Electrons in a weak periodic potential

Assumptions:

1. Static defect-free lattice – perfectly periodic potential.
2. Weak potential – perturbative effect on the free electron states.

Perfect periodicity of the lattice potential implies that any electronic property we deduce will also be influenced by this periodicity.

Bloch states: Average potential at a point is *U(r)*. Assume independent electron picture, the single particle Schrodinger equation is:

$$\mathcal{H}\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + \mathrm{U}(\mathbf{r})\right]\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r})$$

Using Bloch's Theorem; $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}.\boldsymbol{r}}u_k(\boldsymbol{r})$ with $u_k(\boldsymbol{r})$ periodic in the lattice i.e.

$$u_k(\boldsymbol{r}) = u_k(\boldsymbol{r} + \boldsymbol{R})$$

Note that

$$\psi_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{R}) = e^{i\boldsymbol{k}.(\boldsymbol{r}+\boldsymbol{R})}u_k(\boldsymbol{r} + \boldsymbol{R}) = e^{i\boldsymbol{k}.R}\psi_{\boldsymbol{k}}(\boldsymbol{r})$$

implying $\psi_{\boldsymbol{k}}(\boldsymbol{r})$ is not periodic in the real lattice. But ant measurable property will depend on$|\psi_{\boldsymbol{k}}(\boldsymbol{r})|^2 = |u_k(\boldsymbol{r})|^2$ which is periodic in the real lattice.

$u_k(\boldsymbol{r})$ is called the Bloch function. In terms f the Bloc function the Schrodinger equation becomes,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \mathrm{U}(\mathbf{r})\right]e^{i\boldsymbol{k}.\boldsymbol{r}}u_k(\boldsymbol{r}) = \varepsilon_k e^{i\boldsymbol{k}.\boldsymbol{r}}u_k(\boldsymbol{r})$$

or

$$\left[\frac{\hbar^2k^2}{2m} - i\frac{\hbar^2}{m}\boldsymbol{k}.\boldsymbol{\nabla} - \frac{\hbar^2}{2m}\nabla^2 + \mathrm{U}(\mathbf{r})\right]u_k(\boldsymbol{r}) = \varepsilon_k u_k(\boldsymbol{r})\text{----(1)}$$

or

$$\left[\frac{1}{2m}\,(-i\hbar\boldsymbol{\nabla} + \hbar\boldsymbol{k})^2 + \mathrm{U}(\mathbf{r})\right]u_k(\boldsymbol{r}) = \varepsilon_k u_k(\boldsymbol{r})\text{----- (2)}$$

This equation is difficult to solve for any general potential *U(r)* – the periodicity of the lattice lets us see some general features of the solution even without solving.

A. *Quantization of k*: Because of the lattice periodicity it is enough to solve the equation in one primitive cell of the reciprocal lattice thus independent **k** values will have to be confined to the first Brillouin zone $(-\frac{\pi}{a} < k < \frac{\pi}{a})$ - the values of k will be quantized to $\frac{\pi}{L}n$, n being and integer.
B. *How many values of k relevant*: The total number of independent values of k =L/a=N, the number of lattice sites.
C. *Significance of k:*

$$\boldsymbol{p}\psi(\boldsymbol{r}) = -i\hbar\boldsymbol{\nabla}\left(e^{i\boldsymbol{k}.\boldsymbol{r}}u_k(\boldsymbol{r})\right) = \hbar\boldsymbol{k}\psi(\boldsymbol{r}) - \boldsymbol{i}\hbar\boldsymbol{e}^{i\boldsymbol{k}.\boldsymbol{r}}\boldsymbol{\nabla}u_{\boldsymbol{k}}(\boldsymbol{r})$$

implying that the Bloch state is not an eigen state of the momentum operator – this is expected as the translational invariance of the system is broken by the lattice potential. $\boldsymbol{k}$ is called the 'crystal momentum' – it determines the transition rules in scattering problems (we shall see this later in the course when we do phonons)- it also determines the phase factor the wave function picks up as it moves by a lattice translation vector

$$\psi(\boldsymbol{r}+\boldsymbol{R}) = e^{i\boldsymbol{k}.\boldsymbol{R}}\psi(\boldsymbol{r})$$

D. <u>*Formation of energy bands*</u>: Equation (1) is an eigenvalue problem in a box (the primitive lattice) – for a given value of $\boldsymbol{k}$ there will be an infinite number of discrete values of the energy ε_{nk} with the corresponding eigenfunction $\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}.\boldsymbol{r}}u_{n\boldsymbol{k}}(\boldsymbol{r})$. The values of energy for all $\boldsymbol{k}$ for a given *n* form an *energy band*.

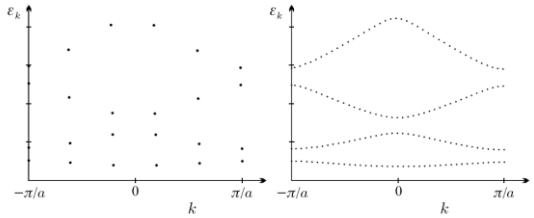

Figure 1:The energy levels of electrons moving in the periodic potential of one dimensional chains made up of 5 and 40 atoms

Note that for a periodic lattice $\boldsymbol{k}$ and $\boldsymbol{k}+\boldsymbol{G}$ denote the same physical states. To see this consider $\boldsymbol{k}'$ outside the 1st Brillouin zone – bring it in using $\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{G}$.

$$\psi_{nk}(\boldsymbol{r}) = e^{i\boldsymbol{k}.\boldsymbol{r}}u_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i(\boldsymbol{k}'-\boldsymbol{G}).\boldsymbol{r}}u_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}'.\boldsymbol{r}}u_{n\boldsymbol{k}'}(\boldsymbol{r})$$

with $u_{n\boldsymbol{k}'}(\boldsymbol{r}) = e^{-i\boldsymbol{G}.\boldsymbol{r}}u_{n\boldsymbol{k}}(\boldsymbol{r})$. Probability of finding an electron at $\boldsymbol{r}$ with 'wave-vector' $\boldsymbol{k}'$ is proportional to $|u_{n\boldsymbol{k}'}(\boldsymbol{r})|^2 = |u_{n\boldsymbol{k}}(\boldsymbol{r})|^2$ which equals to the probability of finding an electron there with 'wave-vector' $\boldsymbol{k} = \boldsymbol{k}' - \boldsymbol{G}$. In this sense the two states $\boldsymbol{k}$ and $\boldsymbol{k}'$are equivalent. For example consider the energy eigenvalues for ε_{nk} and $\varepsilon_{n(k+G)}$. Energy in the state $\boldsymbol{k}'$is given by:

$$\left[\frac{\hbar^2 k'^2}{2m} - i\frac{\hbar^2}{m}\boldsymbol{k}'.\boldsymbol{\nabla} - \frac{\hbar^2}{2m}\nabla^2 + \mathrm{U}(\mathbf{r})\right]u_{n\boldsymbol{k}'}(\boldsymbol{r}) = \varepsilon_{n\boldsymbol{k}'}u_{n\boldsymbol{k}'}(\boldsymbol{r})$$

Substitute $\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{G}$ and use $u_{n\boldsymbol{k}'}(\boldsymbol{r}) = e^{-i\boldsymbol{G}.\boldsymbol{r}}u_{n\boldsymbol{k}}(\boldsymbol{r})$ to get

$$\left[\frac{\hbar^2 k^2}{2m} - i\frac{\hbar^2}{m}\boldsymbol{k}.\boldsymbol{\nabla} - \frac{\hbar^2}{2m}\nabla^2 + \mathrm{U}(\mathbf{r})\right]u_{n\boldsymbol{k}}(\boldsymbol{r}) = \varepsilon_{n\boldsymbol{k}'}u_{n\boldsymbol{k}}(\boldsymbol{r})$$

which tells us that $\varepsilon_{nk} = \varepsilon_{n(k+G)}$ – all equivalent states are associated with the same energy eigenvalue.

<u>Nearly free electron approximation – Empty lattice approximation</u>: Take the Sommerfeld free electron states – treat the lattice as a weak perturbation - free electron states smoothly evolve into the Bloch states as the potential is slowly turned on – we shall see later that the free electron states and the Bloch states in a weak periodic potential differ appreciably only at the centre and at the ends of the Brillouin zones – hence this approach is justified *post priori*.

Writing the potential and the Bloch function in terms of their Fourier components:

$$u_{nk}(\boldsymbol{r}) = \sum_{\boldsymbol{G_j}} c_{\boldsymbol{nk}}(\boldsymbol{G_j}) e^{i\boldsymbol{G_j}.\boldsymbol{r}}$$

and

$$\mathrm{U}(\boldsymbol{r}) = \sum_{\boldsymbol{G_j}} \boldsymbol{U}(\boldsymbol{G_j}) e^{i\boldsymbol{G_j}.\boldsymbol{r}}$$

Substitute it in equation (1), multiply form left by $e^{-i\boldsymbol{G_i}.\boldsymbol{r}}$ and integrate over the volume of the primitive cell to get

$$\left[\frac{\hbar^2}{2m}(\boldsymbol{k}+\boldsymbol{G}_i)^2 - \varepsilon_{nk}\right] c_{nk}(\boldsymbol{G_i}) + \sum_{\boldsymbol{G_j}} U(\boldsymbol{G}_i - \boldsymbol{G}_j)\boldsymbol{c_{nk}}(\boldsymbol{G}_j) = 0$$

In the limit $U \to 0$; the solutions are either

$$c_{\boldsymbol{nk}}(\boldsymbol{G}_i) = 0$$

or

$\varepsilon_{nk} = \frac{\hbar^2}{2m}(\boldsymbol{k}+\boldsymbol{G}_n)^2$ for a particular value of $G_i = G_n$.

The solution in the empty lattice for the band of index *n* is therefore particularly simple: apart from a single $\boldsymbol{G_n}$, all reciprocal-lattice vectors have vanishing coefficients in the expansion. The normalized Bloch function of this state is then

$$\psi_{nk}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}.\boldsymbol{r}} e^{i\boldsymbol{G}_n.\boldsymbol{r}}$$

Thus there is a direct one-to-one correspondence between the band indices *n* and the reciprocal lattice vectors $\boldsymbol{G_n}$.

Band structure of electron in a 1-D lattice

Lattice length L, lattice spacing $a = L/N$. The allowed values of $k = m\frac{2\pi}{L}$ with $-\frac{\pi}{a} < k < \pi/a$; with $-\frac{N}{2} < m < \frac{N}{2}$. $G_n = n\frac{2\pi}{a}$. In the empty lattice approximation:

$$\varepsilon_{nk} = \frac{\hbar^2}{2m}(\boldsymbol{k}+\boldsymbol{G}_n)^2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 (m+nN)^2$$

This looks different form the free electron energy derived using Sommerfeld model,

$$\varepsilon_k = \frac{\hbar^2}{2m}k^2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 m^2$$

The apparent difference becomes clear below.

Different zone schemes:

a. Reduced zone scheme: All the bands are drawn in the first Brillouin zone. (see Figure 2).
b. Repeated/periodic zone scheme: Every band is drawn in every Brillouin zone (see Figure 3).
c. Extended-zone scheme: Different bands are drawn in different Brillouin zones (see Figure 4).

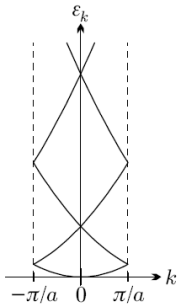

Figure 2: Dispersion relation of free electrons in empty lattice approx in reduced zone representation.

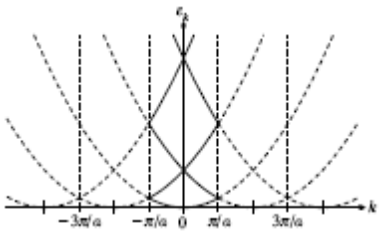

Figure 3: Dispersion relation of free electrons in empty lattice approx in repeated zone scheme

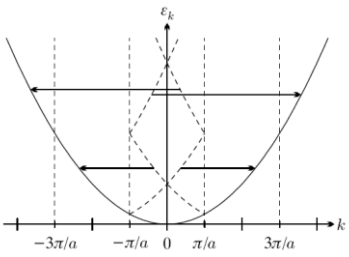

Figure 4: Dispersion relation of free electrons in empty lattice approx in extended zone scheme

The infinite number of solutions associated with a given $\boldsymbol{k}$ can also be distributed among the infinite number of vectors $\boldsymbol{k} + \boldsymbol{G}$ in such a way that one solution should belong to each equivalent vector. The reciprocal lattice can be broken up into Brillouin zones of different orders using the same procedure for creating Wigner-Seitz cell. The assignment of the states to the zones is then done simply by assigning the states of the first band to the wave vectors in the first Brillouin zone, the states of the second band to the wave vectors in the second Brillouin zone, and so forth. This is how the *extended-zone scheme* is obtained.

Conversely energy eigenvalues of the electrons moving through the empty lattice for a given *k* values in the reduced zone scheme can be got from the free-electron dispersion curve by finding the equivalent *k* values inside the first Brillouin zone for each wave number outside of it, and then shifting the energy eigenvalue to this *k* value. This procedure is called *zone folding*.

Fermi surface in empty lattice approximation: Fermi-Dirac statistics determine the filling of the energy levels – Fermi surface important as properties of metals are determined by the electronic density of states at these points - dispersion relation obtained in the extended-zone scheme in the empty lattice approximation is identical to the quadratic dispersion relation of free electrons - the *n*th band is the part of the free-electron spectrum that falls into the *n*th Brillouin zone.

Band structure of electron in a 2-D lattice

Lattice constant a, z electrons per site, N sites – total number of electrons $N_e = zN$. k_F is determined by $2\pi {k_F}^2 \, (L/2\pi)^2 = zN$; giving $k_F = \sqrt{(2z/\pi)}\pi/a$

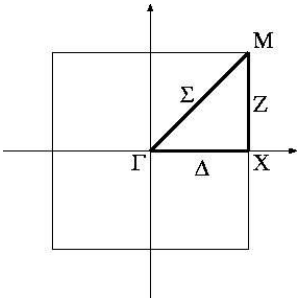

Figure 5: Special points in 2-D Brillouin zone

For $z = 1, k_F = \sqrt{\frac{2}{\pi}\frac{\pi}{a}} < \frac{\pi}{a}$, the boundary of the 1st Brillouin zone. So the Fermi surface lies entirely inside the 1st Brillouin zone.

For $z = 2, k_F = 2\sqrt{\frac{1}{\pi}\frac{\pi}{a}} > \frac{\pi}{a}$, the boundary of the 1st Brillouin zone. In this case k_F is larger than the distance ΓX but smaller than the distance ΓM. Thus, when the lowest-energy states are filled gradually by electrons in the ground state (as required by the Fermi–Dirac statistics), the lowest-lying states in the second band becomes occupied before the highest-lying states in the first band.

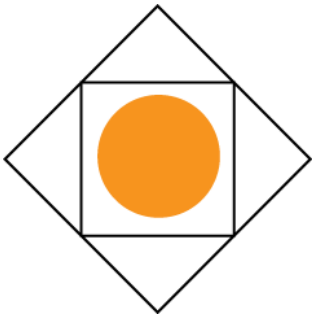

Figure 6: Fermi surface for z=1

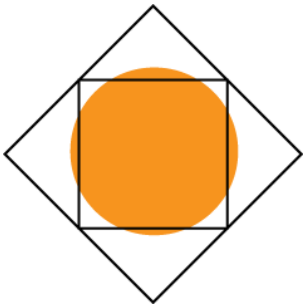

Figure 7: Fermi surface for z=2

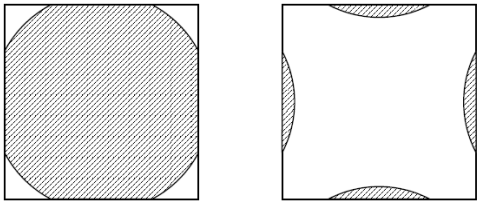

Figure 8: Band structure for z=2 in 2-D lattice in reduced zone scheme

For the case $z = 2$, in reduced zone representation, the Fermi surfaces forms discontinuous structure for the 1st and 2nd band. If the wave vectors are reduced about the points M or X rather than Γ then the 1st and 2nd bands form continuous Fermi surfaces – the 1st band is hole-like and the 2nd band is electron-like.

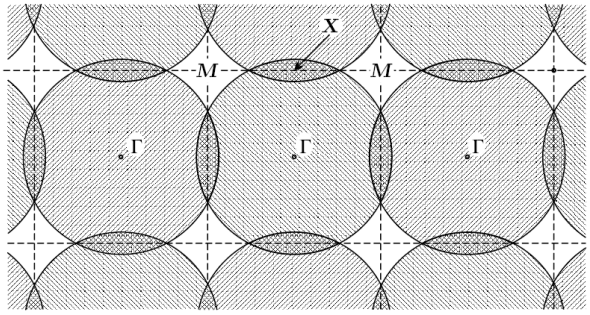

Figure 9: Band structure for z=2 in 2-D lattice in repeated zone scheme

In repeated/periodic zone scheme the n^{th} band is formed of those regions where circles from at least n different zones overlap.

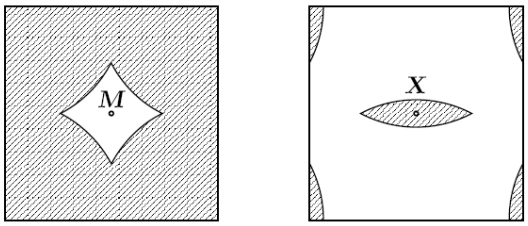

Figure 10: z=2 case reduced about the *M* and *X* points

The bands thus formed can be electron-like or hole-like depending on whether they enclose a filled area or an empty area. Note that in a magnetic field electrons will move along a constant energy surface (remember: magnetic field does not do any work on a moving charge). For a free electron

$$\hbar\frac{d\boldsymbol{k}}{dt} = -e\boldsymbol{v}\times\boldsymbol{B} = -\frac{e}{\hbar}\nabla_{\mathbf{k}}\varepsilon\times\mathbf{B}$$

Particles in electron-like Fermi surface (Figure 11.b) move in a sense opposite to that in hole-like orbits (Figure 11.a).

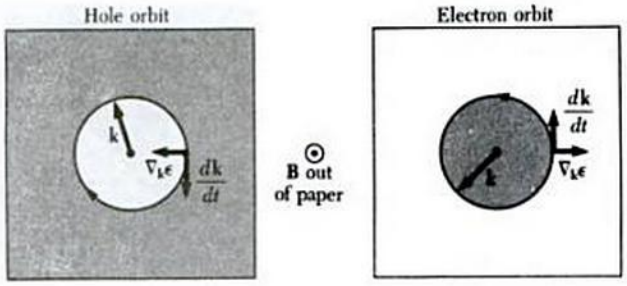

Figure 11: hole-like and electron-like orbits

Band structure of simple cubic lattice with monatomic basis

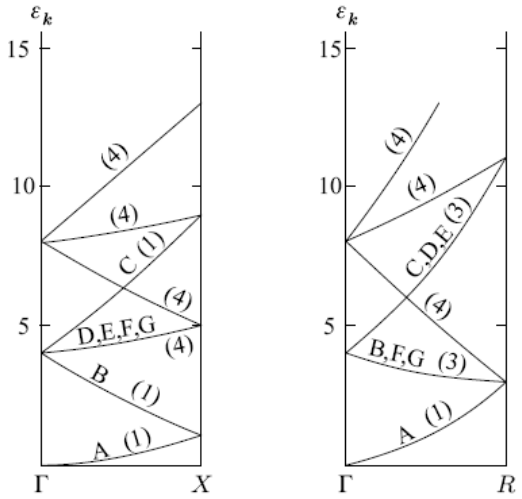

Figure 12: band diagram for simple cubic along two symmetry directions

Figure 12.a is for wave vectors along the line Δ connecting the centre Γ = (0, 0, 0) of the Brillouin zone and $X = (\pi/a)(0, 0, 1)$. The numbers represent the degeneracy of the bands. We

will calculate the energy of the state associated with the wave vector $\left(\frac{\pi}{a}\right)(0,0,k); 0 < k < 1$

Remember the energy is given by $\varepsilon_{nk} = \frac{\hbar^2}{2m}(\boldsymbol{k} + \boldsymbol{G}_n)^2$

The various bands are:

Band A: $G = 0$ $\varepsilon_A = \frac{\hbar^2}{2m}(\boldsymbol{k} + \boldsymbol{G}_n)^2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 k^2$

Band B: $G = \frac{2\pi}{a}(0,0,\bar{1})$ $\varepsilon_B = \frac{\hbar^2}{2m}(\boldsymbol{k} + \boldsymbol{G}_n)^2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 (k-2)^2$

Band C: $G = \frac{2\pi}{a}(0,0,1)$ $\varepsilon_C = \frac{\hbar^2}{2m}(\boldsymbol{k} + \boldsymbol{G}_n)^2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 (k+2)^2$

Band D,E,F,G: $G = \frac{2\pi}{a}(1,0,0), \frac{2\pi}{a}(\bar{1},0,0), \frac{2\pi}{a}(0,1,0), \frac{2\pi}{a}(0,\bar{1},0)$ $\varepsilon_C = \left(\frac{\pi}{a}\right)^2 (k^2+4)$. This band is 4-fold degenerate

Figure 12.b is for wave vectors along the line Λ connecting the centre *Γ* = (0, 0, 0) of the Brillouin zone and *R* = (*π/a*)(1, 1, 1).

Assignment problem: Calculate Figure 12b

Effect of weak lattice potential on the free electron dispersion relation

Treat *U* to be a weak perturbation – need not solve the equation – can get the result applying perturbation theory to the *U*=0 case of free electrons. The results vary appreciably from the free electron model only near the centre and the edges of the Brillouin zones. Take the simple example of system of electrons in a very weak 1-D periodic lattice. At the edge of the Brillouin zone $\left(k = \pm n\frac{\pi}{a}\right)$ the condition for Bragg reflection is satisfied. [Recall: Bragg condition $k = |\boldsymbol{k} - \boldsymbol{G}|$ in 1-D is $k = \pm G/2 = \pm n\pi/a$.] Hence electrons with wave vector at the Brillouin zone edge ($k = \pm\frac{n\pi}{a}$) form standing waves – solutions linear superposition of left moving and right moving waves - two different solutions can be formed from the linear combination of the left-moving $e^{ikx} = e^{i\frac{\pi}{a}x}$ and the right-moving waves $e^{-ikx} = e^{-i\frac{\pi}{a}x}$ –

$$\psi_+ = \frac{e^{i\frac{\pi}{a}x} + e^{-i\frac{\pi}{a}x}}{\sqrt{2}} = \sqrt{2}\cos\left(\frac{\pi x}{a}\right)$$

$$\psi_- = \frac{e^{i\frac{\pi}{a}x} - e^{-i\frac{\pi}{a}x}}{\sqrt{2}} = \sqrt{2}i\sin\left(\frac{\pi x}{a}\right)$$

ψ_+ and ψ_- are the symmetric and anti-symmetric solutions respectively. Charge density associated with ψ_+ is

$$\rho_+ \propto |\psi_+|^2 \propto cos^2\left(\frac{\pi x}{a}\right)$$

Similarly

$$\rho_- \propto |\psi_-|^2 \propto sin^2\left(\frac{\pi x}{a}\right)$$

Density of electrons for ψ_+ maximum near $x = 0, a, \ldots$. *i.e.* at the lattice sites where the potential energy is minimum. Similarly density of electrons for ψ_- maximum near $x = \frac{a}{2}, \frac{3a}{2}$ .... *i.e.* in between the lattice sites where the potential energy is maximum. So the

energies of the two states at the Brillouin zone edge are no longer degenerate – they differ in energies –a band gap opens up of magnitude E_g just below the gap the state is ψ_+ and just above the gap the state is ψ_-.

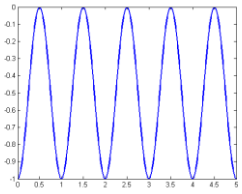

Figure 13: potential energy of electrons in a 1D lattice

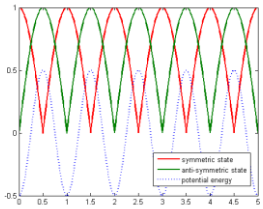

Figure 14: Energy of symmetric and anti-symmetric electronic states at the Bragg plane

Estimate of E_g: Write the potential energy of the electrons as $U(x) = -U_0 \cos\left(\frac{2\pi x}{a}\right)$. The first order difference in the energy between the two states is

$$E_g = \int_0^a dx\, U(x)\,(|\psi_-|^2 - |\psi_+|^2) = U_0$$

So the band-gap is the Fourier component of the potential energy.

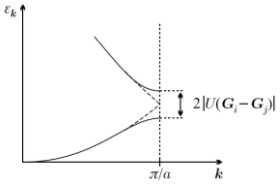

Figure 15: Appearance of band-gap at the Brillouin zone edge

Note: at zone boundaries we have standing waves – group velocity $v_g = \partial\varepsilon/\partial k$=0 implying that the slope of the dispersion relation vanishes at the zone boundary.

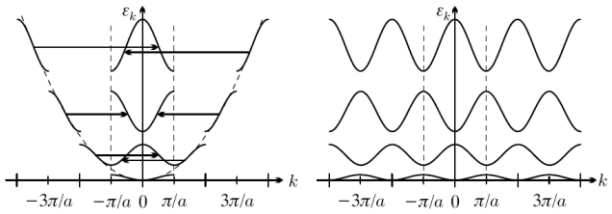

Figure 16: Band structure of nearly free electrons in extended zone scheme and repeated zone scheme

The constant energy surfaces are spherical in the free-electron approximation. In the case of electrons in a weak periodic potential, the surfaces are no longer spherical – they are distorted as the Brillouin edge is approached.

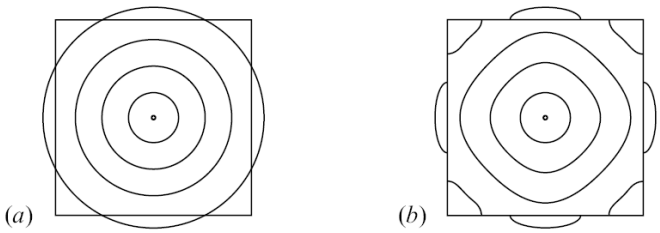

Figure 17: constant energy surfaces for (a) free electrons and (b) electrons in a weak periodic potential