

## 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. As such, it has a distinct flavour from the rest of the book where I have focussed on experimental properties, and then developed theories only to the extent that they are needed to describe the experimental data. My motivation in making this additional section available is that the problem they address is central to understanding what “really happens” inside solids. This central problem is the description of the nature of electronic states in solids.

### The challenge

The challenge can be highlighted by considering two elements: argon and potassium. As solids we know from §6.2 and §7.3, that argon is described as molecular solid. However, when we describe potassium, we would naturally discount the theory for argon as irrelevant, and adopt the description of 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 used 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 some where between these two extremes, and the challenge is to find a way to describe such states. Now the solution of this problem has “been known” for nearly half a century. I use the term “known” in quotation marks because it is not at all clear to be who it is who has been doing the “knowing”. I say this, because 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 to follow the arguments with regard to the tight binding theory is definitely higher than for the topics in the main text.

We shall proceed as follows:

- §W1.2 **k-space and the reciprocal lattice**
- §W1.3 **Free electron theory of metals**
- §W1.4 **Nearly free electron theory of metals and insulators**
- §W1.5 **Tight-binding theory**
- §W1.6 **Understanding band diagrams**

**ALL OF THESE SECTIONS ASSUME THAT YOU HAVE PREVIOUSLY READ CHAPTER 6, SECTION 5**



## W1.1 k-space

### W1.1.1 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  $\mathbf{k}$ -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  $A \cos(\mathbf{k} \cdot \mathbf{r})$  which takes up the whole of the volume of a metal

#### Figure W1.1 Real space and k-space

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.XX

$$k_x = \frac{2m_x \pi}{L_x}, k_y = \frac{2m_y \pi}{L_y}, k_z = \frac{2m_z \pi}{L_z} \quad (6.XX^*)$$

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 extend indefinitely, but it is not a completely barren landscape. There are certain special values of  $\mathbf{k}$  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

### 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 the walls of the box (or in the case of a metal, 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 be surrounded by *identical volumes*.

The differences between this situation and the standing wave situation are illustrated in Figure W1.2. The reader may consider this change to be “trickery”, and 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 depend at all upon the state of the surface of the crystal. The final benefit of using this trick is that we are able to use *travelling wave* solutions to the particle in a box problem.

#### Figure W1.2

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

$$\Psi(-L_x/2) = \Psi(L_x/2) = 0 \quad (W1.1)$$

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.

$$\Psi(x) = \Psi(x + L_x) \quad (W1.2)$$

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

$$\cos(k_x x) = \cos(k_x [x + L_x]) \quad (W1.3a)$$

or

$$\sin(k_x x) = \sin(k_x [x + L_x]) \quad (W1.3b)$$

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's follow one of Equations W1.3 through explicitly to find these conditions for  $k_x$ . The boundary conditions require that:

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

Using the trigonometric identity:

$$\cos(A + B) = \cos A \cos B - \sin A \sin B \quad (W1.5)$$

Equation W1.4 can be rewritten as:

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

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 :

$$k_x L_x = 0, \pm 2\pi, \pm 4\pi, \dots \quad (\text{W1.7})$$

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:

$$k_x = 0, \frac{\pm 2\pi}{L_x}, \frac{\pm 4\pi}{L_x}, \dots \quad (\text{W1.67})$$

or in general when:

$$k_x = \frac{2m_x \pi}{L_x} \quad (\text{W1.68})$$

where  $m_x = 0, \pm 1, \pm 2, \dots$ . Similar equations apply in the  $y$  and  $z$  directions and, as we stated in §6.5 we find:

$$k_x = \frac{2m_x \pi}{L_x}, k_y = \frac{2m_y \pi}{L_y}, k_z = \frac{2m_z \pi}{L_z} \quad (\text{6.XX}^*)$$

#### Note

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.

#### Volume of $k$ -space per quantum state

So, as illustrated in Figure 6.XX, each allowed  $k$ -state occupies a small cuboid of “volume”:

$$\begin{aligned}\Delta k_x \Delta k_y \Delta k_z &= \frac{2\pi}{L_x} \times \frac{2\pi}{L_y} \times \frac{2\pi}{L_z} \\ &= \frac{8\pi^3}{V}\end{aligned}\quad (\text{W1.XX})$$

where  $V$  is the total volume of the crystal. I have used the word “volume” in quotation marks above Equation 6.XX because I am referring to “volume”

on a  $k$ -space graph. As you can see from Equation 6.XX, the “volume” on the  $k$ -space graph actually has the dimensions of inverse volume i.e.  $\text{m}^{-3}$  rather than  $\text{m}^3$ . 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:

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

### 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 that: you will not be alone in finding it a difficult idea!

#### The “metal as a box” approach

Figure 6.XX\* 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:

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}) \quad (\text{W1.68})$$

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 we plot in  $k$ -space, which reflects the periodicity of the crystalline potential. The reciprocal lattice is the set of values of  $\mathbf{k}$  which describe waves, which has *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 only a single crystal structure,

simple cubic. This crystal structure is illustrated in Figure 6.XX and also in Figure W1.X. In Figure W1.X 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 verifying that:

$$\begin{aligned} \cos \frac{2\pi x}{a} &= \cos \frac{2\pi(x+ma)}{a} \\ &= \cos \left[ \frac{2\pi x}{a} + \frac{2\pi ma}{a} \right] \\ &= \cos \left[ \frac{2\pi x}{a} + 2m\pi \right] \end{aligned}$$

So this wave vector does have the same value within every unit cell of the crystal, because all trigonometric functions repeat after any integer number of  $2\pi$  increments. We thus dignify the vector  $\mathbf{k} = (2\pi/a, 0, 0)$  as belonging to the reciprocal lattice of a simple cubic crystal structure. This point, and several other reciprocal lattice vectors, are plotted in Figure W1.X

**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 of them are considerably 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. In the analysis of the diffraction of X-rays by crystals, the reciprocal lattice places a central role.

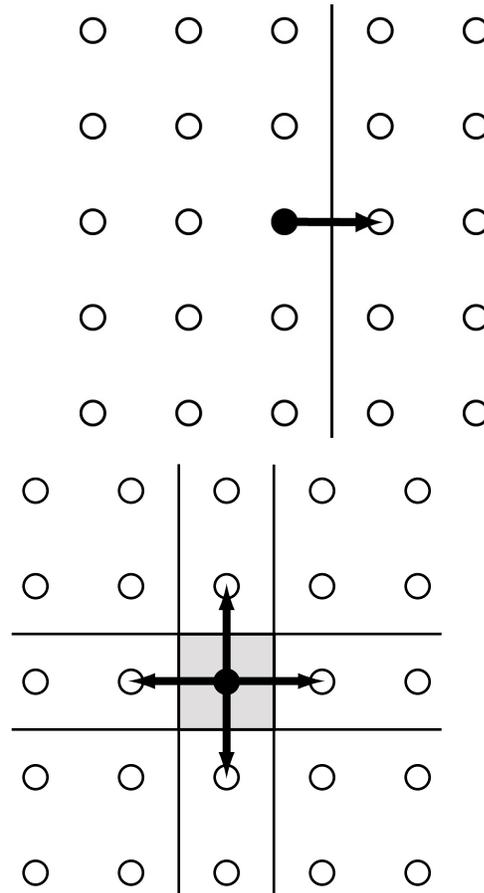
**Brillouin zone**

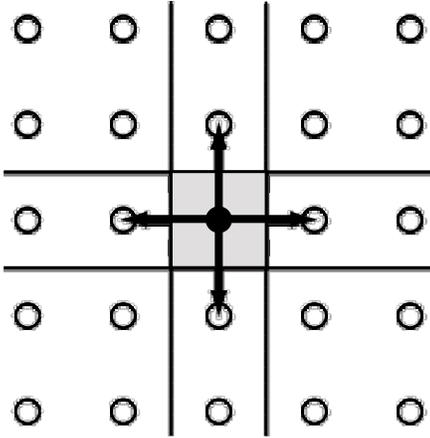
So now we know two features about  $k$ -space. We know that when it comes to finding allowed solutions of the particle in a box problem, only certain allowed values of  $(k_x, k_y, k_z)$  are allowed.

And we also know that there are special sets of values of  $\mathbf{k}$  which are given the symbol  $\mathbf{K}$ , and which 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 complex, in two dimensions the idea is quite simple.

**Brillouin zones in 2- dimensions**

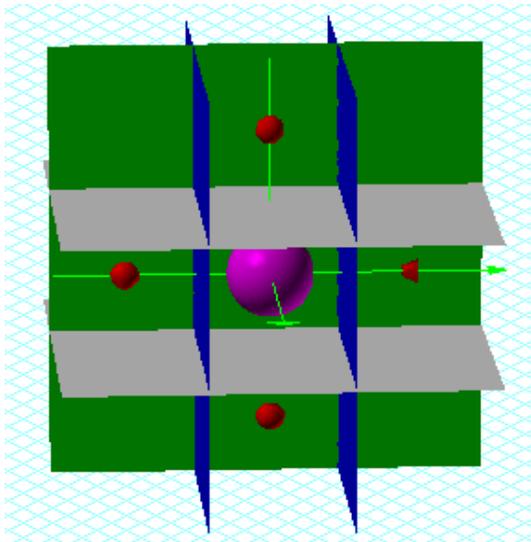
To find the area nearer to a reciprocal lattice point we start at that point, and draw the  $\mathbf{K}$  vectors to nearby reciprocal points. Then we bisect these  $\mathbf{K}$  vectors. The area nearest to the original point is called the *first Brillouin zone*, or often just the *Brillouin zone*.





**Brillouin zones in 3-dimensions**

In 3-dimensions we need to find the *volume* nearest to a reciprocal lattice point. To do this we start at that point, and draw the **K** vectors to nearby reciprocal points. Then we bisect these **K** vectors not with a *line* as in 2-dimensions, but with a *plane*. The *volume* nearest to the original point is called the *first Brillouin zone*, or often just the *Brillouin zone*.



**The significance of the Brillouin zone**

In 3-dimensions we need to find the *volume*

**W1.2 Free electron theory of metals**

**W1.2.1 General description**

The  $k_i$ 's are related to the wavelength of each quantum state. If our waves were just one-dimensional, then we would simply write:

$$\lambda = \frac{2\pi}{k} \quad (W1.XX)$$

In three dimensions, things are a little more complicated. We imagine 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:

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

Equation 6.XX allows us to use the de Broglie relation (2.XX) to infer the momentum and energy of the wave represented by  $(k_x, k_y, k_z)$ . The momentum may be written as:

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

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

$$\begin{aligned} E &= \frac{1}{2} m_e v^2 = \frac{p^2}{2m_e} \\ E &= \frac{\hbar^2 |\mathbf{k}|^2}{2m_e} \\ E &= \frac{\hbar^2}{2m_e} [k_x^2 + k_y^2 + k_z^2] \end{aligned} \quad (W1.XX)$$

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 6.XX 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:

$$|\mathbf{k}| = \sqrt{\frac{2m_e E}{\hbar^2}} \quad (\text{W1.XX})$$

**Figure 6.21**

**The density of states function.**

$$\begin{aligned} g(E) &= \frac{V\sqrt{2m_e^3 E}}{\pi^2 \hbar^3} \\ &= \left[ \frac{V\sqrt{2m_e^3}}{\pi^2 \hbar^3} \right] \sqrt{E} \end{aligned} \quad (\text{W1.77})$$

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

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

**Using the density of states function.**

We can also 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:

$$N = \int_{E=0}^{E=E_F} g(E) dE$$

Substituting for  $g(E)$  from Equation 6.XX and taking the constants outside the integral we find:

$$\begin{aligned} N &= \int_{E=0}^{E=E_F} \left[ \frac{V}{\pi^2} \frac{\sqrt{2m_e^3}}{\hbar^3} E^{1/2} \right] dE \\ &= \left[ \frac{V}{\pi^2} \frac{\sqrt{2m_e^3}}{\hbar^3} \right] \int_{E=0}^{E=E_F} E^{1/2} dE \quad (\text{W1.XX}) \\ N &= \left[ \frac{V}{\pi^2} \frac{\sqrt{2m_e^3}}{\hbar^3} \right] \frac{2}{3} E_F^{3/2} \end{aligned}$$

Rearranging this as an expression for the Fermi energy we find:

$$\begin{aligned} \frac{3n\pi^2 \hbar^3}{2\sqrt{2m_e^3}} &= E_F^{3/2} \\ E_F &= \frac{\hbar^2 (3n\pi^2)^{2/3}}{2m_e} \end{aligned} \quad (\text{W1.XX})$$

which agrees with our previous result (Equation 6.XX).

## Potassium

The previous section has been a rather abstract view of a metal. Let's apply some numbers that might be appropriate to real metals to the model developed in the previous section in order to make its consequences clearer.

### A numerical example

Compare Potassium and copper. Additional electrons in d-states have allowed covalent bonding and dramatically increased the density.

There are several ways to estimate  $n$ , but perhaps the simplest is to look up the *density* of an elemental metal, and to divide by the mass of an atom to get the *number density* of atoms. If we then multiply by the valence we arrive at  $n$ . From Table 7.2 we see that the density of potassium is  $862 \text{ kg m}^{-3}$ , and the mass of an atom is  $39.1 \times 1.66 \times 10^{-27} \text{ kg}$ . Assuming potassium has a valence of one, then our estimate for  $n$  is:

$$\begin{aligned} n &= \frac{1 \times 862}{39.1 \times 1.66 \times 10^{-27}} \\ &= 1.33 \times 10^{28} \text{ electrons m}^{-3} \end{aligned} \quad (\text{W1.85})$$

If we use this estimate for  $n$  in Equation 6.84 for the Fermi wave vector  $k_F$  we find:

$$\begin{aligned} k_F &= (3 \times 1.33 \times 10^{28} \times \pi^2)^{1/3} \\ &= 7.33 \times 10^9 \text{ m}^{-1} \end{aligned} \quad (\text{W1.86})$$

Substituting this in Equation 6.84 for the Fermi Energy  $E_F$  we find:

$$\begin{aligned} E_F &= \frac{(1.054 \times 10^{-34})^2 (7.33 \times 10^9)^2}{2 \times 9.1 \times 10^{-31}} \\ &= 3.28 \times 10^{-19} \text{ J} \\ &= 2.05 \text{ eV} \end{aligned} \quad (\text{W1.87})$$

We can evaluate the  $g(E)$  per unit volume from Equation 6.XX:

$$\frac{g(E)}{V} = \left[ \frac{\sqrt{2 \times (9.1 \times 10^{-31})^3}}{\pi^2 (1.054 \times 10^{-34})^3} \right] \sqrt{E}$$

$$= 1.062 \times 10^{56} \sqrt{E} \text{ states J}^{-1} \text{m}^{-3}$$

Notice that this function has exactly the same value for copper as it did for potassium! And we can evaluate this at the Fermi energy:

$$\frac{g(E_F)}{V} = [1.062 \times 10^{56}] \sqrt{3.28 \times 10^{-19}}$$

$$= 6.08 \times 10^{46} \text{ states J}^{-1} \text{m}^{-3}$$

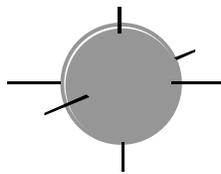
Let's look at the significance of  $k_F$ ,  $E_F$  and  $g(E)$  in turn.

**Potassium: a simple metal.**

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. In this problem we will compare the periodicities encountered in the lattice with those occurring in the Free Electron gas problem. Basically we will discover on what scale to draw the Fermi Sphere.

Potassium crystallises in the bcc structure with a conventional unit cell of side  $a = 0.52 \text{ nm}$ .

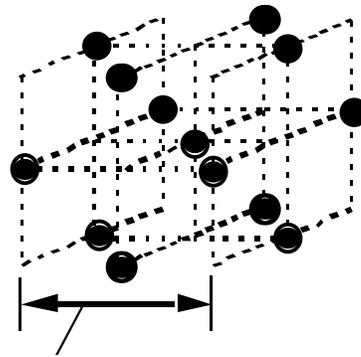
We will work out how big the Fermi Sphere is, both numerically and in units of  $1/a$ , that is we will evaluate  $k_F$ .



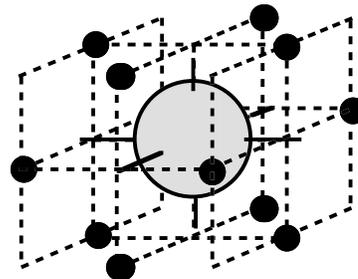
How does the Fermi Sphere fit into the Reciprocal Lattice

What does the reciprocal lattice look like? The reciprocal lattice of bcc of conventional unit cell side  $a$  is fcc with conventional unit cell of side  $4\pi/a \approx 12.6/a \approx 2.4 \times 10^{10} \text{ m}^{-1}$ . So k-space looks something like...

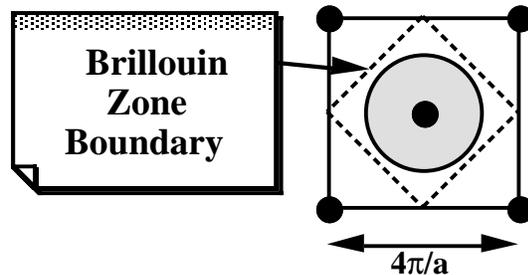
**Remember! k-space is a concept not a place!**



Side =  $4\pi/a$



We can look at this in quantitative detail if we look at a cross section through k-space. Let's look at a plane where the Fermi Sphere comes closest to a neighbouring reciprocal lattice site. We find...



The distance from the origin to the nearest reciprocal lattice point is

$$\sqrt{2} \times \frac{1}{2} \times \frac{4\pi}{a} = 1.709 \times 10^{10} \text{ m}^{-1}$$

and so the distance from the origin to the Brillouin Zone Boundary at its closest point of approach is

$$\frac{1}{2} \left[ \sqrt{2} \times \frac{1}{2} \times \frac{4\pi}{a} \right] = 0.855 \times 10^{10} \text{ m}^{-1}.$$

which compares with the radius of the Fermi Sphere  $k_F = 0.75 \times 10^{10} \text{ m}^{-1}$ . Thus the Fermi Sphere extends 0.75/0.855 = 87.7% of the way to the Brillouin Zone boundary.

*Astonishingly*...one can determine the Fermi Surface of many metals experimentally by means of the de Haas-van Alphen Effect. 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 be correct to within 1% and the "sphere" deviates from sphericity by less than 1 part in  $10^3$ .

The Fermi Surface is "measured" by measuring the magnetisation of a **pure metal at very low temperatures and high magnetic fields**. The magnetic moment of such a sample may show small oscillations called **de Haas-van Alphen Oscillations**. It is from a detailed examination of these wiggles that the Fermi Surface may be reconstructed. Remember! The Fermi Surface is a construction describing the occupancy of quantum states. In other words it is a concept, or an idea, and has no material existence.

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

### W1.4.1 Introduction

In the last section we saw how the energy of an electron state varied with  $\mathbf{k}$ . The electrons we considered 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 the attempt to look at the "corrugations" at the bottom of the box in Figure W1.X. We will find that potential energy also varies with  $\mathbf{k}$  and that, in general, it makes only a small contribution to the total energy. 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  $\mathbf{k}$  is close to the boundary of the Brillouin zone (§W1.3) then the potential energy contribution

becomes very significant.

### W1.4.2 The total energy

The band structure of a material is (essentially), a diagram showing the way the *total* energy of electronic states varies as a function of their quantum number  $\mathbf{k} = (k_x, k_y, k_z)$  i.e. the band structure of a material is nothing more than the relationship  $E(\mathbf{k})$ .

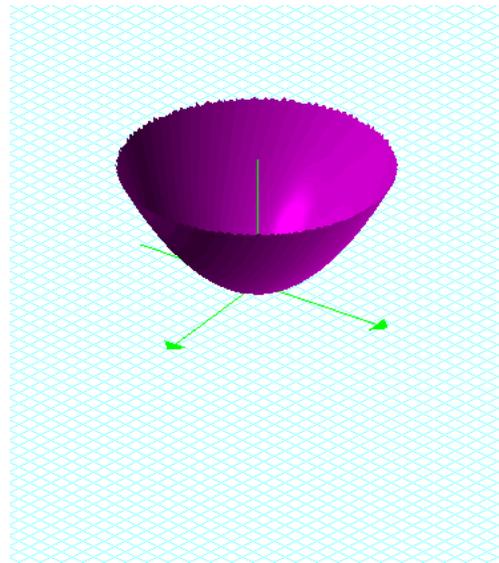
#### Kinetic energy

The kinetic energy contribution is related to the average curvature of the wave function

$$\frac{-\hbar^2}{2m_e} \frac{\partial^2}{\partial x^2} \Psi(x)$$

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:

$$E(k_x) = \frac{-\hbar^2 k_x^2}{2m_e}$$



#### Potential energy

The potential energy contribution  $V(\mathbf{k})$  is caused by the electrostatic (Coulomb) interaction between the electron and all the other electrically charged objects in its vicinity i.e. the ions, and the other electrons.