

§7 – Electron Bands

7.1 Electron Bands

The free electron gas model completely ignored the crystal, which we will now reintroduce.

We saw from the previous section that $k_F \sim \frac{2\pi}{a'}$, where a' is the typical spacing.

If there are two conducting electrons per atom, k_F is even higher.

Thus, we are certain to reach the zone boundary.

An electron, like all particles is both particle-like and wave-like. Thus, like any wave it will undergo *elastic scattering* or diffraction in a periodic crystal lattice.

Recall the definition of the zone boundary. The zone boundary is a locus of points \vec{k} and \vec{k}' satisfying $\vec{k} - \vec{k}' = \vec{G}$.

So all electron wavefunctions with wavevectors \vec{k} that lie on (or near) the zone boundary will scatter strongly into waves of wavevector \vec{k}' differing from it by a reciprocal lattice vector. This has the effect, as we shall see, of opening up a *band gap* in energy at the zone boundary. This will be used to explain the differences between metals and insulators.

7.2 Calculation of the Band Gap Energy

In the presence of strong scattering, the two zone boundary states at $k_x = \frac{\pm\pi}{a}$ have equal amplitude in the electron wavefunction. One of the two states is reflected back on top of the other, and the result is a standing wave. There are two independent combinations:

$$\psi(+)\propto e^{i\frac{\pi}{a}x} + e^{-i\frac{\pi}{a}x} = 2\cos\left(\frac{\pi}{a}x\right) \quad (7.1)$$

$$\psi(-)\propto e^{i\frac{\pi}{a}x} - e^{-i\frac{\pi}{a}x} = 2i\sin\left(\frac{\pi}{a}x\right) \quad (7.2)$$

The atomic cores of the lattice contribute a potential $U(x)$, which unlike our simple free electron model, we no longer neglect.

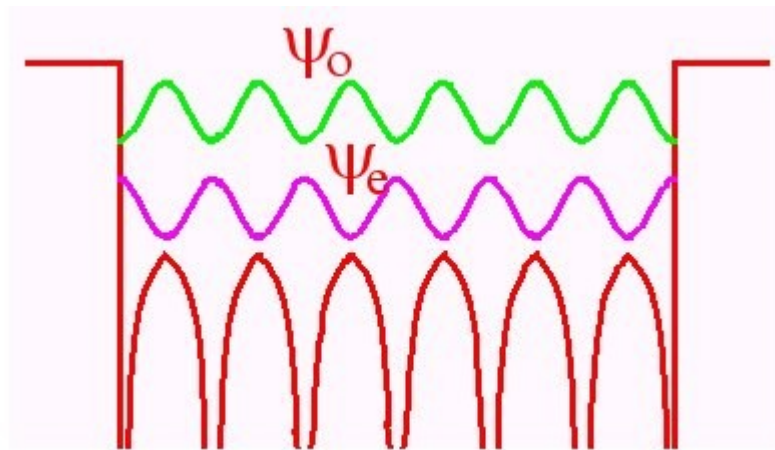
This *nearly-free electron model* considers the potential to be a *perturbation* of the free electron gas

model.

Let H be the **perturbed** Hamiltonian. The Schrödinger (energy eigenvalue) equation is then:

$$H \psi = \left(\underbrace{-\frac{\hbar^2}{2m} \nabla^2}_{\text{unperturbed Hamiltonian}} + \underbrace{U(\vec{r})}_{\text{perturbation}} \right) \psi = E \psi \quad (7.3)$$

In the picture below, the energy is lower for the $\psi(+)$ wavefunction than the $\psi(-)$ wavefunction, because the maximum probability, $|\psi(+)|_{\text{max}}^2$ corresponds to the regions of low potential of the crystal where the ion cores are located. Similarly, $|\psi(-)|^2$ is at a maximum in between the ions.



Since $U(x)$ is the perturbing Hamiltonian, the change in energy is given by the matrix element:

$$\Delta E = \langle \psi | U | \psi \rangle \quad (7.4)$$

Where: $|\psi\rangle$ is an eigenstate corresponding to the wavefunction ψ .

This means that the band gap is given by:

$$E_g = \langle + | U | + \rangle - \langle - | U | - \rangle \quad (7.5)$$

Where: $|+\rangle$ and $|-\rangle$ are eigenstates corresponding to wavefunctions $\psi(+)$ and $\psi(-)$

respectively.

In wavefunction notation, the band gap energy is given by:

$$E_g = \int_0^a U(x) [|\psi(+)|^2 - |\psi(-)|^2] dx \quad (7.6)$$

7.3 Fourier Expansion of $U(x)$

The major strength in considering the reciprocal lattice is that it is the natural basis for Fourier analysis of periodic functions.

This is a key tool in electronic band structure calculations.

Consider a 1-dimensional symmetric periodic function $U(x)$. We can expand this as a Fourier series:

$$U(x) = \frac{1}{2} \sum_{n=-\infty}^{\infty} U_n e^{in\frac{2\pi}{a}x} = \sum_{n>0} U_n \cos\left(n\frac{2\pi}{a}x\right) \quad (7.7)$$

Note:

Since U is symmetric, we can ignore sin terms (since they will be 0). We have also ignored the $n=0$ offset term.

As far as we are concerned, U_n are the set of coefficients U_G , where $G = \frac{2\pi}{a}n$. There is one number for each reciprocal lattice point in 3-dimensions.

Before we continue, we need to normalise the wavefunctions in equations (7.1) and (7.2) :

$$\int_0^a 4 \cos^2\left(\frac{\pi}{a}x\right) dx = 4 \left[\frac{x}{2} + \frac{a \sin\left(\frac{2\pi}{a}x\right)}{4\pi} \right]_0^a = 2a$$

$$\int_0^a 4 \sin^2\left(\frac{\pi}{a}x\right) dx = 4 \left[\frac{x}{2} - \frac{a \sin\left(\frac{2\pi}{a}x\right)}{4\pi} \right]_0^a = 2a$$

Thus, the normalised wavefunctions are:

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$$\psi(+)=\sqrt{\frac{2}{a}}\cos\left(\frac{\pi}{a}x\right) \quad (7.8)$$

$$\psi(-)=i\sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right) \quad (7.9)$$

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Substituting equations (7.7), (7.8) and (7.9) into equation (7.6) gives the band gap energy as:

$$E_g = \frac{2}{a} \int_0^a \sum_{n>0} U_n \cos\left(n \frac{2\pi}{a} x\right) \left[\cos^2\left(\frac{\pi}{a} x\right) - \sin^2\left(\frac{\pi}{a} x\right) \right] dx \quad (7.10)$$

Using the identity $\cos^2\theta - \sin^2\theta = \cos 2\theta$ and separating the first-order correction gives:

$$E_g = \frac{2}{a} \int_0^a U_1 \cos^2\left(\frac{2\pi}{a} x\right) dx + \frac{2}{a} \int_0^a \sum_{n>1} U_n \cos\left(n \frac{2\pi}{a} x\right) \cos\left(\frac{2\pi}{a} x\right) dx \quad (7.11)$$

Now, we can simplify the first integral using the identity $\cos^2\theta = \frac{1}{2}(1 + \cos 2\theta)$:

$$\int_0^a \cos^2\left(\frac{2\pi}{a} x\right) dx = \frac{1}{2} \int_0^a \left(1 + \cos\left(\frac{4\pi}{a} x\right)\right) dx = \frac{1}{2} \left[x + \frac{a}{4\pi} \cos\left(\frac{4\pi}{a} x\right) \right]_0^a = \frac{1}{2} \left[\left(a + \frac{a}{4\pi}\right) - \frac{a}{4\pi} \right] = \frac{a}{2}$$

Thus, we can write the energy gap as:

$$E_g = U_1 + \frac{2}{a} \int_0^a \sum_{n>1} U_n \cos\left(n \frac{2\pi}{a} x\right) \cos\left(\frac{2\pi}{a} x\right) dx \quad (7.12)$$

Although it is not necessarily obvious, the other terms cancel. This can be seen by using various trigonometric identity substitutions. Doing so, and performing the integration yields:

$$E_g = U_1 + \sum_{n>1} U_n \frac{2n \cos(n\pi) \sin(n\pi)}{\pi(n^2 - 1)} \quad (7.13)$$

Thus, the sum cancels since for all $n \in \mathbb{Z}; n > 1$, $\sin(n\pi) = 0$.

Thus, the final solution to the energy gap is:

$$E_g = U_1 \quad (7.14)$$

Thus, the energy gap is simply the first Fourier coefficient of the potential.

This result is completely general, but it is only true **at** the zone boundary. Elsewhere, we need to consider all the coefficients.

We can generalise this argument: the magnitude of the energy gap at the reciprocal lattice vector \vec{G} is $U_{\vec{G}}$.

7.4 Kronig-Penney Model

In this model the potential is approximated by a periodic array of square wells. In the limit of infinitely narrow wells we can obtain an exact solution easily.

Let $U(x)$ be a Dirac-delta function, with weight U_0 .

$$U(x) = U_0 a \sum_s \delta(x - sa) \quad (7.15)$$

We can show by this model that U_G are simply U_0 . This result is true for all the Fourier coefficients

Under this model, all the band gaps are the same size.

7.5 Bloch Model

This is a **very** important theorem in physics, and is invaluable in solid state physics. Bloch's theorem concerns a general solution of the Schrödinger equation for a periodic potential:

$$\psi(\vec{r}) = u_k(\vec{r}) e^{i\vec{k}\cdot\vec{r}} \quad (7.16)$$

Where: $u_k(\vec{r})$ is a periodic function satisfying $u_k(\vec{r} + \vec{T}) = u_k(\vec{r})$.

There is a simple proof for this form for a non-degenerate case.

Assume that a 1-dimensional wavefunction satisfies periodic boundary conditions:

$$\psi(x + Na) = \psi(x) \quad (7.17)$$

This 1-dimensional case is easily generalised. We can make the case general by considering the limit $N \rightarrow \infty$.

We want to look for solutions of equation (7.17) that factorise to separate their lattice periodicity:

$$\psi(x+a) = C(x)\psi(x) \tag{7.18}$$

This is a general solution, since the choice of $C(x)$ is arbitrary.

Applying the periodic boundary condition from equation (7.17):

$$\psi(x+Na) = C(x)^N \psi(x) = \psi(x) \tag{7.19}$$

Thus, we have $C(x)^N = 1$, which means that $C(x) = \sqrt[N]{1}$. Since we have not made any assumption on $C(x)$, then we can write $C(x)$ as the complex equation:

$$C(x) = e^{2\pi i \frac{s}{N}} \tag{7.20}$$

Where $s \in \{0, 1, 2, \dots, N-1\}$

Now, let us choose a periodic function $u(x)$ such that:

$$\psi(x) = u(x) e^{2\pi i \frac{s}{Na} x} \tag{7.21}$$

Now, check that this satisfies periodicity:

$$\psi(x+a) = u(x+a) e^{2\pi i \frac{s}{Na}(x+a)} = \underbrace{e^{2\pi i \frac{s}{N}}}_{C(x)} u(x) \underbrace{e^{2\pi i \frac{s}{Na} x}}_{\psi(x)} \tag{7.22}$$

So, equation (7.22) has the form of equation (7.18), as expected.

This type of wavefunction is called a ***Bloch function***.

In the limit of $N \rightarrow \infty$, we can consider the discrete variable $2\pi \frac{s}{Na}$ to be a continuous variable k .

Thus, we can write the wavefunction in equation (7.21) as:

$$\psi(x) = u(x) e^{ikx} \tag{7.23}$$

For a three dimensional case, we return to the form of equation (7.16).

We have generally considered k to be of this form when we have attempted to model a crystal with periodic boundary conditions.

Note:

These Bloch functions are considerably more general than strictly periodic functions.

We can consider a Bloch function as a wavefunction with a periodic component modulated by a continuously varying phase that represents the wave.

In three dimensions, the wave has 3 components.

We can assemble the Bloch waves into “wave packets”, just as with plane waves.

Bloch waves account for the fact that the wavefunction varies quickly inside the atomic core, but still keeps its long-range coherence.

a) Illustration of Bloch Waves

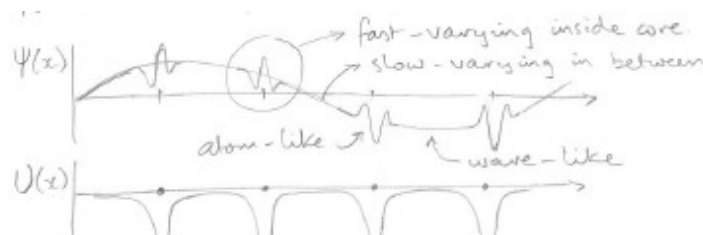


Figure 7.1: a) The Bloch wavefunction as a function of position. Near the ion cores, the wavefunction behaves like in an atom. b) Variation of the potential energy in the field of the ion cores.

The wavefunction of the Bloch wave does **not** have to be an exact solution of the Schrödinger equation inside every core, just within a multiple of the phase factor.

This can be seen as a hybrid solution. Near the atomic cores, the wavefunction is atomic-like, whereas between the cores, the function behaves more like a wave.

We can use this information to explain why electrons do not appear to “see” the nuclei in the metal:

1. Every nucleus has a large, localised potential that strongly influences the wave;
2. At the same time, every nucleus behaves the same, so the phase shift in ψ is the same for each core;
3. Summed over the entire lattice, the phase shifts satisfy the long-range periodic constraint in equation (7.19).

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Thus, in a periodic lattice, the electrons behave as Bloch waves, in an “invisible” lattice.

If there are any defects, such as a lattice vacancy or an atom in an interstitial site, or there is an impurity, or merely an atom out of position due to thermal excitation, then a strong scattering event will occur.

7.6 Electron Bands in 3-Dimensions

Even when we just consider a free electron case, the combined effects of the spherical energy contours with geometrically square reciprocal space lead to a very complicated picture.

The *reduced zone scheme* involves a linear mapping of all energy and wavevectors into the first Brillouin zone.

We showed before that for an umklapp process: $\vec{k}' = \vec{k} + \vec{G}$. We can subtract a reciprocal lattice vector \vec{G} from some \vec{k} in order to translate it into the first Brillouin zone.

In 1-dimension, we have:

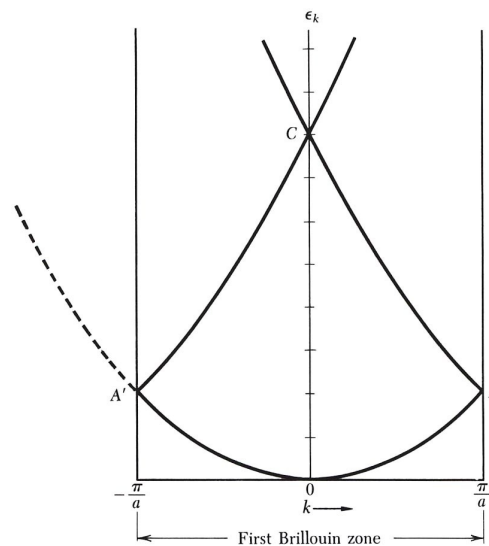


Figure 7.2: Energy-wavevector relation for free electrons in the reduced zone scheme. The branch AC, if displaced by $2\pi/a$ gives the usual curve for negative k in the extended zone scheme, as indicated by the dashed line.

In three dimensions, we need to add more bands, corresponding to the other two dimensions:

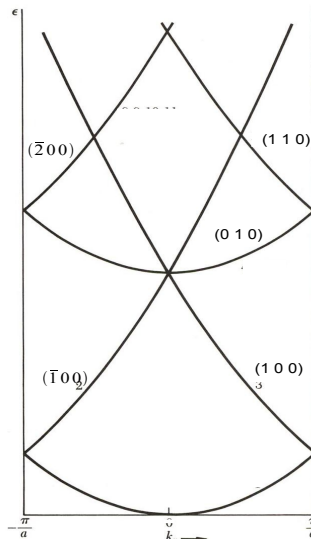


Figure 7.3: Reduced zone scheme for three-dimensions, plotted over $(k_x, 0, 0)$

In all cases, the band gaps open at the zone boundary and the centre of the zone, with $E_g = U_G$.

7.7 Tight Binding Method

This is one of several methods for general calculation of the band-structure.

We will start with neutral, separated atoms, and consider how the energy levels change as the charge-distributions of adjacent atoms overlap as the atoms are brought together to form a crystal.

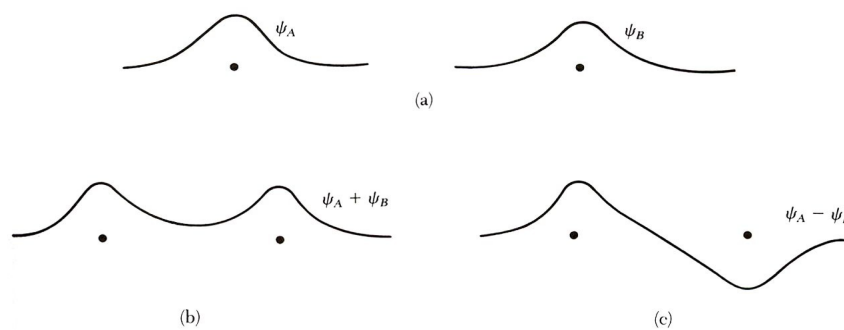


Figure 7.4: a) Schematic drawing of wavefunctions of electrons of two hydrogen atoms with large separation. b) Ground state wavefunction at closer separation (bonding). c) Excited state wavefunction (anti-bonding).

Consider the s-orbitals of two adjacent neighbours.

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When two atoms are brought together, their wavefunctions will overlap. The combined wavefunction will be of the form $\psi_A \pm \psi_B$. These are called **bonding** (+) and anti-bonding (-) orbitals.

An electron in an anti-bonding orbital has **higher** energy than the bonding orbital.

An electron in the bonding orbital spends part of the time in the region midway between two nuclei, and in this region it feels the attractive potential of both nuclei at once, increasing its binding energy.

In the anti-bonding orbital, the probability density vanishes at the midway point, so this extra binding does not occur.

a) Calculating Energy Bands

Suppose the ground state of an electron moving in a potential $U(\vec{r})$ of an isolated atom is given by $\phi(\vec{r})$, which is an s-orbital.

If the influence between atoms is small, we can approximate the wavefunction of an electron in the entire crystal as:

$$\psi_{\vec{k}}(\vec{r}) = \sum_j C_{\vec{k}j} \phi(\vec{r} - \vec{r}_j) \quad (7.24)$$

Where the summation is over all lattice points in the crystal.

We have assumed that the primitive lattices comprises one atom.

This function will be of the form of a Bloch wave if, for a crystal comprising N atoms, the normalised coefficients are:

$$C_{\vec{k}j} = N^{-\frac{1}{2}} e^{i\vec{k} \cdot \vec{r}_j} \quad (7.25)$$

Thus, the (normalised) Bloch wavefunction is given by:

$$\psi_{\vec{k}}(\vec{r}) = N^{-\frac{1}{2}} \sum_j \exp(i\vec{k} \cdot \vec{r}_j) \phi(\vec{r} - \vec{r}_j) \quad (7.26)$$

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Let us prove that equation (7.26) is of the form of a Bloch wave by consider a translation \vec{T} between two lattice points:

$$\psi_{\vec{k}}(\vec{r} + \vec{T}) = N^{-\frac{1}{2}} \sum_j \exp(i \vec{k} \cdot \vec{r}_j) \phi(\vec{r} + \vec{T} - \vec{r}_j)$$

$$\psi_{\vec{k}}(\vec{r} + \vec{T}) = \exp(i \vec{k} \cdot \vec{T}) N^{-\frac{1}{2}} \sum_j \exp[i \vec{k} \cdot (\vec{r}_j - \vec{T})] \phi[\vec{r} - (\vec{r}_j - \vec{T})]$$

By definition of the translational vector \vec{T} both \vec{r}_j and $\vec{r}_j - \vec{T}$ are lattice vectors, and so this is simply:

$$\psi_{\vec{k}}(\vec{r} + \vec{T}) = \exp(i \vec{k} \cdot \vec{T}) N^{-\frac{1}{2}} \sum_j \exp(i \vec{k} \cdot \vec{r}_j) \phi(\vec{r} - \vec{r}_j) = \exp(i \vec{k} \cdot \vec{T}) \psi_{\vec{k}}(\vec{r})$$

This is exactly the Bloch condition, as we expected.

We can find the first-order energy by determining the diagonal matrix elements of the Hamiltonian of the crystal:

$$\langle \vec{k} | H | \vec{k} \rangle = N^{-1} \sum_j \sum_m \exp[i \vec{k} \cdot (\vec{r}_j - \vec{r}_m)] \langle \phi_m | H | \phi_j \rangle \quad (7.27)$$

Where: $\phi_m \equiv \phi(\vec{r} - \vec{r}_m)$.

Let $\vec{\rho}_m \equiv \vec{r}_m - \vec{r}_j$. Then, using the periodicity of the lattice, we have:

$$\langle \vec{k} | H | \vec{k} \rangle = \sum_m \exp(-i \vec{k} \cdot \vec{\rho}_m) \langle \phi'_m | H | \phi \rangle \quad (7.28)$$

Where: $\phi'_m \equiv \phi(\vec{r} - \vec{\rho}_m)$ and $\phi \equiv \phi(\vec{r})$.

Now, we will neglect all terms except those corresponding to the same atom and those between nearest neighbours, connected by $\vec{\rho}$. In a symmetric crystal, all these neighbours will have the same matrix element.

Let $\phi' \equiv \phi(\vec{r} - \vec{\rho})$.

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We can write the matrix elements of the atom and its nearest neighbour as:

$$\langle \phi | H | \phi \rangle = -\alpha \quad (7.29)$$

$$\langle \phi' | H | \phi \rangle = -\gamma \quad (7.30)$$

Finally, substituting equations (7.29) and (7.30) into (7.28) gives the energy bands as:

$$\epsilon_{\vec{k}} = \langle \vec{k} | H | \vec{k} \rangle = -\alpha - \gamma \sum_m \exp(-\vec{k} \cdot \vec{\rho}_m) \quad (7.31)$$

Note:

γ are known as *overlap integrals* (we saw these in the 2nd year when we considered energy levels).

$\vec{\rho}_m$ correspond to the positions of the nearest neighbour atoms in the lattice.

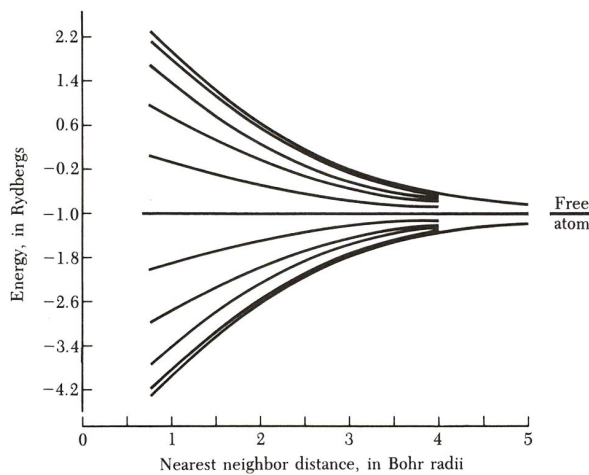


Figure 7.5: The 1s band of a ring of 20 hydrogen atoms. The graph shows the one-electron energy calculated by the tight-binding approximation using the nearest-neighbour overlap integral.

b) Special Cases of Energy Bands

Simple Cubic

This has nearest neighbours at:

$$\vec{\rho}_m = (\pm a, 0, 0); (0, \pm a, 0); (0, 0, \pm a)$$

This means that the energy band is given by:

$$\epsilon_{\vec{k}}(k_x, k_y, k_z) = -\alpha - 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a) \quad (7.32)$$

At the zone centre:

$$\epsilon_{\vec{k}}(0, 0, 0) = -\alpha - 2\gamma(3\cos 0) = -\alpha - 6\gamma$$

And at the furthest (positive) zone boundary:

$$\epsilon_{\vec{k}}(\pi/a, \pi/a, \pi/a) = -\alpha - 2\gamma(3\cos \pi) = -\alpha + 6\gamma$$

Thus, the bandwidth is:

$$\Delta \epsilon = 12\gamma \quad (7.33)$$

BCC Structure

There are 8 nearest neighbours in the bcc structure.

The energy band is given by:

$$\epsilon_{\vec{k}}(k_x, k_y, k_z) = -\alpha - 8\gamma \left[\cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) \right] \quad (7.34)$$

At centre of zone:

$$\epsilon_{\vec{k}}(0, 0, 0) = -\alpha - 8\gamma(\cos 0)^3 = -\alpha - 8\gamma$$

At the zone boundary:

$$\epsilon_{\vec{k}}(0, 0, 2\pi/a) = -\alpha - 8\gamma(\cos(0)^2 \cos(\pi)) = -\alpha + 8\gamma$$

Thus, the bandwidth is:

$$\Delta \epsilon = 16 \gamma \quad (7.35)$$

FCC Structure

There are 12 nearest neighbours in the fcc lattice.

The energy band is given by:

$$\epsilon_k = -\alpha - 4\gamma \left[\cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_z a}{2}\right) \cos\left(\frac{k_x a}{2}\right) + \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \right] \quad (7.36)$$

Thus, the bandwidth is:

$$\Delta \epsilon = 24 \gamma \quad (7.37)$$

7.8 Pseudopotential Methods

This is especially useful for heavy elements.

Take the 5s orbital of Rb ($Z = 36$). This has four radial nodes. The p and d -orbitals have a strong angular structure with positive and negative lobes.

The resulting Bloch waves are unnecessarily complicated.

However, we can simplify this because the cores of the ions have little overlap between sites. Thus, to a very good approximation, we can replace the potential of the core region with an effective potential or *pseudopotential* that gives the same wavefunctions outside the core as are given by the ion cores themselves.