illustrated in (b) to (f).



(a)

(b) $\mathbf{k} = (2\pi/a, 0, 0)$

(c) $\mathbf{k} = (0, 0, 2\pi/a)$

(d) $\mathbf{k} = (2 \times 2\pi/a, 0, 0)$

(e) $\mathbf{k} = (2\pi/a, 2\pi/a, 0)$

(f) $\mathbf{k} = (2\pi/a, 2\pi/a, 2\pi/a)$

(g) Reciprocal lattice

W1.1.4 The Brillouin zone

So now we know two features about *k*-space.

- We know that when it comes to finding allowed solutions of the particle in a box problem, only certain allowed values of (k_x, k_y, k_z) are allowed.
- And we also know that there are special sets of values of **k** which are given the symbol **K**., These tell us which wave vectors are special to the crystal lattice that plays host to our electrons.

Let me now introduce a new feature: the *Brillouin zone*. This is the region of *k*-space around each reciprocal lattice point which is nearer to that reciprocal point than it is to any other. Sounds complicated? Not really. Although the Brillouin zones of three-dimensional crystals in are indeed quite difficult to visualise, in two dimensions the idea is quite simple.

Brillouin zones in 2- dimensions

A two-dimensional Brillioun zone is *the area* of a lattice which is nearer to a particular reciprocal lattice point than to any other reciprocal lattice point. To find this area we proceed as follows:

- Start at the reciprocal lattice point and draw the **K** vectors to nearby reciprocal lattice points.
- Bisect these **K** vectors with lines.
- The area enclosed by all the bisectors is the area nearest to the original point. This is called the *first Brillouin zone*, or often just the *Brillouin zone*.

This procedure is illustrated in FigureW1.3

Brillouin zones in 3-dimensions

A three-dimensional the procedure is similar. The Brillioun zone is *the volume* which is nearer to a particular reciprocal lattice point than to any other reciprocal lattice point. To find this volume we proceed as follows:

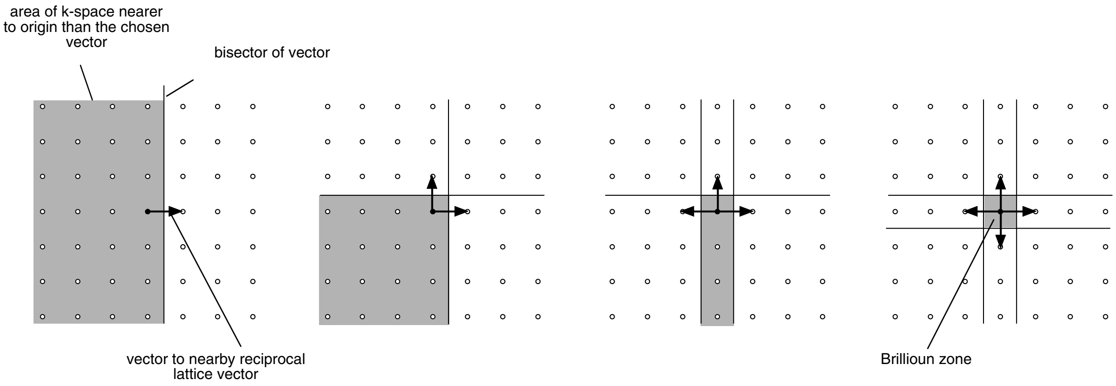
- Start at the reciprocal lattice point and draw the **K** vectors to nearby reciprocal lattice points.
- Bisect these **K** vectors with planes perpendicular to the **K** vectors.
- The volume enclosed by all the bisecting planes is the volume nearest to the original point. This is called the *first Brillouin zone*, or often just the *Brillouin zone.*

The result of applying this procedure to a three dimensional simple cubic lattice is illustrated in FigureW1.4

The ‘volume ‘of the Brillouin zone

For a crystal with exactly *N* lattice sites, the Brillouin zone contains exactly *N* allowed values of **k**. This is important. Suppose we are using *k*-space to visualise the occupancy of states of a particle in a box problem i.e. the free electron gas. We recall

Figure W1.3 Illustration of the way in which a Brillioun zone is constructed.



(§6.5) that each allowed value of **k** can ‘accommodate’ two quantum states with opposite values of intrinsic electron spin. This was summarised n Equation W1.11 where we saw that the 'volume of k-space per allowed quantum state was:

$$\Delta\mathbf{k} = \frac{4\pi^3}{V} \qquad (*\text{W1.11})$$

Thus, if there is one atom at each lattice site (N) which donates one electron to the electron gas ($N \times 1$), then the total ‘volume’ of occupied states is:

$$N \times 1 \times \Delta\mathbf{k} = N \times \frac{4\pi^3}{V} \qquad (\text{W1.15})$$

Since volume of the crystal is just Na^3 we find that the ‘volume’ of occupied states in *k*-space is:

$$N \times \frac{4\pi^3}{Na^3} = \frac{4\pi^3}{a^3} \qquad (\text{W1.16})$$

Notice that this does not depend at all on the size of the crystal, but does depend on its lattice constant a.

The Brillioun zone of a simple cubic lattice is a cube of side $2\pi/a$ and so has volume given by:

$$\left[\frac{2\pi}{a}\right]^3 = \frac{8\pi^3}{a^3} \qquad (\text{W1.17})$$

By comparing Equations W1.16 and W1.17 we see that exactly half the quantum states in the Brillioun zone (i.e. half the volume of the Brillioun zone) would be occupied by electrons from a monovalent metal. Similarly, all the quantum states in the Brillioun zone would be occupied by electrons from a divalent metal.

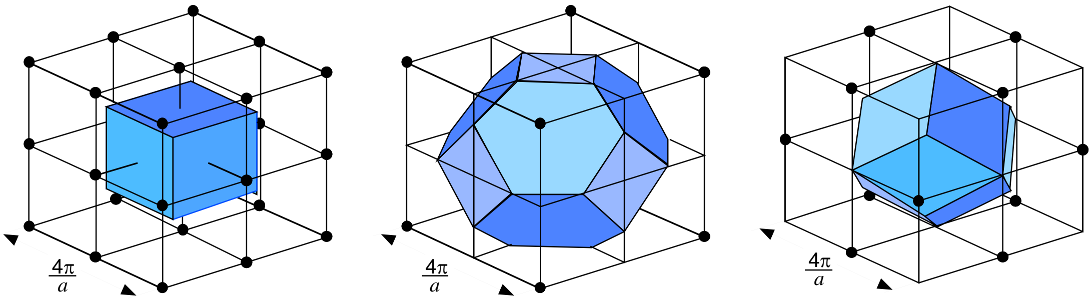
This result, that exactly half of the quantum states in the Brillioun zone would be occupied by electrons in a monovalent metal is not restricted to simple cubic lattices but applies to all lattices:

The significance of the Brillouin zone

Why have I introduced the idea of a Brillouin zone? What is the significance of the Brillouin zone boundaries? After 20 years of studying this subject I can find no obvious significance, *in themselves*. However, I find that time and time again interesting physics occurs in a crystal when any kind of wave takes a value near a Brillouin zone boundary. For each different type of wave (X-rays, electrons, phonons) the physics is slightly different, but it is always interesting

Figure W1.4 Illustration of the 3 dimensional Brillioun zones of (a) the simple cubic (sc), (b) the face centred cubic (fcc) direct lattice and (c) the body-centred cubic (bc) direct lattice. .(a) The sc direct lattice has a reciprocal lattice which also forms a sc pattern with a lattice constant of side 2π/a and the first Brillioun zone forms a cube of side 2π/a . (b) The fcc direct lattice has a reciprocal lattice which forms a bcc pattern with a cube of side 4π/a and the first Brillioun zone forms a 14-sided shape which can be described as a *truncated octahedron.* (c) The bcc direct has a reciprocal lattice which forms an fcc pattern with a cube of side 4π/a and the first Brillioun zone forms a 12 sided shape known as a *regular rhombic dodecahedron.* Notice that for all of the figures drawn:

- The origin of k-space lies at the centre of the shape depicted.
- The region inside the shape depicted is closer to the origin than it is to any other reciprocal lattice point.



W1.2 Free electron theory of metals

W1.2.1 General description

We have already presented the basic ideas of the free electron theory of a metal in §6.5. Here we will remind ourselves of the relationships between the **k** vector that describes each electron quantum state and (a) the momentum and (b) the energy, of the particle occupying that state. However as we make our calculations, we are now in a position to keep in mind the 'landscape' in which these electron states belong: the reciprocal lattice that we described in §1.1. It will turn out to be important to understand the relationship between:

- the wave vectors describing the electron quantum states, and
- the wave vectors describing the reciprocal lattice,

If the electronic quantum states were one-dimensional, then we could relate the wave vector to the wavelength of the wave by:

$$\lambda = \frac{2\pi}{k} \tag{W1.18}$$

In three dimensions, things are a little more complicated. Recall that the k_i's are components of a vector **k** that points from the origin to the point $\mathbf{k} = (k_x, k_y, k_z)$. Now the wavelength of the wave represented by $\mathbf{k} = (k_x, k_y, k_z)$ is given by:

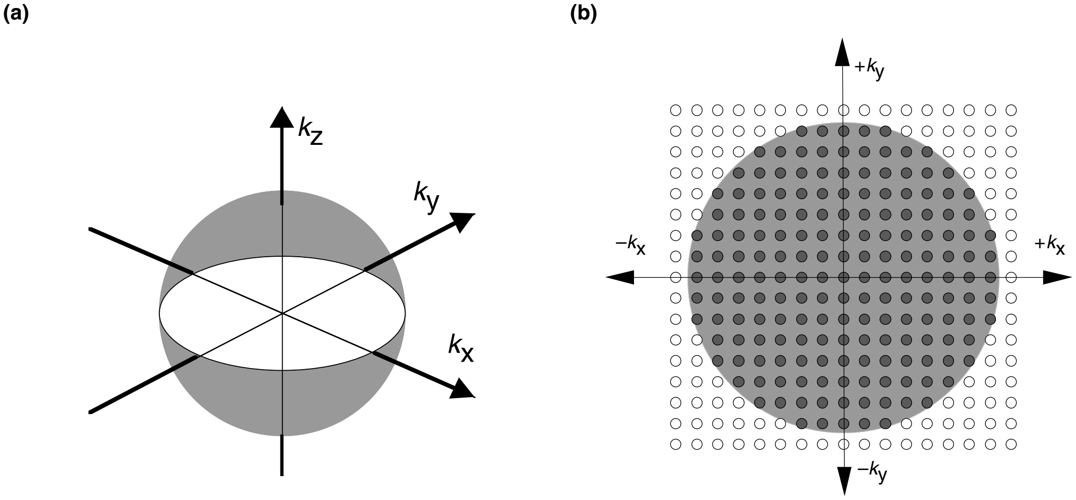
$$\begin{aligned} \lambda &= \frac{2\pi}{|\mathbf{k}|} \\ &= \frac{2\pi}{\sqrt{k_x^2 + k_y^2 + k_z^2}} \end{aligned} \tag{W1.19}$$

Equation 6.63 allows us to use the de Broglie relation (Equation 2.42) to infer the momentum and energy of the wave represented by (k_x, k_y, k_z). The momentum may be written as:

$$\begin{aligned} p &= \frac{h}{\lambda} = \frac{h}{\frac{2\pi}{|\mathbf{k}|}} = \hbar|\mathbf{k}| \\ p &= \hbar\sqrt{k_x^2 + k_y^2 + k_z^2} \end{aligned} \tag{W1.20}$$

Notice that the quantum states with small amounts of momentum have small values of $|\mathbf{k}|$. Thus in *k*-

Figure W1.5 (a) In three-dimensions the occupied states form a sphere in *k*-space known as the *Fermi sphere* which is shown shaded in the figure. If we imagine slicing through the Fermi sphere in plane where $k_z = 0$ we would find a situation represented in (b). Each small circle represents an allowed travelling wave solution to the Schrödinger Equation. The filled circles represent occupied quantum states and the unfilled circles represent empty quantum states. At absolute zero, only the lowest energy states (low *k* = long wavelength = low energy) are occupied. For any macroscopic piece of metal the quantum states would be much more densely packed than in the figure.



space they will be represented by points near the origin. The energy, which is just the kinetic energy of a free particle, may be written as:

$$E = \frac{1}{2} m_{\mathrm{e}} v^2 = \frac{p^2}{2m_{\mathrm{e}}}$$

$$E = \frac{\hbar^2 |\mathbf{k}|^2}{2m_{\mathrm{e}}} \qquad \text{(W1.21)}$$

$$E = \frac{\hbar^2}{2m_{\mathrm{e}}}\left[k_{\mathrm{x}}^2 + k_{\mathrm{y}}^2 + k_{\mathrm{z}}^2\right]$$

Notice again that the low-energy quantum states have small values of $|\mathbf{k}|$. Thus in *k*-space they will be represented by points near the origin. Importantly, the last Equation in W1.21 is the equation of a sphere. Thus, all quantum states with energy E will be represented by points in *k*-space which lie on the surface of a sphere with radius:

$$|\mathbf{k}| = \sqrt{\frac{2m_{\mathrm{e}}E}{\hbar^2}} \qquad \text{(W1.22)}$$

The density of states function.

The density of states function $g(E)$ is the function which answers the question 'How many quantum states are there with energy between E and $E + \mathrm{d}E$ '. We derived an expression for this in §6.5.2 where we found:

$$g(E) = \frac{V\sqrt{2m_{\mathrm{e}}^3 E}}{\pi^2 \hbar^3} = \left[\frac{V\sqrt{2m_{\mathrm{e}}^3}}{\pi^2 \hbar^3}\right]\sqrt{E} \qquad \text{(*6.70 \& W1.23)}$$

Notice that $g(E)$ depends only a group of fundamental constants, and increases as the square root of the energy.

We can derive an expression for the Fermi energy using the density of states function. To do this we note that at the absolute zero of temperature, all of the quantum states below the Fermi energy will be occupied, and all the states above the Fermi energy will be empty. So, we can write that:

$$N = \int_{E=0}^{E=E_{\mathrm{F}}} g(E)\,\mathrm{d}E \qquad \text{(W1.24)}$$

Substituting for $g(E)$ from Equation W1.23 and taking the constants outside the integral we find:

$$N = \int_{E=0}^{E=E_{\mathrm{F}}} \left[\frac{V}{\pi^2}\frac{\sqrt{2m_{\mathrm{e}}^3}}{\hbar^3} E^{1/2}\right] \mathrm{d}E$$

$$= \left[\frac{V}{\pi^2}\frac{\sqrt{2m_{\mathrm{e}}^3}}{\hbar^3}\right] \int_{E=0}^{E=E_{\mathrm{F}}} E^{1/2}\,\mathrm{d}E \qquad \text{(W1.25)}$$

$$N = \left[\frac{V}{\pi^2}\frac{\sqrt{2m_{\mathrm{e}}^3}}{\hbar^3}\right] \frac{2}{3} E_{\mathrm{F}}^{3/2}$$

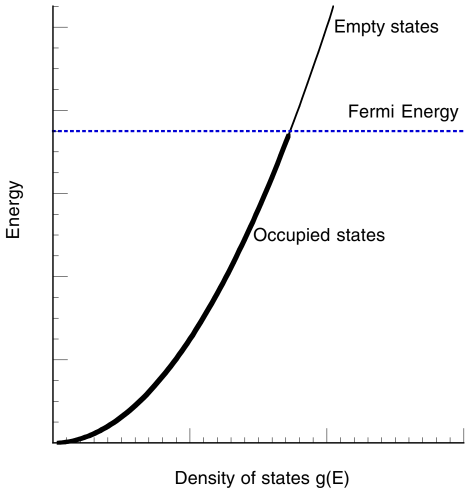
Rearranging this as an expression for the Fermi energy:

$$\frac{3n\pi^2\hbar^3}{2\sqrt{2m_{\mathrm{e}}^3}} = E_{\mathrm{F}}^{3/2}$$

$$E_{\mathrm{F}} = \frac{\hbar^2\left(3n\pi^2\right)^{2/3}}{2m_{\mathrm{e}}^2} \qquad \text{(W1.27)}$$

which agrees with Equation 6.73.

Figure W1.6 Showing g(E) occupied up to the Fermi energy.



Potassium: a simple metal

In §6.5 we worked out the free electron estimates for the Fermi parameters of the metal copper. Here we compare those estimates with those for potassium. Potassium is a group 1 metal which should satisfy well our idea of a material which 'ionises' easily in the solid, leaving a gas of electrons relatively free to move through the metal. We expect each atom to 'donate' one electron to the electron gas.

As in §6.5, we estimate the *number density* of electrons from the *mass density* of the elemental metal. First we divide the mass density by the mass of an atom to get the number density of *atoms*. We then multiply by the valence to arrive at *n*. From Table 7.2 we see that the density of potassium is $862\ \mathrm{kg\ m^{-3}}$, and the mass of an atom is $39.1 \times 1.66 \times 10^{-27}$ kg. Assuming potassium has a valence of one, then our estimate for *n* is:

$$\begin{aligned} n &= \frac{1\times 862}{39.1\times 1.66\times 10^{-27}} \\ &= 1.33\times 10^{28}\ \text{electrons m}^{-3} \end{aligned} \qquad \text{(W1.27)}$$

which we can compare with $n_{\mathrm{Cu}} = 8.47 \times 10^{28}$ electrons $\mathrm{m^{-3}}$ for copper. It is interesting to note that copper has an electron density some six times greater than potassium. As discussed in §7.2, this is due to the effect of additional covalent bonding between copper atoms by the *d*-electrons.

Table W1.1 Free electron parameters for potassium and copper. Notice that in the free electron approximation, the density of states function *g*(*E*) is the same for all metals.

	Potassium	Copper
k_{F}	$7.33\times 10^{9}\ \mathrm{m^{-1}}$	$13.6\times 10^{9}\ \mathrm{m^{-1}}$
E_{F}	2.05 eV	7.06 eV
$g(E)$	$1.062\times 10^{56}\sqrt{E}$ states $\mathrm{J^{-1}m^{-3}}$	
$g(E_{\mathrm{F}})$	6.08×10^{46} states $\mathrm{J^{-1}m^{-3}}$	1.13×10^{47} states $\mathrm{J^{-1}m^{-3}}$

Similarly we can estimate the Fermi wave vector, Fermi energy, density of states and the density of states at the Fermi energy as we did for copper. The results are summarised in Table W1.1

A metal in a lattice.

We can now compare the periodicities encountered in the lattice with those occurring in the free electron gas. We will use the fact that potassium crystallises in the *bcc* structure with a conventional unit cell of side $a = 0.52$ nm to compare the size of the Fermi sphere with the size of the Brillouin zone. In particular, for reasons which will become clear in the next section, we will find out whether the Fermi sphere fits entirely within the Brillouin zone.

The reciprocal lattice of a bcc crystal

What does the reciprocal lattice of a bcc crystal look like? The reciprocal lattice of *bcc* of conventional unit cell side *a* is *fcc* with conventional unit cell of side $4\pi/a$. Numerically, this amounts to $\approx 12.6/a$ or (for $a = 0.532$ nm) the lattice constant amounts to $2.36\times 10^{10}\mathrm{m^{-1}}$. The reciprocal lattice is illustrated in Figures W1.4 and W1.7.

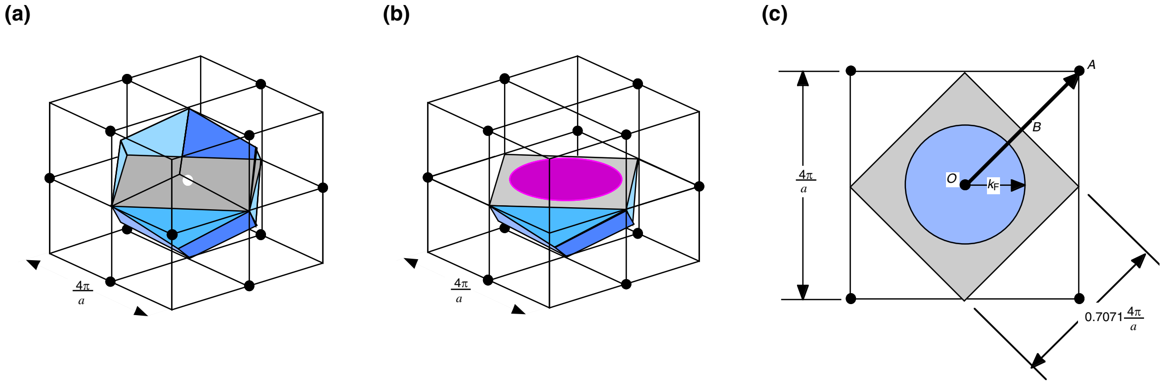
Figure W1.7 gives an impression of the Brillouin zone with the Fermi sphere illustrated inside the zone. Although three-dimensional geometry is hard, we can make a relatively simple calculation if we confine our attention to a cross-section of the Fermi sphere in the $k_z = 0$ plane.

First we need to calculate the distance from the origin to the point on the Brillouin zone boundary which most closely approaches the origin. This is at the midpoint of the line joining the origin to the (1,1,0) reciprocal lattice point. From the scale of the diagram we can see that this distance (*OA*) from the origin to the nearest reciprocal lattice point is:

$$\sqrt{2}\times\frac{1}{2}\times\frac{4\pi}{a} = 1.67\times 10^{10}\ \ \mathrm{m^{-1}} \qquad \text{(W1.28)}$$

and so the distance (*OB*) from the origin to the Brillouin zone boundary at its closest point of approach is:

Figure W1.7 Illustration of the relationship between the size of the Fermi sphere and Brillioun zone for potassium, a monovalent metal with a bcc crystal structure. (a) Shows the fcc reciprocal lattice of the bcc direct lattice showing the Brillioun zone from Figure W1.4 and the $k_z = 0$ plane. The origin is shown as a white dot in this picture and the other reciprocal lattice points are shown as black dots. (b) The first Brillioun zone 'chopped' in $k_z = 0$ plane showing the Fermi sphere. (c) Detailed view of the $k_z = 0$ plane showing the relative sizes of the Fermi sphere and Brillioun zone.



$$\frac{1}{2}\left[\sqrt{2}\times\frac{1}{2}\times\frac{4\pi}{a}\right] = 0.835\times10^{10}\ \ \mathrm{m}^{-1} \qquad \text{(W1.29)}$$

We now need to compare this distance with the radius of the Fermi sphere, k_F.. At the risk of boring you, let us do this calculation yet again. Recall that the Fermi sphere must 'accommodate' N electrons, each of which occupies a 'volume' given Equation W1.11.

$$\frac{4}{3}\pi k_F^3 = N\times\frac{4\pi^3}{V} \qquad \text{(W1.30)}$$

Remembering that the total volume of the crystal is just N times the volume of a unit cell containing one atom we write:

$$V = N\frac{a^3}{2} \qquad \text{(W1.31)}$$

Substituting this result into Equation W1.30

$$\frac{4}{3}\pi k_F^3 = N\times\frac{4\pi^3}{N\dfrac{a^3}{2}} = \frac{8\pi^3}{a^3} \qquad \text{(W1.32)}$$

and solving for k_F we find:

$$k_F^3 = \frac{3}{4\pi}\frac{8\pi^3}{a^3} = \frac{3}{4\pi}\left[\frac{2\pi}{a}\right]^3$$

$$k_F = \left(\frac{3}{4\pi}\right)^{1/3}\left[\frac{2\pi}{a}\right] \qquad \text{(W1.33)}$$

$$k_F = 0.620\left(\frac{2\pi}{a}\right)$$

Evaluating this for $a = 0.532$ nm we find:

$$k_F = 0.73\times10^{-10}\ \mathrm{m}^{-1} \qquad \text{(W1.34)}$$

Comparing Equation W1.34 with W1.29 we see that the Fermi sphere extends 0.73/0.84 ≈ 87% of the way to the Brillouin zone boundary. So, based solely on an estimate of electron density, the free electron theory predicts that the Fermi sphere lies entirely within the Brillouin zone. This quite a simple prediction, and as we mention in just a moment, an amazingly accurate one.

Is this correct?

In the next section (§W1.5), on the nearly-free electron model of a metal, we shall see that the prediction that the Fermi surface of potassium is a sphere is true *because* it does not come near the Brillioun zone boundary. In §W1.5 on the tight binding model we will see that it is possible to have Fermi surfaces which are quite different in shape from a sphere. Astonishingly, in my opinion at least, one can determine the Fermi surface of many metals *experimentally*. The best established technique for achieving this is by means of the *de Haas-van Alphen effect*. This effect gives rise to tiny oscillations in the magnetisation of very pure metals at very low temperatures (<≈ 1 K) and in very high magnetic fields (>≈ 3 T). From a detailed examination of these oscillations, in particular their periodicity as the magnetic field is varied, the Fermi surface may be reconstructed.

Using techniques such as this, the Fermi surface of potassium is found to be in excellent agreement with this simple theory. The diameter of the Fermi sphere is found to agree with the simple estimates we made to within 1% and the 'sphere' deviates from being a perfect sphere by less than 1 part in 10^3. To put this in perspective, it is a more perfect sphere than a typical snooker (pool) ball.

So consider this: the free electron theory (which is based solely on an estimate of electron density and has no free parameters, correctly predicts the electronic structure of at least one *real* metal to within one percent! This result is even more astounding than the predictions for the bulk modulus of potassium that we calculated in §7.3 where the agreement was only at the 10% level.

However, there is a 'fudge' here. It is that we had to decide arbitrarily what the valence was. Thus the theory does not tell us what we asked at the start of the chapter, namely, it does not tell us that argon (one electron and one proton less than potassium) will not be a metal. So the free electron theory is sometimes surprisingly good, but there are some questions for which it is not able to provide answers.

W1.4 The nearly-free electron theory of metals and insulators

W1.4.1 Introduction

In the last section we considered the case of electrons which were free to move within the metal and so the only contribution to their energy was their kinetic energy:

In this section we will consider how the electrons are affected by the crystalline potential arising from the ion cores. Essentially, this is an attempt to look at the effect of the 'corrugations' at the bottom of the box in Figure W1.8. As long as the corrugations are not too large, we will find that the energy varies with **k** in a way which is similar to that predicted by the free-electron model. This supports the use of the free electron model that we considered in the last section where we ignored the potential energy completely! However, we will find that when **k** is close to the boundary of the Brillouin zone then the potential energy contribution becomes significant. We will also find that we are able to take a first step towards understanding how to represent materials that are not metals.

W1.4.2 The total energy

The *band structure* of a material is (essentially), a description of the way the *total* energy of electronic states varies as a function of their quantum number. $\mathbf{k} = (k_x, k_y, k_z)$. In other words, the band structure of a material is a statement of the total energy relationship $E(\mathbf{k})$, which is in turn the sum of the kinetic and potential energy contributions.

Kinetic energy

The kinetic energy contribution is related to the average curvature of the wave function which in one dimension is given by:

$$\frac{-\hbar^2}{2m_\mathrm{e}}\frac{\partial^2}{\partial x^2}\Psi(x) \tag{W1.35}$$

In the free electron approximation the potential energy contribution is assumed to be zero. The wave functions are plane waves with the general form $A\cos k_x x$ and the total energy is just the kinetic energy:

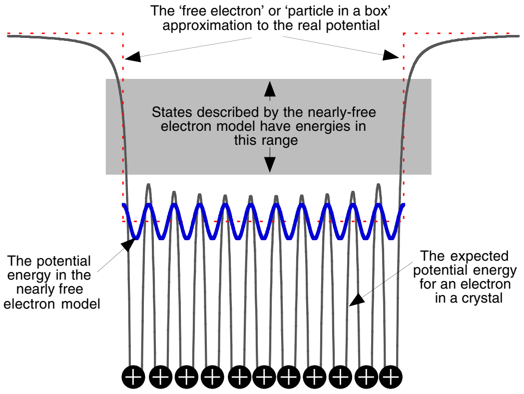
$$E(k_x) = \frac{-\hbar^2 k_x^2}{2m_\mathrm{e}} \tag{W1.36}$$

Potential energy

The potential energy contribution $V(\mathbf{k})$ is caused by the electrostatic (Coulomb) interactions between the electron and all the other electrically charged objects in its vicinity i.e. the ions, and the other electrons. In the nearly-free electron model we acknowledge that a potential energy contribution exists, but we assume that it is (a) small compared to the kinetic energy contribution and (b) has the same periodicity as the crystal.

Introducing the potential energy in this way is obviously not very realistic. However, even at this level of approximation it introduces an important physical feature which is also true of more complex theories. This is that the energy of a plane wave is no longer determined solely by the wave vector **k**. It can also depend on the *phase* of the wave function. In this case it means that the function Ψ = sinkx can have a different energy than the function Ψ = coskx. This is a feature of all more complex theories and the nearly-free electron theory is the simplest theory which includes this feature.

Figure W1.8 Illustration of the potential energy in the nearly-free electron model.



Total energy

The total energy is the sum of the kinetic energy and the potential energy. However, we need to take account of the fact that the potential energy depends not just on **k**, but on the phase of the wave function. Thus we shall need to list separately the way in which total energy of sine-based wave functions depends on **k**, and then way in which total energy of cosine-based wave functions depends on **k**. Using the labels *A* and *B* to indicate sine- and cosine-based wave functions respectively we write:

$$\begin{aligned} E_\mathrm{A}(\mathbf{k}) &= KE(\mathbf{k}) + V_\mathrm{A}(\mathbf{k}) \\ E_\mathrm{B}(\mathbf{k}) &= KE(\mathbf{k}) + V_\mathrm{B}(\mathbf{k}) \end{aligned} \qquad \text{(W1.37)}$$

W1.4.2 A ‘simple’ calculation

Let us now follow our introductory discussion by making some estimates of the effect of introducing a periodic potential into the free-electron ‘box’.

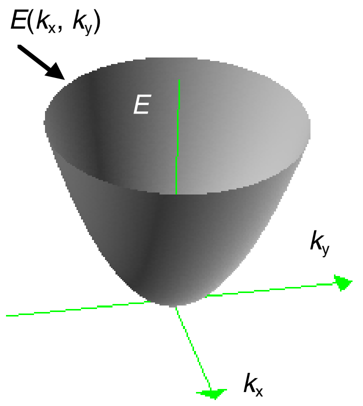
Considering only one-dimension, we will consider the effect a periodic potential of the form:

$$V(x) = V_\mathrm{o}\cos\left[\frac{2\pi x}{a}\right] \qquad \text{(W1.38)}$$

We will evaluate this for electron wave functions of the form:

$$\Psi_\mathrm{A} = \sqrt{\frac{2}{L_\mathrm{x}}}\sin k_\mathrm{x}x \qquad \text{(W1.39)}$$

Figure W1.9 Illustration of the kinetic energy parabola in two dimensions.



$$\Psi_\mathrm{B} = \sqrt{\frac{2}{L_\mathrm{x}}}\cos k_\mathrm{x}x \qquad \text{(W1.40)}$$

where L_x is the size of the ‘box’ in the *x*-direction. We will work out the total energy in four stages:

- First, we will demonstrate that Equations W1.39 and W1.40 are *normalised*.
- Second, we will calculation the kinetic energy
- Third, we will calculation the potential energy
- Finally, we will add the potential and kinetic energies and then describe a more accurate way of calculating the total energy

Stage 1: Normalisation

Firstly, let us notice that these wave functions are *normalised*. This means that if we evaluate the probability of finding the electron *anywhere* the answer is unity. This reflects the fact that the electron *must* be some somewhere. Mathematically we write:

$$\int_{all\ space} \Psi_\mathrm{A}^{*}\Psi_\mathrm{A} = 1 \qquad \text{(W1.41)}$$

We now substitute using W1.39 to find:

$$I_\mathrm{A} = \int_0^{L_\mathrm{x}} \sqrt{\frac{2}{L_\mathrm{x}}}\sin k_\mathrm{x}x \times \sqrt{\frac{2}{L_\mathrm{x}}}\sin k_\mathrm{x}x\,\mathrm{d}x \qquad \text{(W1.42)}$$

Taking the constants outside the integral yields:

$$\begin{aligned} I_\mathrm{A} &= \sqrt{\frac{2}{L_\mathrm{x}}}\sqrt{\frac{2}{L_\mathrm{x}}}\int_0^{L_\mathrm{x}} \sin^2 k_\mathrm{x}x\,\mathrm{d}x \\ &= \frac{2}{L_\mathrm{x}}\int_0^{L_\mathrm{x}} \sin^2 k_\mathrm{x}x\,\mathrm{d}x \end{aligned} \qquad \text{(W1.43)}$$

If we had started with Ψ_B we should have found

$$I_\mathrm{B} = \frac{2}{L_\mathrm{x}}\int_0^{L_\mathrm{x}} \cos^2 k_\mathrm{x}x\,\mathrm{d}x \qquad \text{(W1.44)}$$

To proceed with either integral we need to simplify the kernel of the integral using the trigonometric identities:

$$\cos^2\theta = \frac{1}{2}[1 + \cos 2\theta] \qquad \text{(W1.45)}$$

$$\sin^2\theta = \frac{1}{2}[1-\cos 2\theta] \qquad \text{(W1.46)}$$

We can now treat the two wave functions *A* and *B* at the same time by writing:

$$I_{\mathrm{A/B}} = \frac{2}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \frac{1}{2}\left[1 \pm \cos 2k_{\mathrm{x}}x\right]\mathrm{d}x \qquad \text{(W1.47)}$$

where wave function *A* takes the lower option (–) of the ± sign and wave function *B* takes the upper option (+). The integral can then be separated into two integrals as follows:

$$\begin{aligned} I_{\mathrm{A/B}} &= \frac{2}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \frac{1}{2}\left[1 \pm \cos 2k_{\mathrm{x}}x\right]\mathrm{d}x \\ &= \frac{1}{L_{\mathrm{x}}}\left[\int_0^{L_{\mathrm{x}}}\mathrm{d}x \pm \int_0^{L_{\mathrm{x}}}\left[\cos 2k_{\mathrm{x}}x\right]\mathrm{d}x\right] \end{aligned} \qquad \text{(W1.48)}$$

Now the first integral is straightforward and the second integral is conveniently very small. We can see that this is so because the integral itself evaluates to somewhere between 1 and –1 as for any oscillating function, but the pre-factor $1/L_{\mathrm{x}}$ makes the integral extremely small for any reasonably large crystal. We thus write:

$$\begin{aligned} I_{\mathrm{A/B}} &= \frac{1}{L_{\mathrm{x}}}\left[\int_0^{L_{\mathrm{x}}}\mathrm{d}x \pm \int_0^{L_{\mathrm{x}}}\left[\cos 2k_{\mathrm{x}}x\right]\mathrm{d}x\right] \\ &= \frac{1}{L_{\mathrm{x}}}\left[\int_0^{L_{\mathrm{x}}}\mathrm{d}x \pm 0\right] \\ &= \frac{1}{L_{\mathrm{x}}}\left[L_{\mathrm{x}} \pm 0\right] \\ I_{\mathrm{A/B}} &= 1 \end{aligned} \qquad \text{(W1.49)}$$

So we conclude that these are indeed normalised wave functions.

Stage 2: Kinetic energy

We estimate the kinetic energy using the *kinetic energy operator*:

$$-\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right] \qquad \text{(W1.50)}$$

which can be written in one-dimension as:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \qquad \text{(W1.51)}$$

The kinetic energy is found by evaluating the expectation value of the kinetic energy operator :

$$KE_{\mathrm{A}} = \int_0^{L_{\mathrm{x}}} \Psi_{\mathrm{A}}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\Psi_{\mathrm{A}}^{*}\mathrm{d}x \qquad \text{(W1.52)}$$

$$KE_{\mathrm{A}} = \int_0^{L_{\mathrm{x}}} \sqrt{\frac{2}{L_{\mathrm{x}}}}\sin k_{\mathrm{x}}x\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\sqrt{\frac{2}{L_{\mathrm{x}}}}\sin k_{\mathrm{x}}x\,\mathrm{d}x \qquad \text{(W1.53)}$$

$$KE_{\mathrm{A}} = -\frac{\hbar^2}{2m}\frac{2}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \sin k_{\mathrm{x}}x\left[\frac{\partial^2}{\partial x^2}\right]\sin k_{\mathrm{x}}x\,\mathrm{d}x \qquad \text{(W1.54)}$$

Differentiating in two stages we find:

$$KE_{\mathrm{A}} = -\frac{\hbar^2}{2m}\frac{2}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \sin k_{\mathrm{x}}x\left[\frac{\partial}{\partial x}\right]k_{\mathrm{x}}\cos k_{\mathrm{x}}x\,\mathrm{d}x \qquad \text{(W1.55)}$$

and then:

$$KE_{\mathrm{A}} = -\frac{\hbar^2}{2m}\frac{2}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \sin k_{\mathrm{x}}x\left[-k_{\mathrm{x}}^2\right]\sin k_{\mathrm{x}}x\,\mathrm{d}x \qquad \text{(W1.56)}$$

which simplifies to:

$$KE_{\mathrm{A}} = \frac{\hbar^2 k_{\mathrm{x}}^2}{2m}\frac{2}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \sin^2 k_{\mathrm{x}}x\,\mathrm{d}x \qquad \text{(W1.57)}$$

Similarly we find for Ψ_{B} that:

$$KE_{\mathrm{B}} = \frac{\hbar^2 k_{\mathrm{x}}^2}{2m}\frac{2}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \cos^2 k_{\mathrm{x}}x\,\mathrm{d}x \qquad \text{(W1.58)}$$

and so in general we can write:

$$KE_{\mathrm{A/B}} = \frac{\hbar^2 k_{\mathrm{x}}^2}{2m}\frac{2}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \frac{1}{2}\left[1 \pm \cos 2k_{\mathrm{x}}x\right]\mathrm{d}x \qquad \text{(W1.59)}$$

As we saw in Equations W1.47 to W1.49, the integral evaluates to $L_{\mathrm{x}}/2$ and so we find:

$$KE_{\mathrm{A/B}} = \frac{\hbar^2 k_{\mathrm{x}}^2}{2m} \tag{W1.60}$$

which does not depend on the phase of the wave function (sine or cosine). Now let us consider the potential energy terms.

Stage 3: Potential energy

We estimate the potential energy of these wave functions in this cosine potential using the *potential energy operator* $V(\mathbf{r})$

$$PE_{\mathrm{A}} = \int_0^{L_{\mathrm{x}}} \Psi_{\mathrm{A}}^*\left[V(\mathbf{r})\right]\Psi_{\mathrm{A}}\,\mathrm{d}x \tag{W1.61}$$

which in one dimensions reduces to:

$$PE_{\mathrm{A}} = \int_0^{L_{\mathrm{x}}} \Psi_{\mathrm{A}}^*\left[V(x)\right]\Psi_{\mathrm{A}}\,\mathrm{d}x \tag{W1.62}$$

$$PE_{\mathrm{A}} = \int_0^{L_{\mathrm{x}}} \Psi_{\mathrm{A}}^*\left[V_{\mathrm{o}}\cos\left(\frac{2\pi x}{a}\right)\right]\Psi_{\mathrm{A}}\,\mathrm{d}x \tag{W1.63}$$

Substituting for Ψ_{A} we find:

$$PE_{\mathrm{A}} = \int_0^{L_{\mathrm{x}}} \sqrt{\frac{2}{L_{\mathrm{x}}}}\sin k_{\mathrm{x}}x\left[V_{\mathrm{o}}\cos\left(\frac{2\pi x}{a}\right)\right]\sqrt{\frac{2}{L_{\mathrm{x}}}}\sin k_{\mathrm{x}}x\,\mathrm{d}x \tag{W1.64}$$

$$\begin{aligned} PE_{\mathrm{A}} &= \frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \sin k_{\mathrm{x}}x\left[\cos\left(\frac{2\pi x}{a}\right)\right]\sin k_{\mathrm{x}}x\,\mathrm{d}x \\ &= \frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \sin^2 k_{\mathrm{x}}x\left[\cos\left(\frac{2\pi x}{a}\right)\right]\mathrm{d}x \end{aligned} \tag{W1.65}$$

Again we use the trick of writing $\sin^2$ in terms of the cosine of twice the angle to find:

$$PE_{\mathrm{A}} = \frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \frac{1}{2}\left[1-\cos 2k_{\mathrm{x}}x\right]\left[\cos\left(\frac{2\pi x}{a}\right)\right]\mathrm{d}x \tag{W1.66}$$

If we had started with wave function B we would have found

$$PE_{\mathrm{B}} = \frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \frac{1}{2}\left[1+\cos 2k_{\mathrm{x}}x\right]\left[\cos\left(\frac{2\pi x}{a}\right)\right]\mathrm{d}x \tag{W1.67}$$

and so in general we can write:

$$PE_{\mathrm{A/B}} = \frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \frac{1}{2}\left[1\pm\cos 2k_{\mathrm{x}}x\right]\left[\cos\left(\frac{2\pi x}{a}\right)\right]\mathrm{d}x \tag{W1.68}$$

Where Ψ_{A} corresponds to the lower option of the ± sign and Ψ_{B} corresponds to the upper option. Multiplying out this bracket yields:

$$\begin{aligned} PE_{\mathrm{A/B}} &= \frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \cos\left(\frac{2\pi x}{a}\right)\mathrm{d}x \\ &\quad \pm\frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \cos 2k_{\mathrm{x}}x\cos\left(\frac{2\pi x}{a}\right)\mathrm{d}x \end{aligned} \tag{W1.69}$$

which amounts to:

$$PE_{\mathrm{A/B}} = 0\pm\frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \cos 2k_{\mathrm{x}}x\cos\left(\frac{2\pi x}{a}\right)\mathrm{d}x \tag{W1.70}$$

Notice that the first integral in Equation W1.69 is zero because we are integrating over a function with period a, and L_{x} (the length of the crystal) is an integer number of unit cell spacings in length.

Now we arrive at an interesting integral. If k_{x} takes almost any value then the integral is zero for the same reason we just discussed. However, if k_{x} takes on the value $\pm\pi/a$, then the integral is not zero and we find:

$$PE_{\mathrm{A/B}} = \pm\frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \cos^2\left(\frac{2\pi x}{a}\right)\mathrm{d}x \tag{W1.71}$$

Which can be written in terms of the same trigonometric identity we discussed in Equation W1.45

$$PE_{\mathrm{A/B}} = \pm\frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \frac{1}{2}\left[1+\cos\left(\frac{4\pi x}{a}\right)\right]\mathrm{d}x \tag{W1.72}$$

$$\begin{aligned} PE_{\mathrm{A/B}} &= \pm\frac{V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}}\left[1\right]\mathrm{d}x \\ &\quad \pm\frac{2V_{\mathrm{o}}}{L_{\mathrm{x}}}\int_0^{L_{\mathrm{x}}} \frac{1}{2}\left[\cos\left(\frac{4\pi x}{a}\right)\right]\mathrm{d}x \end{aligned} \tag{W1.73}$$

Once again the second term is zero because it is a periodic function integrated over an integer number of periods and we find:

$$\begin{aligned} PE_{\mathrm{A/B}} &= \pm\frac{V_{\mathrm{o}}}{L_{\mathrm{x}}}\left[L_{\mathrm{x}}\right] \\ &= \pm V_{\mathrm{o}} \end{aligned} \qquad \text{(W1.74)}$$

or explicitly:

$$\begin{aligned} PE_{\mathrm{A}} &= -V_{\mathrm{o}} \\ PE_{\mathrm{B}} &= +V_{\mathrm{o}} \end{aligned} \qquad \text{(W1.75)}$$

Stage 4: Total energy: a more complete calculation

The results of our nearly-free electron calculation can be summarised as follows:

$$E_{\mathrm{A}}(k_{\mathrm{x}}) = \begin{cases} \dfrac{\hbar^2 k_{\mathrm{x}}^2}{2m_{\mathrm{e}}} & \text{if } k_{\mathrm{x}} \neq \pm\dfrac{\pi}{a} \\ \dfrac{\hbar^2 k_{\mathrm{x}}^2}{2m_{\mathrm{e}}} - V_{\mathrm{o}} & \text{if } k_{\mathrm{x}} = \pm\dfrac{\pi}{a} \end{cases} \qquad \text{(W1.76)}$$

$$E_{\mathrm{B}}(k_{\mathrm{x}}) = \begin{cases} \dfrac{\hbar^2 k_{\mathrm{x}}^2}{2m_{\mathrm{e}}} & \text{if } k_{\mathrm{x}} \neq \pm\dfrac{\pi}{a} \\ \dfrac{\hbar^2 k_{\mathrm{x}}^2}{2m_{\mathrm{e}}} + V_{\mathrm{o}} & \text{if } k_{\mathrm{x}} = \pm\dfrac{\pi}{a} \end{cases} \qquad \text{(W1.77)}$$

These equations indicate that energy is the same as for the free electron model, except when the wave vector is *exactly* $k_{\mathrm{x}} = \pm\pi/a$. The physical difference between the two cases *A* and *B*, and the significance of the special case when $k_{\mathrm{x}} = \pm\pi/a$, is illustrated in Figure W1.10 and described in the legend to the figure.

The result encapsulated in Equations W1.76 and W1.77 is interesting, but in fact is only approximately correct. It has been arrived using what is called *first-order perturbation theory.* A more accurate calculation (using, for example, *second-order perturbation theory*) would take account of the fact that in response to the potential $V(x)$ the wave functions change slightly from simple sine and cosine waves. Before we go on to see what second-order perturbation theory tells us, it is important to note again the key result of first order theory: it tells us that 'something happens' at $k_{\mathrm{x}} = \pm\pi/a$. Those with a keen memory will recall that this exactly at the *Brillioun zone boundary.*

Second-order results

The results of the second-order calculation are in some ways only slightly different from the first-order calculation, but they will change the way we think about electrons in solids profoundly. The second-order calculation takes account of the fact that wave functions are composed of linear superpositions of sine and cosine wave functions. For most values of k_{x} the sine and cosine functions are degenerate (i.e. have the same energy), just as we calculated in first order theory. Because of the degeneracy, the actual wave functions are composed of equal amounts of sine and cosine functions. However, near the *Brillioun zone boundary*, the sine and cosine functions are no longer degenerate (as revealed by the first-order calculation) and the actual wave functions are composed of primarily *either* sine *or* cosine functions. The effects are twofold:

- The energy of all the states is slightly lowered. We will neglect this small change in what follows.
- The energy of states *close to* $k_{\mathrm{x}} = \pm\pi/a$ is affected in a manner similar to the way in which states with *exactly* $k_{\mathrm{x}} = \pm\pi/a$ were affected in the first-order calculation.

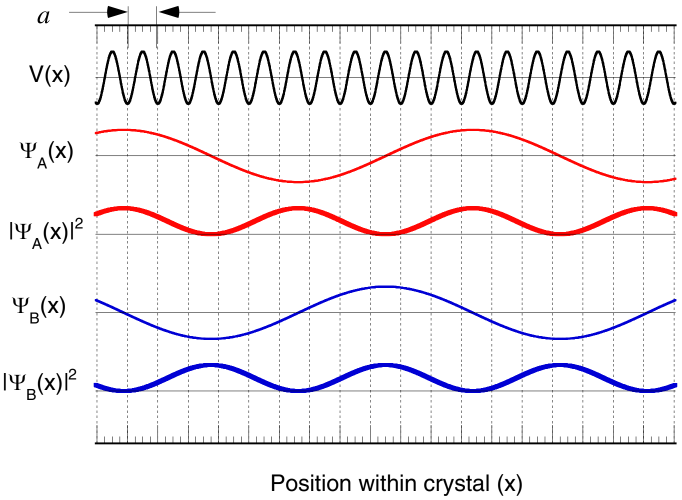
These results are graphed in Figure W1.11. Now we see that the potential has introduced a gap (known as a *band gap* or *energy gap*) in the spectrum of possible electron energies. This is the key result of this nearly-free electron analysis and the result is quite general. It tells us that if we consider the amount of energy required to move an electron from one quantum state to another, then normally this quantity is infinitesimally small. However if we consider quantum states on two sides of a Brillioun zone boundary then:

- To cross the Brillioun zone boundary associated with a potential $V_{\mathrm{o}}\cos(2\pi x/a)$we must provide an additional $2V_{\mathrm{o}}$ of energy.

Before we can see why this is so important, we need to take two more steps: we need to see the effect of a more realistic potential, and then we need to consider the effect of a periodic potential in more than one dimension.

Figure W1.10 Illustration of the meaning of the results of the nearly-free electron calculation summarised in Equations W1.76 and W1.77

(a) The top curve shows the cosine potential (Equation W1.38) which has the periodicity of the lattice (*a*). We imagine that the minima of the potential correspond to the atomic positions. The lower curves show the wave functions and charge densities associated with solutions A and B (Equation W1.39 and W1.40) when the wave vector is small, far away from a Brillioun zone boundary. The example shown corresponds to k ≈ 0.17 π/a. Notice that in this case the charge density is large in some unit cells and small in others. On average this causes the perturbation to the energy of the both states A and B to remain nearly unaffected by the potential.



(b) This is the equivalent graph to (a) for the case where k ≈ π/a. Notice that now (in contrast with the case in (a)) the charge density for each solution A or B is exactly the same in every unit cell of the crystal. The detailed nature of the functions are shown for a single unit cell in (c). In case A the charge density in every unit cell is concentrated in the region of lowest potential, and so this solution has lower energy than case B, where the charge density in every unit cell is concentrated in the region of highest potential.

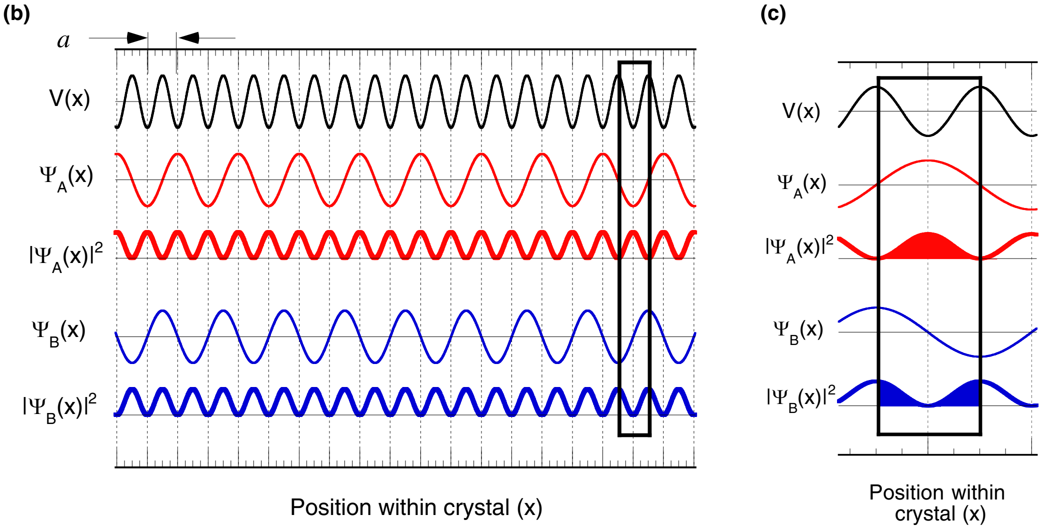
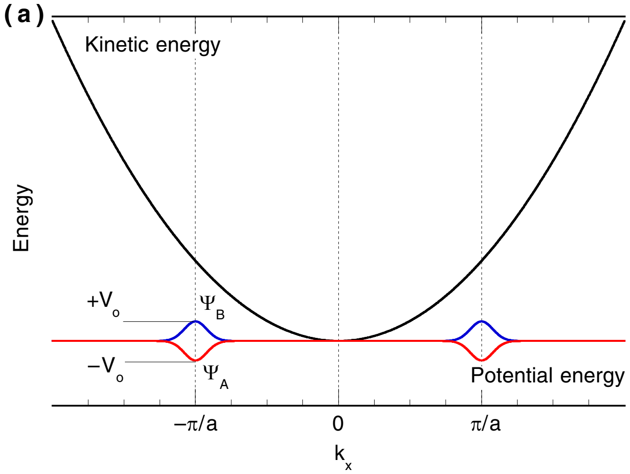
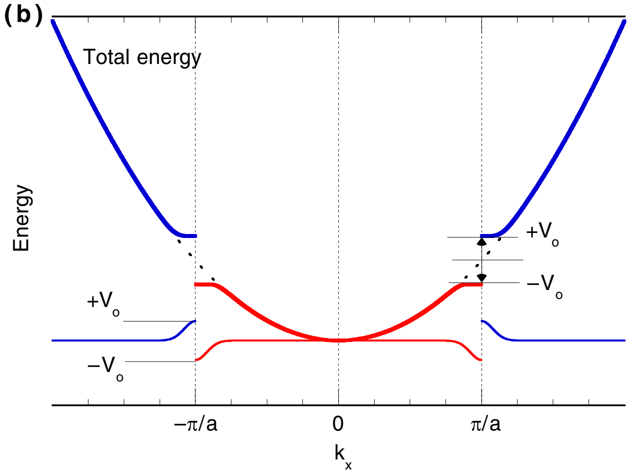


Figure W1.11 Illustration of the effect of a weak periodic potential on the one-dimensional *E*(*k*).

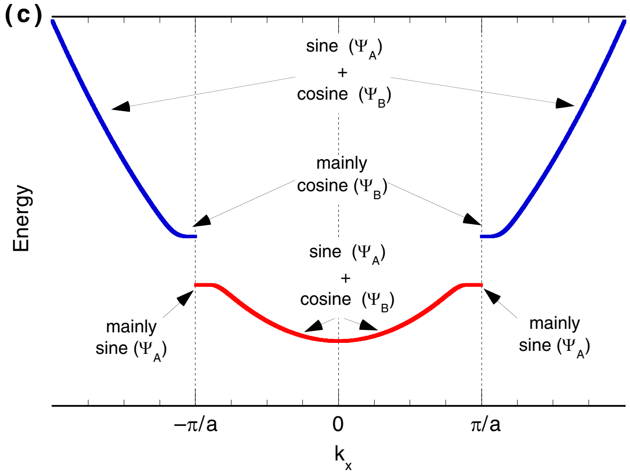
(a) The free electron parabola (corresponding to the kinetic energy of an electron) is shown along with the potential energy contributions for each solution A and B (Equation W1.39 and W1.40).



(b) The result of the correct calculation of the energy is shown together with the free electron parabola (dotted). In this calculation, the composition of the wave functions changes across the curve.



(c) In the parts of the curve which are 'free-electron-like', the wave functions are composed of equal amounts of sine and cosine functions. However, near the Brillioun zone boundary, the functions are *either* like or sine *or* cosine functions.



Making the potential more realistic

Does the nearly-free electron model allow us to use a 'model' potential closer to the 'actual' potential? Fortunately, the answer to this is 'Yes'. To do this we write the potential as a *Fourier sum* of cosine (and sine) terms. For example, consider the one dimensional potential:

$$V(x) = V_o \cos\left(\frac{2\pi x}{a}\right) + V_1 \cos\left(\frac{6\pi x}{a}\right) \quad \text{(W1.78)}$$

This potential (Figure W1.12) is more 'pointed' than the simple sinusoidal potential and represents at least a step towards the atomic potentials shown on the bottom of Figure W1.8.

The first thing to notice about Equation W1.78 is that the new wave vector we have added ($k = 6\pi/a$) belongs to the reciprocal lattice. In fact, as we synthesise the new potential, we can only include wave vectors which have the same periodicity as the lattice i.e. those which belong to the reciprocal lattice.

$$V(x) = \sum_{n=1,2\ldots} V_n \cos\left(\frac{[2n+1]2\pi x}{a}\right) \quad \text{(W1.79)}$$

Now, in the same way that the main component of the potential ($k = 2\pi/a$) only affects the energy of the quantum states with wave vectors ($k = \pm\pi/a$), so the additional component ($k = 6\pi/a$) only affects the energy of the quantum states with wave vectors ($k = \pm 3\pi/a$). (These bisectors of the successive reciprocal lattice vector are known as the second, third, fourth etc. *Brillioun zone boundaries*.) This result dramatically simplifies our analysis.

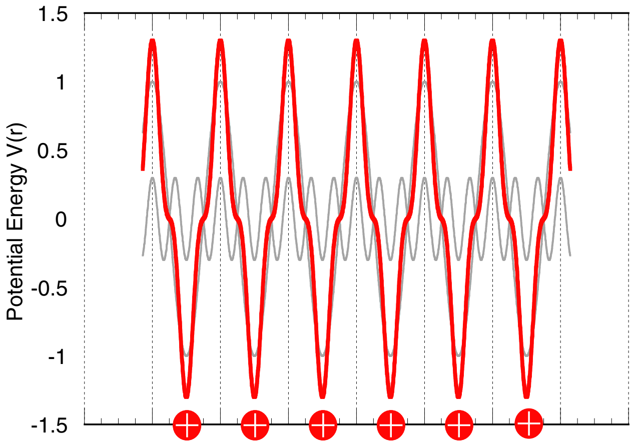
In metals, electrons only occupy quantum states with wave-vectors less than (or of the order of) k_F. So, if k_F is less than (for example) $3\pi/a$, then (in this analysis) we can simply ignore the effect of the higher order components of the potential. In other words, no matter how complex the potential energy curve, (in the nearly-free electron approximation) it will simply make no difference to the energy of the quantum states. This remains true as long as the components of the potential are not too large.

Potassium

Recall that for potassium, k_F was small enough that there were no occupied states in the region of the Brillioun zone boundary (Equation W1.33, Figure W1.7), i.e. $k_F < \pm\pi/a$. So now we can understand why the free-electron theory gave such anomalously good predictions of the basic electronic properties of potassium. Because the occupied quantum states have wave vectors smaller than even the first Brillioun Zone boundary, there is no component of the electronic potential that affects their energy. Another way of stating this is to say that the *wavelengths* of the occupied electron wave functions are all *so long* that the details of the potential are effectively averaged across many unit cells. This is exactly the result illustrated in Figure W1.10

Figure W1.12 Illustration of the potential in Equation W1.78 for the case when $V_1 = 0.3\ V_o$. The two 'component' potentials are shown in grey and their sum is shown bold. Also shown are positions of the ion cores.

The sum potential has a little more of the character of the sharp potential seen in Figure W1.8.



Moving to more than one dimension

Two-dimensions

It is only when we consider a hypothetical two-dimensional crystal that we can appreciate fully how the nearly-free electron model allows us to describe a much richer variety of physics than does the free-electron model. Remember that the free-electron model describes a substance which is a metal. The nearly-free electron model allows us to describe a material which can be either a metal or an insulator depending on the strength of the interaction V_o.

Consider a two-dimensional square lattice with an 'egg box' potential:

$$V(x,y) = V_o \cos[2\pi x / a]\cos[2\pi y / a] \quad \text{(W1.80)}$$

This is illustrated in Figure W1.13. The variation of energy across the first Brillioun zone of the reciprocal lattice for this two-dimensional lattice is shown in Figure W1.14. Notice that the distance from the origin to the boundary of the first Brillioun zone does not have a unique value.

- If one considers the quantum states of electrons travelling in the x- or y-directions i.e. $\mathbf{k} = (k, 0)$ or $\mathbf{k} = (0, k)$ then one reaches the Brillioun zone boundary at the point where $k = \pi/a$. At this point the energy of the quantum state is approximately

$$\frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2 (\pi/a)^2}{2m_e}$$

- If one considers quantum states of electrons travelling in between the x- and y-directions i.e. $\mathbf{k} = (k, k)$ then one reaches the Brillioun zone boundary at the point where $k = \sqrt{2}\pi / a$. At this point the energy of the quantum state is approximately.

$$2 \times \frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2 \left(\sqrt{2}\pi/a\right)^2}{2m_e}$$

Figure W1.13 The two dimensional 'egg-box' potential

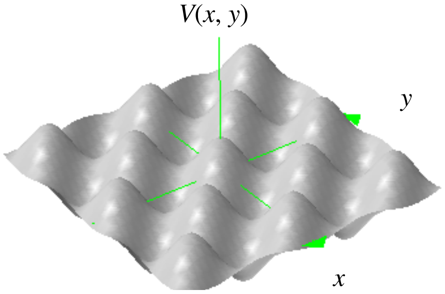


Figure W1.15 shows how the energy varies as one proceeds from the origin along lines joining the origin to the point (0, π/a) and to the point (π/a, π/a). Notice that the magnitude of the parameter V_o in Equation 1.80 now becomes very important.

- If V_o is large compared with the maximum energy of a quantum state in the first Brillioun zone, then *all* the quantum states in the second Brillioun Zone will have energies higher than *any* quantum state in the first Brillioun Zone. In this situation there is what is known as a *band gap* between states in the two zones.
- However, if V_o is small compared with the maximum energy of a quantum state in the first Brillioun zone, then *some* of the quantum states in the *second* Brillioun Zone will have energies lower than *some* quantum states in the *first* Brillioun Zone. In this situation there is said to be *band overlap* between states in the two zones.

The significance of this comes when we imagine populating the quantum states.

Populating the quantum states

One electron per lattice site

In Section W1.1.4 we saw that the Brillioun zone contains enough quantum states for exactly two electrons per lattice site in the crystal. So if we consider the case of a monovalent substance which donates one electron per atom to the electron gas then the first zone will always be large enough to accommodate all the electrons. There will then always be regions where the highest-energy *occupied* quantum states have empty quantum states *immediately* above them.

This is illustrated for the two dimensional case in Figure W1.14. In two dimensions, donating one electron per lattice site corresponds to filling half the *area* of the zone. It is clear from the figure that even if $E(\mathbf{k})$ was such that the occupied states reached the zone boundary, there would always be occupied states with adjacent empty states. Thus an excitation of the electron system (thermal or electrical) would allow electrons to move into unoccupied states with infinitesimal expenditure of energy. This describes a substance that we would call a metal.

Two electrons per lattice site

If a material donates exactly two electrons per lattice site in the crystal, then the situation is more complex. The properties of the resulting substance then depend on the magnitude of the perturbation parameter V_o.

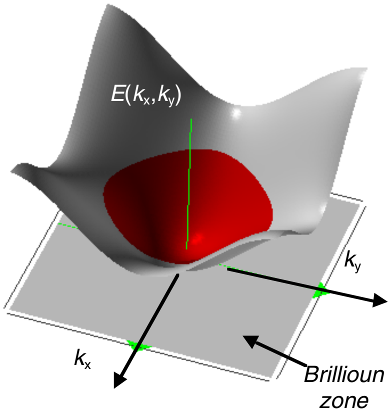
If V_o is large, then the lowest energy states in the second Brillioun zone have energies which are greater than the highest energy state in the first Brillioun zone. In this case, all the states in the first Brillioun zone will be occupied and all the states in the second Brillioun zone will be empty. We say that such a substance has a *band gap*. This case is illustrated in Figure W1.15(a), (b) and (c).

We cannot tell much about this material from its $E(\mathbf{k})$ relationship until we draw in the Fermi Energy. At T = 0, this has an energy half way between the last occupied level and the next unoccupied level. Drawing on the Fermi energy for the case of two electrons per quantum state, we can see that a material such as this would not be a metal, but an insulator.

To appreciate this, consider how an electron in a state in the first Brillioun zone could respond to an applied electric field. In order to respond, it would need to move into an empty quantum state, and the only empty states are in the second Brillioun zone. In order to move into this empty state it would therefore need $\approx 2V_0$ of energy. If we consider the case where V_0 is of the order a few electron volts, then such large energies are extremely unlikely to be available from thermal sources. Thus, such a substance would be an electrical insulator. (§7.7.4 to §7.7.9)

If V_o is small, then the lowest energy states in the second Brillioun zone have energies which are *less than* the highest energy state in the first Brillioun zone. In this case, most, *but not all* the states in the first Brillioun zone will be occupied and most, *but not all* the states in the second Brillioun zone will be empty. We say that such a substance has a *band overlap*. This case is illustrated in Figures W1.15(d) (e) and (f). A material such as this would still be a metal, but probably with a lower conductivity than a monovalent metal.

Figure W1.14 Illustration of the occupancy of quantum states. The figure shows a two dimensional $E(\mathbf{k})$ relation (grey) with occupied states (dark) corresponding to approximately half the area of the Brillioun zone. Note that the highest energy occupied states have adjacent empty states into which they can be easily excited.



To understand this, notice that if the bands only just overlap, although there are a large number of occupied states in the first zone, few of these occupied states have adjacent empty states. Similarly, there are very few occupied states in the second zone. Thus if an electric field were applied to this material, a relatively small number of electrons would be able to change quantum state in response to the field. The precise number would depended on precisely the extent of the overlap between the bands. Such a material might be called a metal if the overlap were quite large, or a *semimetal* if the overlap were small.

Summary of nearly-free electron model

Before moving on to ever more complex models of materials, it is worth pausing to summarise what we are the achievements and limitations of the nearly-free electron model.

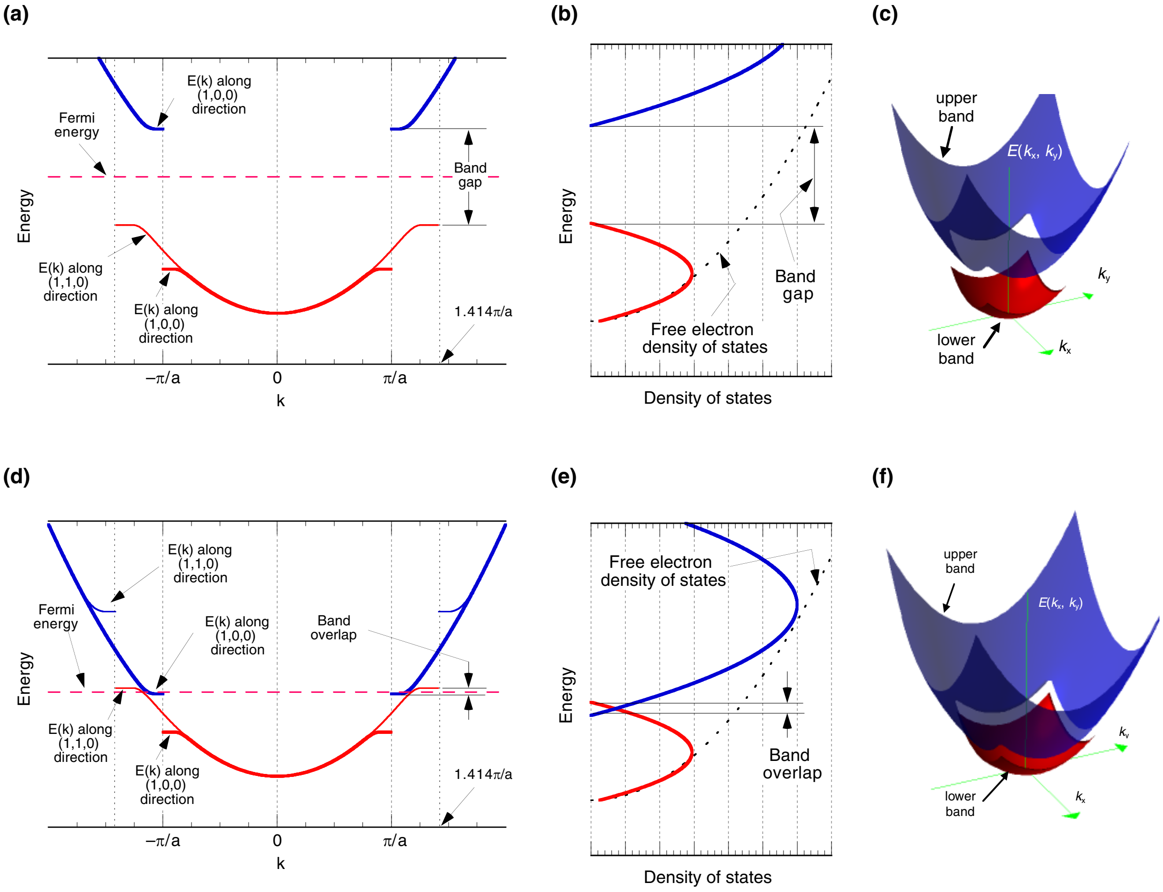
Achievements

The most impressive achievement of this model is that, in a relatively simple way, it allows us to describe an electronic structure which can exhibit *either* metallic *or* insulating properties. Just by altering the strength of the parameter V_0 and the filling of the quantum states, we can describe materials which are either metals, semi-metals or insulators.

Limitations

The main limitation of the nearly-free electron model is that it is (fairly obviously) not very realistic! It is useful pedagogically, and it can also be used to describe *some* simple states in *some* metals. However for the most part, the quantum states that solve the Schrödinger equation in real metals are simply not at all like plane waves (or simple sums of plane waves). The nearly-free electron model can be useful when the kinetic energy derived from the regions *in between* the ion cores dominates the kinetic and potential energy derived from the regions *close to* the ion cores. This is most commonly true for states derived from valence states in atoms, and *s*-states in particular. The bands produced in this approach are all broad, and perturbed from their parabolic form only at the Brillouin zone boundaries.

Figure W1.15 Illustration of the results of two-dimensional, nearly-free electron calculation for the case of two electrons per lattice site. (a) (b) and (c) correspond to the case when V_0 is large and (d) (e) and (f) to the case when V_0 is small. (a) and (d) show the structure of E(k) along k,0,0 and k,k,0 directions (b) and (e) show the resulting density of states. Notice that in (b) the density of states at the Fermi energy is zero which is indicative of insulator. (c) and (f) show three dimensional views of the band structure in the two bands



The nearly-free electron approximation is *not* applicable to electronic states derived from *p*-, *d*- and *f*- orbitals because for these states the bulk of the contribution to the energy comes from the region close to the ion cores. To describe such states we need to use the so-called *tight-binding model*.

Change in the meaning of *k*

Before moving onto the tight-binding model, we should note that there has been one development in the nearly-free electron model to which I have not specifically drawn your attention. This is that the meaning of the term of term **k** has changed.

In the free electron discussion, the wave functions were plane waves (cosine and sine), and **k** was their wave vector. In the nearly-free electron discussion we have continued to use **k** to label the quantum states but now the wave functions are no longer pure sine and cosine waves. Recall that when we described the effect of a weak periodic potential, we noted that wave functions which solved the Schrödinger equation were no longer simple sine and cosine waves. However, we kept the label **k** because as long as the potential was not too large, the wave functions could be fairly described as being a superposition of:

- *mainly* sine or cosine waves with wave vector **k**, plus
- some other parts which we did not describe in detail.

It is not difficult to see that if the perturbing potential became too large then the solutions to the Schrödinger equation would become quite distorted and not at all well-described by a wave vector **k**. You might think then that the meaning of **k** would have been lost, but surprisingly this is not so. To see why this is so requires you to read even the following section on the tight-binding theory of solids, but I am sure you were going to do that anyway.

W1.5 Tight-binding theory

Introduction

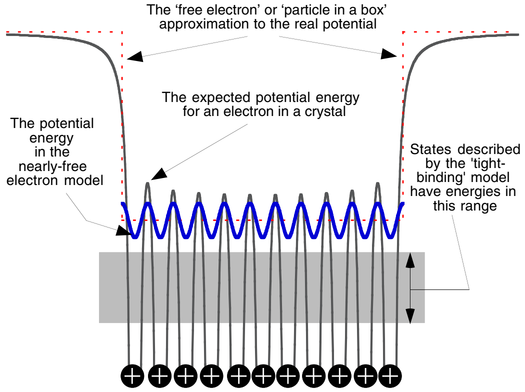
The *tight-binding theory* of electronic states in solids starts from the premise that the quantum states within a solid are similar to those states which exist on isolated atoms.

- For so-called *core states* deep within an atom this is certainly true: for these states the intense electric field of the 'parent' nucleus is much greater than the electric field due to other atoms in a solid.
- In contrast, for the electrons in states deriving from valence *s*-states this is probably *not* a very good description.

The tight-binding theory is relevant to states that fall in between these two extremes. These are typically states such as *p*- and *d*- valence states.

Such states are quite complicated even when they are based on a single isolated atom. In the tight-binding theory, however we wish to examine the effects that occur when electrons occupying such complicated states are brought close to each other, as occurs with neighbouring atoms in a solid. This may sound tremendously difficult (and its not easy!), but our task is made much easier by appreciating the results of *Bloch's theorem*.

Figure W1.16 The range of energies in which tight-binding solutions to the Schrödinger equation are reasonable. (See also Figure W1.8)



Bloch's theorem

Bloch's theorem tells us that any solution to the Schrödinger equation in a *periodic potential* has to have a rather simple form. More precisely Bloch's theorem states that:

- in a Bravais lattice: i.e. in a lattice where any lattice site can be reached at from any other lattice site by integer multiple steps of three basic lattice vectors:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \qquad \text{(W1.81)}$$

- in the independent electron approximation i.e. in the approximation that electrons do not interact strongly with each other. This is not really a good approximation, but for a number of complex reasons, it often gives acceptable results

then the electron wave functions may *always* be written as a product of two parts:

- A plane wave;

$$\exp(i\mathbf{k}\cdot\mathbf{r}) \qquad \text{(W1.82)}$$

- A function $u_\mathrm{n}(\mathbf{k},\mathbf{r})$ with the periodicity of the lattice i.e.

$$u_\mathrm{n}(\mathbf{k},\mathbf{r}) = u_\mathrm{n}(\mathbf{k},\mathbf{r}+\mathbf{R}) \qquad \text{(W1.83)}$$

where **R** is a Bravais lattice vector and *n* is a so-called *band index*. So, subject to the approximations above, Bloch's theorem states that electron wave functions in a lattice may always be written as the product of Equations W1.82 and W1.83 i.e.:

$$\Psi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r}) \times u_\mathrm{n}(\mathbf{k},\mathbf{r}) \qquad \text{(W1.84)}$$

Functions of this type are called *Bloch functions*. We should note that Bloch functions solutions are explicitly *not appropriate* in quite a few common situations. For example:

- near impurities in a lattice,
- in random alloys,
- in amorphous materials,
- near surfaces of otherwise periodic crystals.

In these situations Bloch's theorem does not apply, and the nature of the electronic states becomes more difficult to calculate. So on the whole

Bloch's theorem should be considered as a 'good thing'. Figure W1.17 illustrates graphically the simple truths of Bloch's theorem.

Tight binding

The wave functions of electrons in isolated atoms, $\chi(\mathbf{r})$, are calculated by solving the Schrödinger equation for electrons in the potential of :

- all the other electrons on an atom, and
- the nuclear charge.

The single electron (i.e. the hydrogenic) solutions ignore other electrons except in the crudest sense. These solutions are the familiar set of $1s$, $2s$, $2p$ etc. functions. In complicated many-electron atoms, the wave functions are more complicated, but are often qualitatively similar to the hydrogenic wave functions. Pictorial representations of these functions can be found at the web site for this book (`www.physicsofmatter.com`) and, no doubt, in several other places.

In a solid, the potential the electrons experience can be considered as being equal to the sum of

- the original atomic potential *plus*
- an extra contribution from the surrounding atoms.

In the tight-binding approximation, we assume that this extra potential is relatively small compared to the atomic potential. We then assume that the wave functions can be described by Bloch functions that are simply linear combinations of atomic orbitals from *different* atomic sites. Using this approach we can approximate the effect of the crystalline environment on electronic states that are too deep in the atomic potential for the nearly-free electron approximation to be valid. Perhaps surprisingly, such states again give rise to bands. To see how, we will proceed as follows:

- First, we will make an educated guess for a wave function which should (at least approximately) solve the Schrödinger equation. We know that this function must have the general form of a Bloch function.
- Second we will work out how the energy of the wave function depends on **k**.

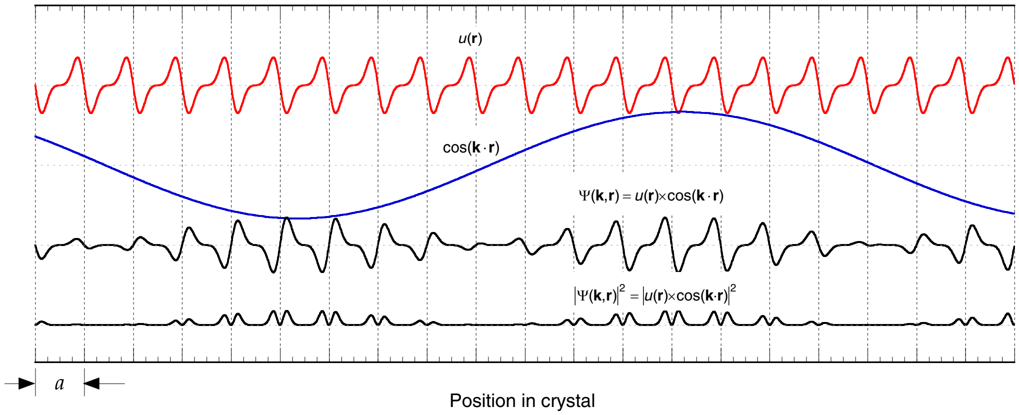
Constructing the wave function

The exact Schrödinger equation for the atomic orbital $\chi(\mathbf{r})$ in an isolated atom is:

$$-\frac{\hbar^2}{2m_{\mathrm{e}}}\chi(\mathbf{r})+V_{\mathrm{atomic}}\chi(\mathbf{r})=E_{\mathrm{atomic}}\chi(\mathbf{r}) \qquad \text{(W1.85)}$$

where E_{atomic} is the energy of the state $\chi(\mathbf{r})$. We take the function $u_{\mathrm{n}}(\mathbf{k},\mathbf{r})$ to be the same as the

Figure W1.17 Illustration of the nature of states in a periodic lattice. The figure shows a function u(**r**) which has the same periodicity as the lattice and a modulation factor with wave vector k ≈ 0.125 π/a. Below these is plotted the Bloch function which is the result of multiplying the two together. At the bottom of the figure is shown the charge density which would be associated with such a wave function. **Note**: I have assumed that the atomic wave functions are entirely real and shown only the real component of the modulation factor and the resulting real components of the wave functions.



isolated atom wave function $\chi(\mathbf{r})$. This is a simple choice for $u_n(\mathbf{k},r)$ in that it has no dependence on **k**. We then construct our approximate solution to the Schrödinger equation for the crystal by adding together the atomic wave functions on neighbouring sites as follows:

$$\Psi(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{R}} \exp(i\mathbf{k}\cdot\mathbf{R})\chi(\mathbf{r}-\mathbf{R}) \quad \text{(W1.86)}$$

This function is illustrated in Figure W1.18.

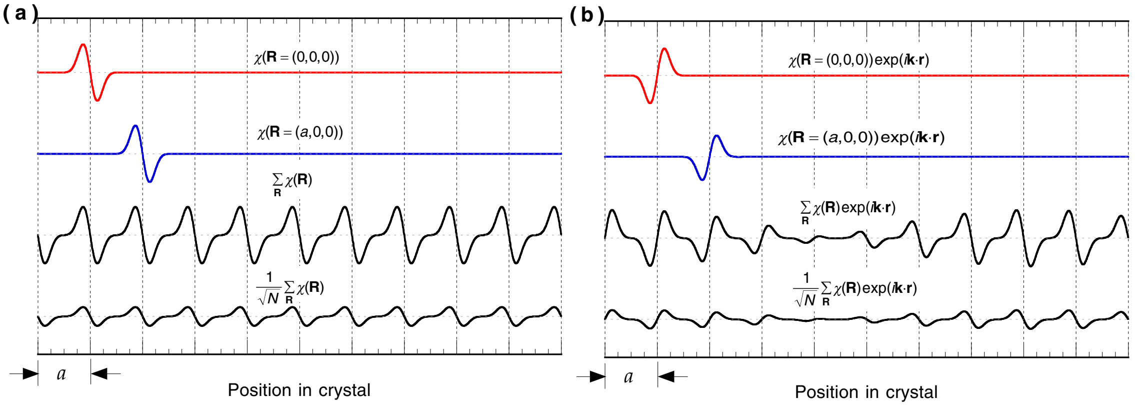
Calculating *E*(*k*): Where do the 'bands' come from?

Now we need to solve the Schrödinger equation using the wave function in Equation W1.86. When we do this we will see explicitly how its energy depends on the **k** We proceed as we did in the nearly-free electron case i.e. we evaluate the expectation value for the *total energy* using the wave function we have just defined.

- **In the NFE case** our wave functions were plane waves and their unperturbed energy depended strongly on **k**. The perturbation to the free electron case was a weak periodic potential. The effect of the perturbation in first order was to add a *potential energy* to electrons occupying quantum states with wave vectors **k** close to a Brillouin zone boundary.
- **In the tight binding case** the wave functions are linear superpositions of atomic wave functions added together with a phase shift exp(***i*****k.r**) between the functions on neighbouring sites. If these Bloch functions are constructed for atoms which are far apart, then their energy does not depend upon the phase shift (i.e. upon **k**) and their energy is just given by E_{atomic}, the energy of the atomic state upon which the Bloch function is based. The perturbation to the atomic case is that when the atoms are close together (as in a crystal), the potential is no longer $V_{\text{atomic,}}$ because the atoms at neighbouring sites have affected the potential energy. The effect of this perturbation (in first order) is to introduce a dependence of the energy on the phase shift between neighbouring sites. The magnitude of this dependence is proportional to:
  - the extent of the *overlap* of wave functions on adjacent sites, and
  - the extent to which (in the region of wave functions overlap), the potential differs from the free atom potential energy.

This dependence on the phase shift is essentially a *kinetic energy* term associated, not with motion around an atom, but with motion *between* atoms i.e. with motion through the lattice.

Figure W1.18 Illustration of the way in which atomic wave functions centred on different sites are added together to make functions which have the form of Bloch functions (Equation W1.84). Recall that it is known (from Bloch's theorem) that solutions to the Schrödinger equation in a periodic potential *must* have this form. (a) Two atomic wave functions χ have the same shape, but are centred on different sites within the crystal. Also shown is the summation of all such atomic functions, and the normalised summation which accommodates just one electron. (b) This figure is similar (a) but includes additionally the effect of the phase shift between neighbouring atomic functions. **Note**: To simplify the presentation I have assumed that the atomic wave functions are entirely real and I have shown only the real component of the modulation factor and the resulting real components of the wave functions.



Calculating E(k).

So let us begin our total energy calculation. The kinetic energy (*KE*) operator is:

$$-\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right] \quad \text{(W1.87)}$$

and the potential energy operator is:

$$V_{\text{crystal}}(\mathbf{r}) = V_{\text{atomic}}(\mathbf{r}) + \Delta V(\mathbf{r}) \qquad \text{(W1.88)}$$

Notice that we have written the potential energy as the sum of two terms, where the term $\Delta V(\mathbf{r})$ is the *additional potential* which an electron experiences as a result of being in the crystal (Figure W1.19 (a)). Numerically this is usually negative because the potential energy of the valence electrons is generally lower in a solid.

Now we use some intelligence: notice that as a first approximation the sum of the kinetic energy and potential energy terms deriving from the *atomic* potential will just result in E_{atomic}, the energy of the unperturbed atomic state. We are interested in the difference between:

- the energy of the state in an isolated atom, and
- the energy of the state in the crystal.

This difference depends mainly on $\Delta V(\mathbf{r})$, the difference between the potential energy in these two situations. So we may evaluate the total energy as:

$$\begin{aligned}
E &= \int_{\text{all space}} \Psi^*\left[KE + V_{\text{crystal}}(\mathbf{r})\right]\Psi \mathrm{d}\mathbf{r} \\
E &= \int_{\text{all space}} \Psi^*\left[\underbrace{KE + V_{\text{atomic}}(\mathbf{r})}_{E_{\text{atomic}}} + \Delta V(\mathbf{r})\right]\Psi \mathrm{d}\mathbf{r} \\
E &= \int_{\text{all space}} \Psi^*\left[E_{\text{atomic}} + \Delta V(\mathbf{r})\right]\Psi \mathrm{d}\mathbf{r} \\
E &= E_{\text{atomic}} + \int_{\textit{all space}} \Psi^* \Delta V(\mathbf{r})\Psi \mathrm{d}\mathbf{r}
\end{aligned} \qquad \text{(W1.89)}$$

The final term in the last of Equations W1.89 makes clear the nature of the perturbation that we need to evaluate. It involves the term $\Delta V(\mathbf{r})$ and our constructed wave function. Now we recall that our wave function (and its complex conjugate) is written as:

$$\begin{aligned}
\Psi(\mathbf{k},\mathbf{r}) &= \frac{1}{\sqrt{N}}\sum_{\mathbf{R}} \exp(i\mathbf{k}\cdot\mathbf{R})\chi(\mathbf{r}-\mathbf{R}) \\
\Psi^*(\mathbf{k},\mathbf{r}) &= \frac{1}{\sqrt{N}}\sum_{\mathbf{R}'} \exp(-i\mathbf{k}\cdot\mathbf{R}')\chi^*(\mathbf{r}-\mathbf{R}')
\end{aligned} \qquad \text{(W1.90)}$$

Substituting for this in the expression for the total energy yields an expression which looks very complicated:

$$\begin{aligned}
E = E_{\text{atomic}} &+ \\
&\frac{1}{N}\sum_{\mathbf{R}'}\sum_{\mathbf{R}} \exp(i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}'))\times \\
&\int_{\textit{all space}} \chi^*(\mathbf{r}-\mathbf{R}')\Delta V(\mathbf{r})\chi(\mathbf{r}-\mathbf{R})
\end{aligned} \qquad \text{(W1.91)}$$

However, the double summation make things look much more complicated than they really are. We note that for each chosen value of **R'**, the sum over **R** has the same value (because each lattice site **R'** in a crystal is equivalent to any other). So we can just evaluate the sum for **R'** = **0**,.and then multiply the answer by *N*, the number of unit cells in the crystal. We can then replace one of the summations by a factor *N* which we can subsequently cancel:

$$\begin{aligned}
E = E_{\text{atomic}} &+ \frac{1}{N} N \sum_{\mathbf{R}} \exp(i\mathbf{k}\cdot\mathbf{R})\times \\
&\int_{\textit{all space}} \chi^*(\mathbf{r}-\mathbf{R}')\Delta V(\mathbf{r})\chi(\mathbf{r}-\mathbf{R})
\end{aligned} \qquad \text{(W1.92)}$$

$$\begin{aligned}
E = E_{\text{atomic}} &+ \sum_{\mathbf{R}} \exp(i\mathbf{k}\cdot\mathbf{R})\times \\
&\int_{\textit{all space}} \chi^*(\mathbf{r}-\mathbf{R}')\Delta V(\mathbf{r})\chi(\mathbf{r}-\mathbf{R})
\end{aligned} \qquad \text{(W1.93)}$$

We can now write this integral in a more compact form and look at the origin of each of the terms:

$$E(\mathbf{k}) = E_{\text{atomic}} + \sum_{\mathbf{R}} \exp(i\mathbf{k}\cdot\mathbf{R})A(\mathbf{R}) \qquad \text{(W1.94)}$$

where $A(\mathbf{R})$ is given by:

$$A(\mathbf{R}) = \int \chi^*(\mathbf{r})\Delta V(\mathbf{r})\chi(\mathbf{r}-\mathbf{R})\mathrm{d}\mathbf{r} \qquad \text{(W1.95)}$$

Let us look at more closely at the integral $A(\mathbf{R})$. It involves the 'overlap' between the atomic wave functions centred at $\mathbf{R} = \mathbf{0}$ and at $\mathbf{R}$. Notice that $A(\mathbf{R})$ is a function only of the overlap of wave functions on neighbouring sites. So it is a function of $\mathbf{R}$, but not of $\mathbf{r}$. So for the overlap of:

- any particular orbital, at
- a particular separation between atoms, and
- with a given change in potential.

$A(\mathbf{R})$ simply has a value in units of energy, typically a few electron volts. So our expression for the energy becomes

$$E(\mathbf{k}) = E_{\text{atomic}} + \sum_{\mathbf{R}} A(\mathbf{R}) \exp(i\mathbf{k}\cdot\mathbf{R}) \qquad \text{(W1.96)}$$

where the sum is over all the lattice sites in the crystal. Now this expression looks a whole lot simpler than Equation W1.91. In fact we can clarify matters a little further by noticing that one term in the summation of Equation W1.96 is generally much larger than all the rest. The case when $\mathbf{R} = \mathbf{0}$ involves the 'overlap' between an orbital and itself. This is generally much larger than the overlap between functions on neighbouring sites when $\mathbf{R} \neq \mathbf{0}$ (Figure W1.19 (b)). We thus consider these two cases separately:

$$\alpha = A(\mathbf{0}) = \int \underbrace{\chi^*(\mathbf{r})}_{\substack{\textit{atomic}\\ \textit{wavefunction}\\ \textit{at site } \mathbf{R}=0}} \quad \Delta V(\mathbf{r}) \quad \underbrace{\chi(\mathbf{r})}_{\substack{\textit{atomic}\\ \textit{wavefunction}\\ \textit{at site } \mathbf{R}=0}} \quad d\mathbf{r} \qquad \text{(W1.97)}$$

$$A(\mathbf{R}) = \int \underbrace{\chi^*(\mathbf{r})}_{\substack{\textit{atomic}\\ \textit{wavefunction}\\ \textit{at site } \mathbf{R}=0}} \quad \Delta V(\mathbf{r}) \underbrace{\chi(\mathbf{r}-\mathbf{R})}_{\substack{\textit{atomic}\\ \textit{wavefunction}\\ \textit{at site } \mathbf{R}\neq 0}} d\mathbf{r} \qquad \text{(W1.98)}$$

Using this new terminology our expression for the energy becomes:

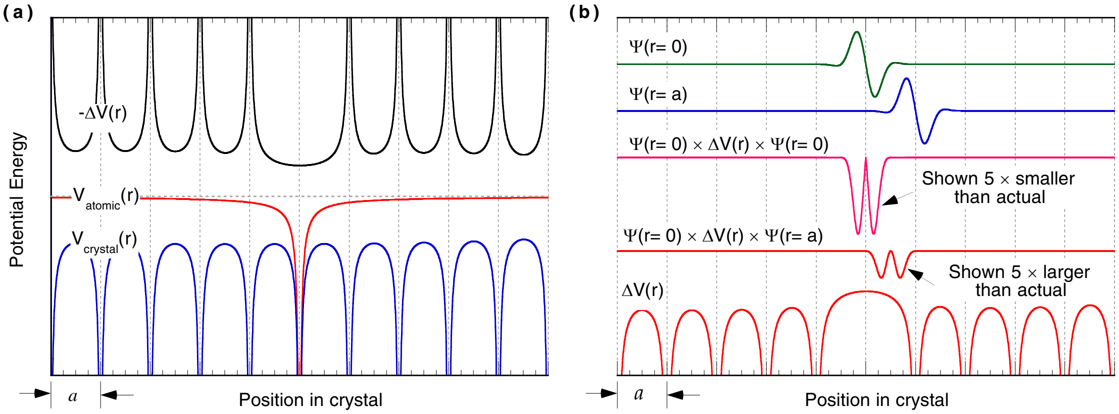
$$E(\mathbf{k}) = E_{\text{atomic}} + A(\mathbf{R}=\mathbf{0}) \exp(i\mathbf{k}\cdot 0) + \sum_{\mathbf{R}\neq\mathbf{0}} A(\mathbf{R}) \exp(i\mathbf{k}\cdot\mathbf{R})$$

$$E(\mathbf{k}) = E_{\text{atomic}} + A(\mathbf{R}=\mathbf{0}) + \sum_{\mathbf{R}\neq\mathbf{0}} A(\mathbf{R}) \exp(i\mathbf{k}\cdot\mathbf{R})$$

$$E(\mathbf{k}) = \underbrace{E_{\text{atomic}}}_{\substack{\textit{The energy}\\ \textit{of the}\\ \textit{original}\\ \textit{atomic}\\ \textit{orbital}}} + \underbrace{\alpha}_{\substack{\textit{The change}\\ \textit{in energy}\\ \textit{of the}\\ \textit{atomic}\\ \textit{orbital}\\ \textit{due to the}\\ \textit{crystalline}\\ \textit{environment}}} + \underbrace{\sum_{\mathbf{R}\neq\mathbf{0}} A(\mathbf{R}) \exp(i\mathbf{k}\cdot\mathbf{R})}_{\substack{\textit{The change in energy of the}\\ \textit{atomic orbital that depends}\\ \textit{on the overlap of between}\\ \textit{an orbital and the same type}\\ \textit{of orbital on a neighbouring site.}\\ \textit{It depends on the phase shift}\\ \textit{between the two states}}} \qquad \text{(W1.99)}$$

The term α is just the change in energy of the

Figure W1.19 Illustration of the meaning of some of the functions and integral kernels from Equations W1.88 to W1.99. (a) The difference between the potential energy of an electron within an atom and within a crystal ΔV(r). In order to show the function clearly, the function plotted is actually *minus* ΔV(r). (b) Illustration of the difference in magnitude between the kernels of the so-called *direct* integral α (Equation W1.97).and the so-called *transfer* integral *A*(**R**≠**0**) (Equation W1.98). The value of the integrals is the area underneath the curves shown. The direct kernel is shown *reduced* in scale by a factor 5 and the transfer kernel is shown *amplified* by a factor 5.



atomic orbital χ caused by the presence of the other ions. Since $\Delta V(\mathbf{r})$ is always negative (Figure W1.19(a)), the term α always represents a lowering of the energy level in the crystal as compared with the isolated atom (Figure W1.20).

It is from this final term that the bands arise i.e. the dependence of E upon **k**. It involves the overlap of orbitals centred on *neighbouring* sites. Examination of the form of $A(\mathbf{R})$ shows that the integral is only large when the potential differs significantly from what it was in the atomic case. Notice that $E(\mathbf{k})$ can take on different values as **k** changes, and shifts the phases of the contributions to the sum i.e. the phase of the wave function in adjacent unit cells is shifted (Figure W1.20).

An example

Let us find an expression for the energies of a tight-binding band in a crystal with a simple cubic lattice and a basis of one atom placed at each lattice site. We will assume the atomic orbital $\chi(\mathbf{r})$ is real and spherically symmetric and take the integral $A(\mathbf{R})$ to be 0, except for the case of nearest neighbours.

Evaluating E(k)

The unit cell of the simple cubic lattice is a cube of side a. Placing one lattice site at the origin of our co-ordinate system we find it has nearest neighbours at:

$$\begin{aligned}\mathbf{R} &= (\pm a,0,0)\\ \mathbf{R} &= (0,\pm a,0)\\ \mathbf{R} &= (0,0,\pm a)\end{aligned} \qquad \text{(W1.100)}$$

Our final expression for the energy of a tightly-bound state is:

$$E(\mathbf{k}) = E_{\text{atomic}} + \alpha + \sum_{\mathbf{R}\neq\mathbf{0}} A(\mathbf{R})\exp(i\mathbf{k}\cdot\mathbf{R}) \qquad \text{(*W1.99)}$$

where $A(\mathbf{R}) = \int \chi^*(\mathbf{r})\Delta V(\mathbf{r})\chi(\mathbf{r}-\mathbf{R})d\mathbf{r}$ is an integral involving the overlap of orbitals at **R** = **0** with orbitals at **R**. In this case, we consider only nearest neighbours, of which there are six (Figure W1.21). Because of the spherical symmetry of the orbitals, all six integrals are equal. Let us call the value of this integral A.

Evaluating $\mathbf{k}\cdot\mathbf{R}$ for $\mathbf{R} = (a,0,0)$ we find:

$$\begin{aligned}\mathbf{k}\cdot\mathbf{R} &= k_x x + k_y y + k_z z\\ &= k_x \times a + k_y \times 0 + k_z \times 0\\ &= k_x a\end{aligned} \qquad \text{(W1.101)}$$

Similarly, we can find results for the other five orbitals. Evaluating $\exp(i\mathbf{k}\cdot\mathbf{R})$ for each of the six terms in the sum we find:

Figure W1.20 Energy level diagram showing meaning of terms in Equation W1.99

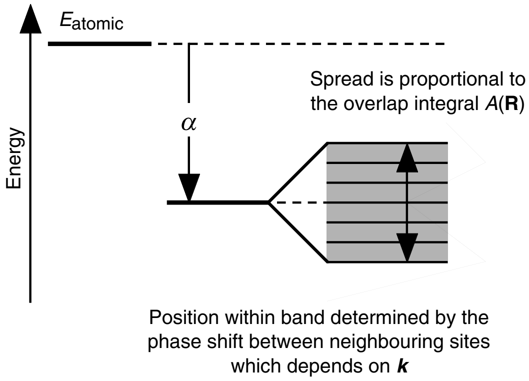
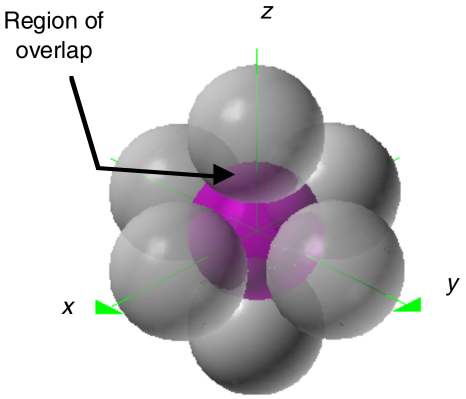


Figure W1.21: Each sphere represents an *s* orbital centre on a different lattice site.



$$E(\mathbf{k}) = E_{\text{atomic}} + \alpha + \\ + A\left[\exp(ik_x a) + \exp(-ik_x a)\right] \\ + A\left[\exp(ik_y a) + \exp(-ik_y a)\right] \\ + A\left[\exp(ik_z a) + \exp(-ik_z a)\right] \tag{W1.102}$$

Simplifying this using the standard definition of the cosine function we find:

$$E(\mathbf{k}) = E_{\text{atomic}} + \alpha + \\ + A\left[2\cos k_x a\right] \\ + A\left[2\cos k_y a\right] \\ + A\left[2\cos k_z a\right] \tag{W1.103}$$

which simplifies to:

$$E(\mathbf{k}) = E_{\text{atomic}} + \alpha + 2A\left[\cos k_x a + \cos k_y a + \cos k_z a\right] \tag{W1.104}$$

Finding the bandwidth

Looking at the expression for α we see:

$$\alpha = A(\mathbf{0}) = \int \underbrace{\chi^*(\mathbf{r})}_{\substack{\text{atomic}\\ \text{wavefunction}\\ \text{at site } \mathbf{R}=0}} \Delta V(\mathbf{r}) \underbrace{\chi(\mathbf{r})}_{\substack{\text{atomic}\\ \text{wavefunction}\\ \text{at site } \mathbf{R}=0}} \, d\mathbf{r} \tag{W1.105}$$

As shown in Figures W1.19 and W1.20, the crystalline potential is always lower than the atomic potential. So $\Delta V(\mathbf{r})$ is always negative, and since $\int \chi^*(\mathbf{r})\chi(\mathbf{r})d\mathbf{r}$ is just equal to 1, then α is always negative i.e. it corresponds to a lowering of the energy of an atomic state by an amount |α|.

The sign of the integral A can in general be either positive or negative, but in this case it is negative. This is because the orbitals χ are real so terms like $|\chi|^2$ will be positive, and because, as we saw above, $\Delta V(\mathbf{r})$ is negative. Thus A will be a negative number. The expression for the energy thus becomes:

$$E(\mathbf{k}) = E_{\text{atomic}} - |\alpha| \\ - 2|A|\left[\cos k_x a + \cos k_y a + \cos k_z a\right] \tag{W1.106}$$

This has a minimum value of:

$$E_{\min} = E_{\text{atomic}} - |\alpha| - 6|A| \tag{W1.107}$$

when all the cosine terms are equal to 1 i.e. at **k** = **0**, and a maximum value of

$$E_{\max} = E_{\text{atomic}} - |\alpha| + 6|A| \tag{W1.108}$$

when all the cosine terms have value –1 i.e. at $\mathbf{k} = (\pi/a, \pi/a, \pi/a)$. The *bandwidth* is equal to the difference between the maximum and the minimum energies is given by 12|A| i.e. it is directly proportional to integral involving:

- The overlap between neighbouring atomic orbitals,
- The difference between the crystalline and the atomic potential energy i.e.

$$A(\mathbf{R}) = \int \chi^*(\mathbf{r})\Delta V(\mathbf{r})\chi(\mathbf{r}-\mathbf{R})d\mathbf{r} \tag{*W1.95}$$

We can see that this makes sense.

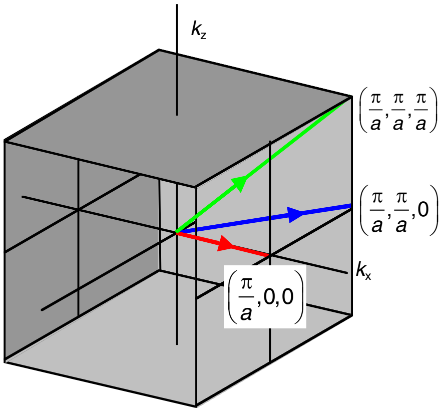
- Firstly, notice that if the crystalline potential is the same as the atomic potential then the quantum states will be the same in the crystal as they were in the atom. This makes $\Delta V(\mathbf{r}) = 0$ and hence $A(\mathbf{R}) = 0$ and hence the bandwidth is zero. This describes a return narrow atomic-like states.
- Similarly, if the overlap between the wave functions is zero i.e. if $\chi^*(\mathbf{r}) = 0$ whenever $\chi(\mathbf{r}-\mathbf{R}) \neq 0$ and vice versa then the bandwidth will also be zero.

These two cases describe the situation of the deepest ‘core’ states on atoms within a solid. However, if the crystalline potential differs from the atomic potential, then the corresponding quantum states will be different in the crystal and the atom. Thus the Bloch functions we constructed will not be accurate. In this tight-binding approximation we have neglected this effect and evaluated only the change in energy of the original quantum states.

How to visualise *E*(**k**)

The total energy *E*(**k**) that we have calculated (Equation W1.104) is a function that takes a single value at each point in the three-dimensional (k_x, k_y, k_z) 'volume' of the Brillioun zone. This makes visualising how the energy varies with **k** quite taxing. There has evolved a standard solution to this problem. The energy is calculated along special paths through the Brillioun zone. These paths are chosen to follow certain high symmetry directions within the zone. Graphs then show how the energy varies along the route.

Figure W1.22 Illustration of special 'representative' paths within the Brillioun zone as described in Equations W1.109 to W1.114



Let us calculate how the energy varies as one moves out from the centre of the zone **k** = (0,0,0) along lines joining the origin to:

- the centre of the square face of the Brillioun zone $(\pi/a, 0, 0)$
- the midpoint of the line joining two adjacent corners $(\pi/a, \pi/a, 0)$
- a corner of the zone $(\pi/a, \pi/a, \pi/a)$

How do we set about this problem?

E(k) along the (1,0,0) direction

The general expression for the energy anywhere within the Brillioun zone is given by:

$$E(\mathbf{k}) = E_{\text{atomic}} - |\alpha| \\ -2|A|\left[\cos k_x a + \cos k_y a + \cos k_z a\right] \tag{*W1.106}$$

If we now substitute $k_y = 0$ and $k_z = 0$ we find:

$$E(\mathbf{k}) = E_{\text{atomic}} - |\alpha| \\ -2|A|\left[\cos k_x a + \cos(0) + \cos(0)\right]$$

$$E(\mathbf{k}) = E_{\text{atomic}} - |\alpha| \ -2|A|\left[\cos k_x a + 2\right] \tag{W1.109}$$

so the energy increases as $\cos k_x a$. The energy at the Brillouin Zone Boundary is therefore:

$$\begin{aligned} E(\mathbf{k}) &= E_{\text{atomic}} - |\alpha| \ -2|A|\left[\cos\frac{\pi}{a}a + 2\right] \\ &= E_{\text{atomic}} - |\alpha| \ -2|A|[-1+2] \\ &= E_{\text{atomic}} - |\alpha| \ -2|A| \end{aligned} \tag{W1.110}$$

E(k) along the (1,1,0) direction

We start again with the general expression for the energy anywhere within the Brillioun zone:

$$E(\mathbf{k}) = E_{\text{atomic}} - |\alpha| \\ -2|A|\left[\cos k_x a + \cos k_y a + \cos k_z a\right] \tag{*W1.106}$$

Along this special direction we now substitute $k_z = 0$ and $k_x = k_y = k$ to find:

$$E(\mathbf{k}) = E_{\text{atomic}} - |\alpha| \ -2|A|[2\cos ka + 1] \tag{W1.111}$$

and the energy increases as $2\cos ka$. The energy at the zone boundary is therefore:

$$\begin{aligned} E\left(\frac{\pi}{a},\frac{\pi}{a},0\right) &= E_{\text{atomic}} - |\alpha| \ -2|A|\left[2\cos\frac{\pi}{a}a + 1\right] \\ &= E_{\text{atomic}} - |\alpha| \ -2|A|[2(-1)+1] \\ &= E_{\text{atomic}} - |\alpha| \ -2|A|[-1] \\ &= E_{\text{atomic}} - |\alpha| \ +2|A| \end{aligned} \tag{W1.112}$$

E(k) along the (1,1,1) direction

We start again with the general expression for the energy anywhere within the Brillioun zone:

$$E(\mathbf{k}) = E_{\text{atomic}} - |\alpha| - 2|A|\left[\cos k_x a + \cos k_y a + \cos k_z a\right] \quad (*\text{W1.106})$$

Along this special direction we now substitute and $k_x = k_y = k_y = k$ to find:

$$E(\mathbf{k}) = E_{\text{atomic}} - |\alpha| - 2|A|[3\cos ka] \quad (\text{W1.113})$$

and the energy increases as $3\cos ka$. The energy at the zone boundary is therefore:

$$\begin{aligned} E\left(\frac{\pi}{a},\frac{\pi}{a},\frac{\pi}{a}\right) &= E_{\text{atomic}} - |\alpha| - 2|A|\left[3\cos\frac{\pi}{a}a\right] \\ &= E_{\text{atomic}} - |\alpha| - 2|A|[3(-1)] \\ &= E_{\text{atomic}} - |\alpha| - 2|A|[-3] \\ &= E_{\text{atomic}} - |\alpha| + 6|A| \end{aligned} \quad (\text{W1.114})$$

Visualisation and interpretation

So now we can calculate how the energy of electronic states varies with the character of the quantum state (as described by its position in the Brillioun zone). For many advanced calculations, this kind of calculation is exactly what is required to understand some particular property of a solid. However, for many solids the details required as inputs to the band structure calculation (such as the value of overlap integrals), are not well known. This makes the detailed results of calculations unreliable, but such calculations can still reveal the *general form* of the band structure. In particular, the position of the Fermi energy relative to the calculated band structure is central to understanding a material's properties.

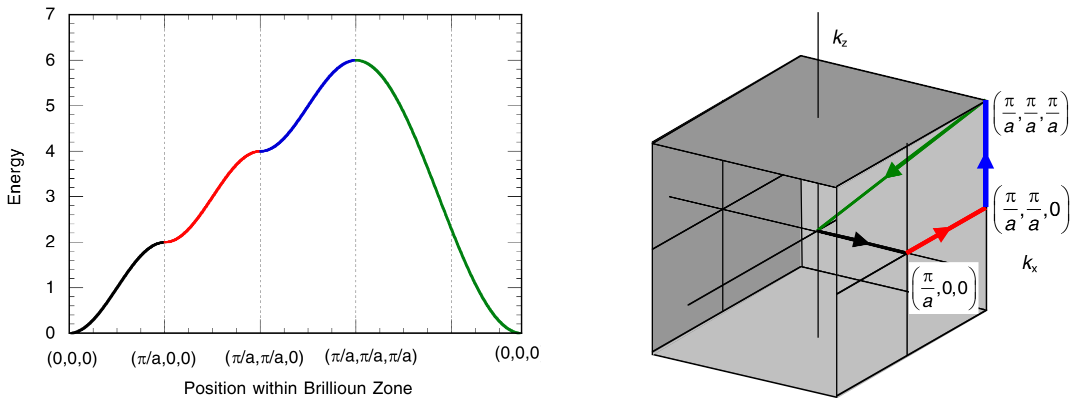
Before proceeding to analyse this situation in more depth, we will just pause to remind ourselves of the status of concepts such as 'band structures' and 'Brillioun zones'. They are *explanatory concepts* which (while they exist only in our heads) will allow us to calculate and discuss the properties of widely different solids using a unified framework.

A band structure diagram

Figure W1.23 illustrates what we mean by a 'band structure' diagram. It is a graph showing how the energy of electron quantum states varies with position in the Brillioun zone. It does not show the energy of all the states in the zone, rather it shows how the energy of states varies as a standard path through the zone is traversed.

While plotting the band structure is in itself an achievement, is it is not until we add a line indicating the position of the Fermi energy that the

Figure W1.23 Illustration of the band structure described by Equation W1.106. (a) A graph of energy versus **k** along the path through the Brillioun zone shown in (b). Notice that (b) is *not* the same as Figure W1.22.



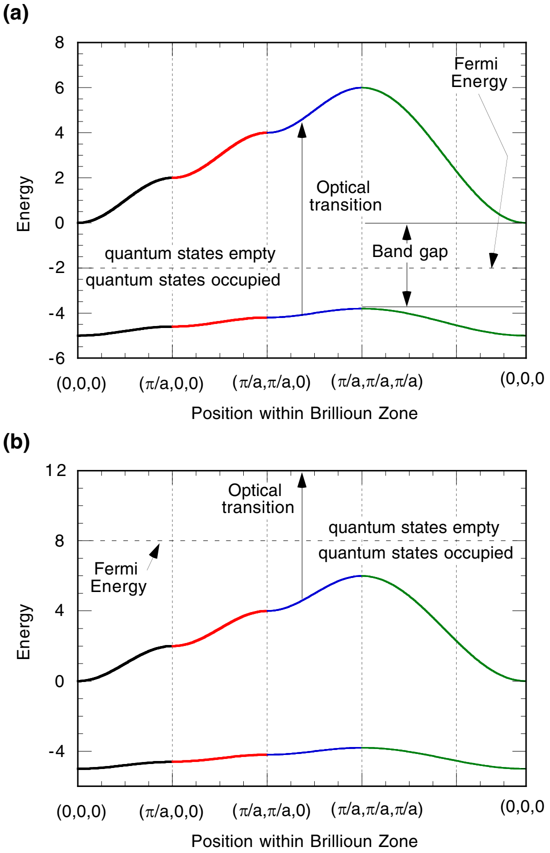
band structure acquires any physical significance. There are three cases to consider:

- The Fermi energy is lower than the lowest energy in this band.
- The Fermi energy is greater than the highest energy in this band.
- The Fermi energy lies in the energy range spanned by this band.

Let us consider each of these cases in turn. If the Fermi energy is lower than the lowest energy in this band, then no states within this band are occupied (Figure W1.24(a)). The band can still affect the optical properties of the solid by providing empty quantum states into which electrons (from lower energy bands) may be excited by photons of an appropriate energy. Typically this energy would be of the order of a few electron volts which would correspond to light in the near infra red, optical or ultra violet regions of the spectrum.

Normally a material described by a band diagram such as that in Figure W1.24 (a) would correspond to that of an insulator. However, if the band gap is relatively small (≈ 1 electron volt) then it is possible for a population of electrons to be thermally excited from quantum states in the lower occupied band to empty quantum states in the band under consideration. These electrons would then be able to conduct electricity. Although the number density of this excited population is tiny in comparison with a metal, it is very large in comparison with insulators. Such materials are described as *semiconductors* (§7.7.8 and §7.7.9).

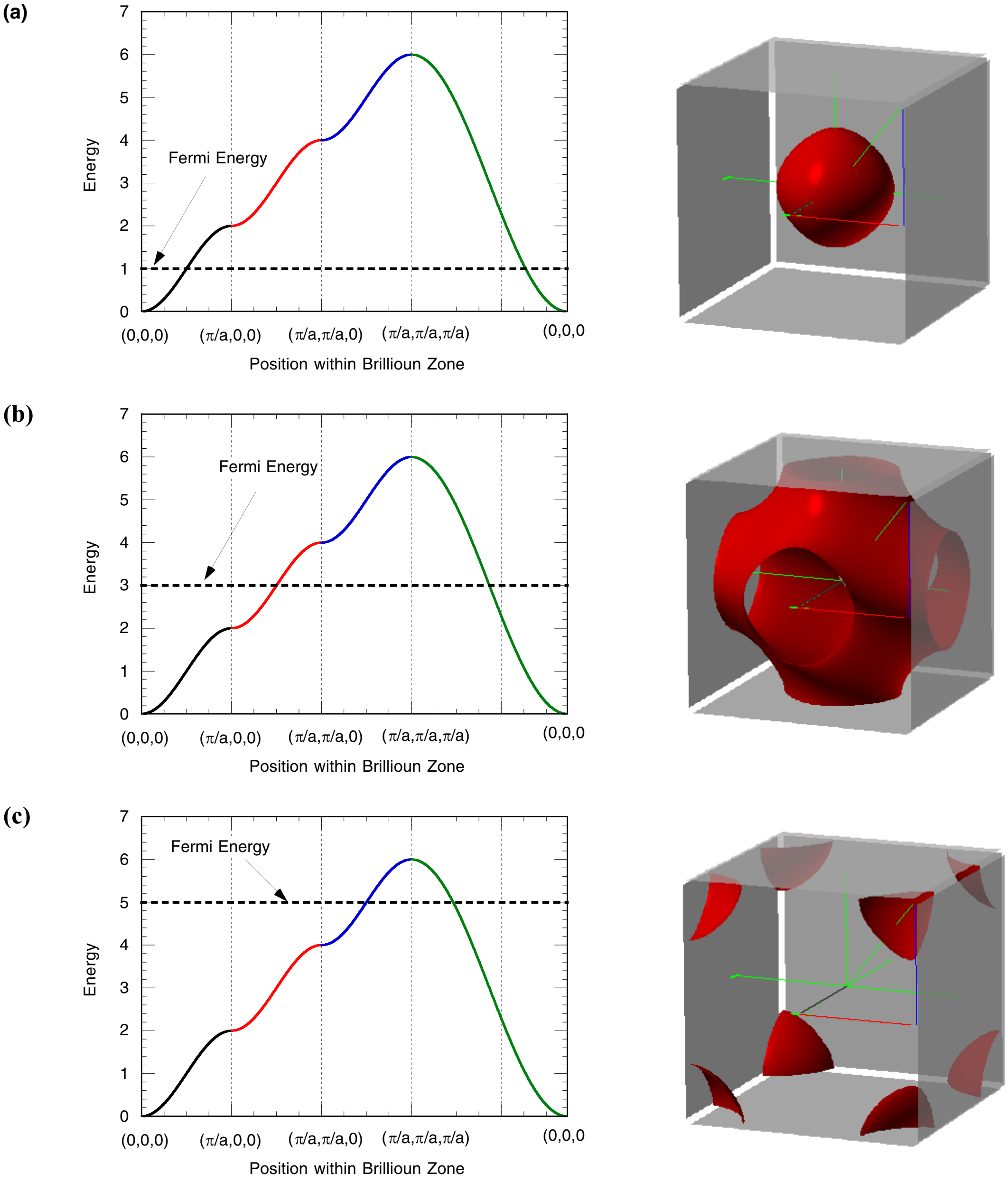
Figure W1.24 Illustration of the cases described in text in which the Fermi energy lies (a) below the band of states under consideration and (b) above the band of states under consideration. The Figures show two bands of quantum states based on different atomic orbitals. The upper band is the one considered in the text and plotted in Figure W1.23.



Alternatively, if the Fermi energy is higher than the highest energy in this band, then all states within this band are occupied (Figure W1.24(b)). Perhaps surprisingly, this means that the band of occupied states contributes nothing to the conductivity. This is because there are no easily accessible quantum states into which electrons may move. Thus when an electric field is applied to the substance, electrons in this band of states are unable to easily change quantum state in response to the electric field. The band can still affect the *optical* properties of the solid by providing a source of electrons which may be excited by photons of an appropriate energy into empty, higher energy quantum states. Typically this energy would be of the order of a few electron volts which would correspond to light in the near infra red, optical or ultra violet regions of the spectrum.

As for the previous case, we should add the qualification that if a band of empty states is available with energies within ≈ 1 electron volt of the highest energy in the band, then again the material would be described as a semiconductor.

Figure W1.25 Illustration of the effect of changing the Fermi energy for the fixed hypothetical band structure described by Equation W1.106. (a) When the Fermi energy is just above the low edge of the band, the occupied states are all near the zone centre and the Fermi surface is only slightly distorted froma sphere. (b) When the Fermi energy is in the middle of the band, the occupied states are all near the zone centre and the Fermi surface (i.e. a surface of constant energy with energy E_{F}) is complex in shape. (c) When the Fermi energy is near the top of the band, nearly all the states are occupied and the Fermi surface is complex in shape is very much reduced in area.



Finally, we consider the case when Fermi energy lies in the energy range spanned by this band. In this case the material will be a metal. We can see this because the Fermi energy separates occupied from empty states (at $T = 0$ K). Since the Fermi energy lies within a band of states, electrons will be able to find empty quantum states only infinitesimally above the Fermi energy. Thus even a weak applied electric field will be able to cause electrons to change states (i.e. conduct). Since the substance is a metal, it will possess a *Fermi surface* (which is the energy contour in *k*-space separating occupied from empty states (at $T = 0$ K). However, as Figure W1.25 makes clear, depending on where the Fermi energy lies within the band, the Fermi surface can be quite different in shape from the Fermi spheres that we have discussed previously.

W1.5 Summary

W1.5.1 So what?

Let me explain again why I embarked on writing these 36 theoretical pages to accompany the 400 or so decidedly phenomenological pages of *Understanding the properties of matter*. I sought to explain how we can develop a language for describing electronic quantum states in solids To this end, we developed the *nearly-free electron model* that allowed us to see how a material might be an insulator or a metal depending on the strength of a perturbing potential energy. We also developed the *tight binding model* which was considerably more complex, but generally more plausible. This again allowed us to understand how a substance could display insulating or metallic properties depending on some calculable properties of the electronic orbitals of the atoms of the substance.

So, in terms of the problem that I stated at the start of this chapter, we can now discuss the properties of solid argon and solid potassium using the *same theoretical model*. In solid argon, the Fermi energy lies *in between* bands of states and so the material is an insulator. In solid potassium, the Fermi energy lies *within* a band of states and so the material is a metal. This may seem an unspectacular conclusion the Chapter, but that is what it has all been for.

W1.5.2 What next?

If you wish to find out more about the band theory of solids then there is no better introductory text than *Solid State Physics* by N.W. Ashcroft and N.D. Mermin. (ISBN: 0030839939).