

# Review of Electronic structure of metals

*See Kittel, Ashcroft, ....*

## Sommerfeld theory of metals – Electron in a box

Like the Drude theory it assumes that electrons move freely inside the metal. However, the electrons behave as quantum particles and obey Fermi –Dirac statistics. This leads to the important fundamental concept of **electron in a box**.

The Schrödinger equation governs the motion of the electrons:

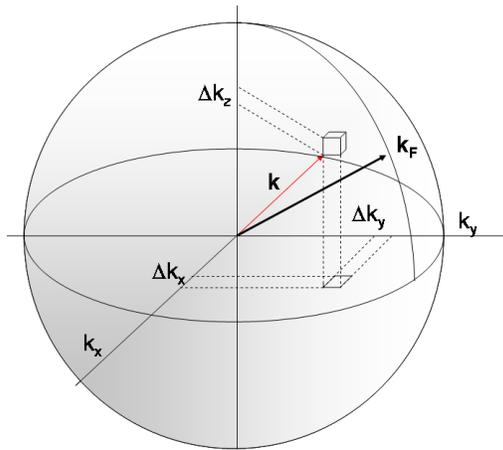
$$-\frac{\hbar^2}{2m} \cdot \nabla^2 \psi(\mathbf{r}) = \mathbf{E} \cdot \psi(\mathbf{r})$$

Which has as solutions plane waves:  $\Psi(\mathbf{r},t) = \psi_0 \cdot e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$ , with energy  $E = \hbar^2 k^2 / 2m$

*Periodic boundary conditions:*

$e^{ik_x L_x} = 1 \rightarrow k_x L_x = 2\pi n$ , and similar conditions for y and z.  $k_x = 2\pi n / L_x$ , n = integer

The volume per state is  $\Delta k_x \cdot \Delta k_y \cdot \Delta k_z = (2\pi)^3 / V$  and the density of states in k-space is  $V / 8\pi^3$



In each state we can put 2 electrons, with spin up and down (Pauli Exclusion Principle)

At 0K, if the box contains N electrons the sphere in k-space that contains all the occupied states has a radius  $k_F$  called the Fermi wave-vector:

$$\frac{4}{3} \pi k_F^3 \cdot \frac{2V}{8\pi^3} = N, \text{ and using } n = N/V \text{ we get:}$$

$$k_F = (3\pi^2 n)^{1/3}. \text{ Typically } n \sim 10^{22} \text{ cm}^{-3}$$

The Fermi wavelength is  $\lambda_F = 2\pi / k_F$ , and the **Fermi energy**  $E_F = \hbar^2 k_F^2 / 2m$

The volume per electron is  $1/n = 3\pi^2 / k_F^3 = 4/3 \cdot \pi r_s^3$

Typical values:

$k_F = 1.92 / r_s$ , for most metals  $r_s \sim 1 \text{ \AA}$ ;  $k_F \sim 1 \text{ \AA}^{-1}$ ;  $E_F \sim 10 \text{ eV}$ ;  $T_F \sim 10^4 \text{ K}$ ;  $v_F \sim 10^6 \text{ m/s}$   
The mean free path  $l = v_F \cdot \tau = 10^{-8} \text{ m} = 100 \text{ \AA}$ , which is about 100 times larger than the Drude theory value.

## Density of states in 3-dimensions

The density of states as a function of energy,  $D(E)$ , is defined as the number of states with energy  $E$  per unit energy, i.e., the number of states between  $E$  and  $E+dE$  divided by  $dE$

To calculate  $D(E)$  we consider the volume between a sphere of radius  $k$  and a sphere of radius  $k+dk$ , which contains  $4\pi k^2 \cdot dk \cdot (V/8\pi^3)$  states.

Since  $E = \hbar^2 k^2 / 2m \rightarrow dE = \hbar^2 k / m \cdot dk$ .

Substituting we find:

$D(E) = (V/2\pi^2) \cdot (2m/\hbar^2)^{3/2} \cdot E^{1/2}$ , (2 electrons per state).

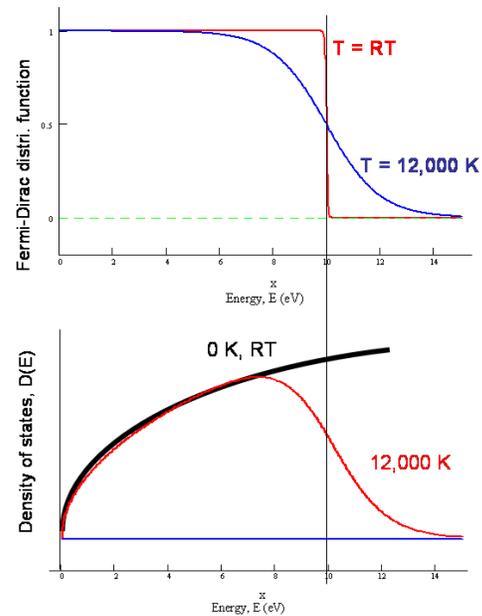
Since  $N = (V/3\pi^2) \cdot (2mE_F/\hbar^2)^{3/2}$

We obtain  $D(E_F) = 3/2 \cdot N/E_F$

This calculation is valid for  $T = 0$  K

$$f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1}$$

Fermi-Dirac statistics :

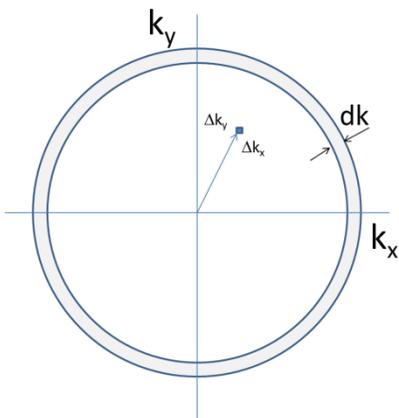


## Density of states in 2-dimensions

We proceed as before but now we have only a square box of sides  $L_x$  and  $L_y$ .

The boundary conditions are similar:  $e^{ik_x L_x} = 1 \rightarrow k_x L_x = 2\pi n$ , with  $n = \text{integer}$ . And similar for  $y$ .

The volume per state is  $\Delta k_x \cdot \Delta k_y = (2\pi)^2 / V$  (where  $V = L_x \cdot L_y = \text{area of the 2-D space}$ ). The density of states in  $k$ -space is therefore  $V/4\pi^2$ .



The density of states in  $k$ -space is:  $2\pi k \cdot dk \cdot 2 \cdot V/4\pi^2$  (2 times because of 2 spins values)

Since  $E = \hbar^2 k^2 / 2m$ ,  $dE = \hbar^2 k / m \cdot dk$

Finally we have:

$$N(E) = V \cdot m / (\pi \hbar^2) = \text{constant}$$

## Density of states in 1-dimension

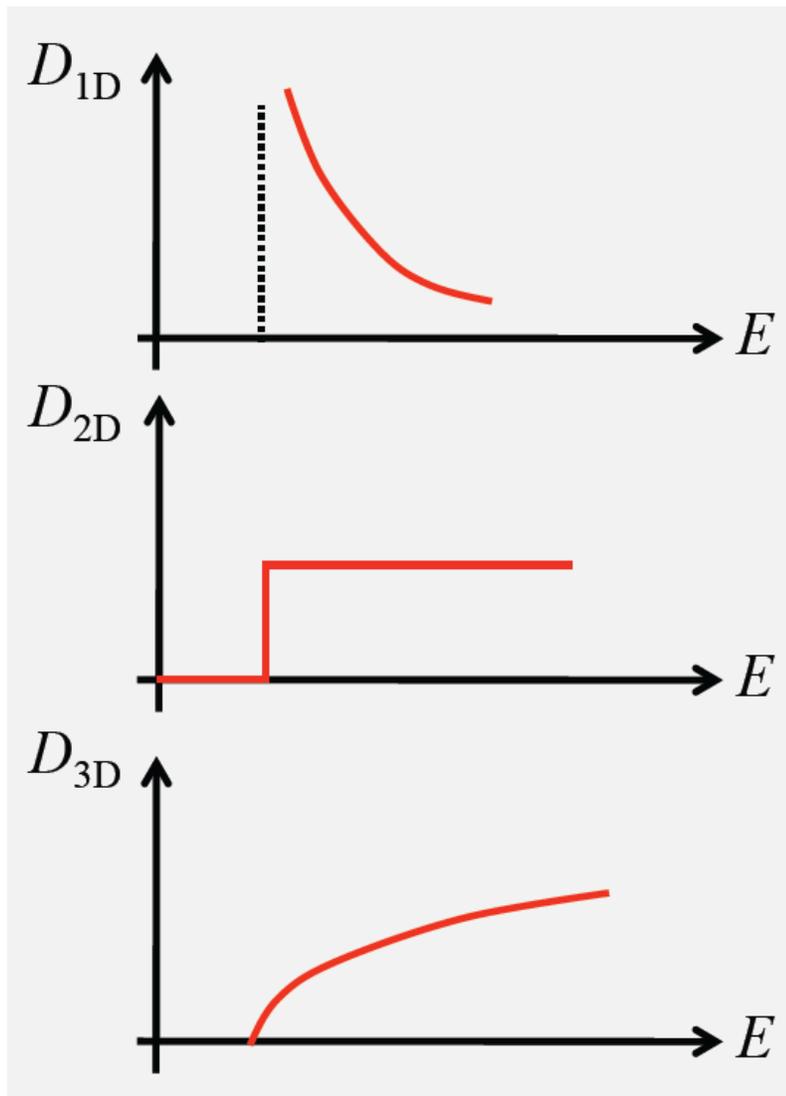
Using similar arguments as before:

$\Delta k_x = (2\pi)/V$  where  $V = L_x$ . The density of states in k-space is:  $2.V/(2\pi).dk$  (again 2 because of spin up and spin down states).

From  $dE = \hbar^2 k/m.dk$  and substituting, we get:

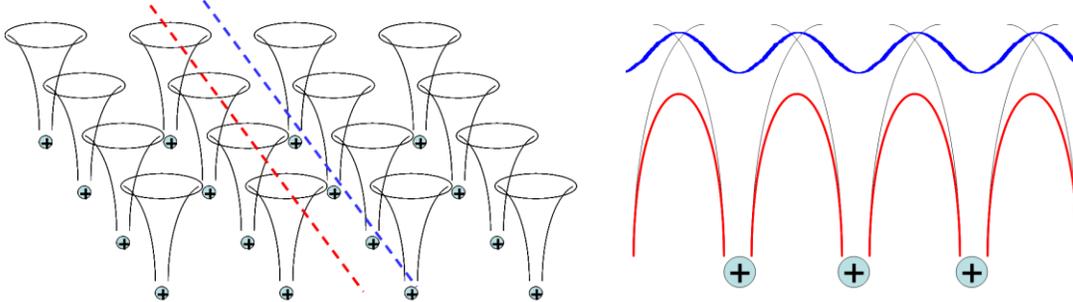
$$N(E) = V/(\pi\hbar).(2mE)^{-1/2}$$

In summary:



## Band theory of solids (See Kittel, Ascroft, etc.)

This is one of the most important topics in this course as it will allow us to understand the reason for the existence of metals, insulators and semiconductors. The idea is to introduce into the “electron in a box” model of Sommerfeld, discussed above, the periodic electrostatic potential of the ion cores. So far, they ions provide just the right amount of + charge, equal to the total charge of the free electrons, to make the “box”



neutral. They only contributed as “obstacles” to the moving electrons giving thus rise to the resistivity. Now we will assume that they create a periodic potential  $V(\mathbf{r})$ , with the periodicity of the Bravais lattice. In the non-interaction electron model,  $V$  is the simple superposition of the individual ionic potentials, as shown in the figure for an array of ions. The potential of an electron moving on a line through the ions and between the ions would look like in the figure.

The Fourier theorem tells us that  $V(\mathbf{r})$  can be expressed as a combination of periodic functions with the periodicity of the lattice:

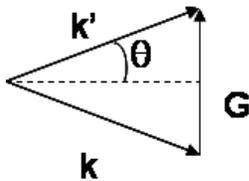
$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \cdot e^{i\mathbf{G} \cdot \mathbf{r}}, \quad \mathbf{G} \text{ being vectors of the reciprocal lattice.}$$

If  $\mathbf{R}$  represents any Bravais lattice vector, then  $V(\mathbf{r}+\mathbf{R}) = V(\mathbf{r})$ , by definition of  $V$  being periodic. Using the above equation:  $V(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{G} \cdot \mathbf{R}} \cdot V(\mathbf{r})$  in line with the condition of the reciprocal lattice definition:  $e^{i\mathbf{G} \cdot \mathbf{R}} = 1$

Since the potential must be a real function,  $V(\mathbf{r}) = V(\mathbf{r})^*$  the \* meaning the complex conjugate. This implies  $V_{\mathbf{G}}^* = V_{-\mathbf{G}}$

If the crystal has inversion symmetry we can choose the origin such that  $V(\mathbf{r})=V(-\mathbf{r})$ , which implies that  $V_{-\mathbf{G}} = V_{\mathbf{G}}$ , in other words, the  $V_{\mathbf{G}}$  are real numbers.

We saw that the wavelength of electrons inside the box is of the order of 1 Å, which is also the typical distance between ions. We thus expect strong diffraction effects when the Laue conditions are satisfied. This occurs whenever the wave vector  $\mathbf{k}$  has a component along one reciprocal vector  $\mathbf{G}$  of half its length. If  $\mathbf{G}$  is in the x-direction, the condition is  $k_x = \frac{1}{2} |\mathbf{G}|$ . If the periodicity of the lattice in the x-direction is  $a$ , then  $k_x = n\pi/a$ , with  $n = \text{all integers } + \text{ and } -$ .



For these particular electrons, there will be strong diffraction and the wave will be reflected back and forth, building up standing waves that do not propagate in the x-direction. The wave function will be a combination of the incident and reflected waves

$$\psi(x) = e^{ikx} \pm e^{-ikx} = 2\cos(\pi x/a); \text{ and } = 2i\sin(\pi x/a)$$

These two combinations will not have the same energy because one has larger amplitude over the ions and the other between the ions.

More rigorously, we have to solve the Schrödinger equation with a periodic potential  $V(\mathbf{r})$ :

$$-\frac{\hbar^2}{2m} \cdot \nabla^2 \psi(\mathbf{r}) + \mathbf{V}(\mathbf{r}) \cdot \psi(\mathbf{r}) = \mathbf{E} \cdot \psi(\mathbf{r})$$

We wish to express  $\psi(\mathbf{r})$  as a linear combination of the plane wave function of the Sommerfeld model, as they constitute a complete base.

$\psi(\mathbf{r}) = \sum_{\mathbf{k}} \mathbf{c}(\mathbf{k}) \cdot \mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}}$ , with  $k_x = 2\pi n/L_x$ ,  $n = \text{integer } (0, \pm 1, \pm 2, \dots)$  and similar expressions for the y and z components.  $L_{x,y,z}$  = dimensions of the box in the x,y, and z directions.

The Schrödinger equation will now read (using  $\lambda_{\mathbf{k}} = \hbar^2 \mathbf{k}^2 / 2m$ ):

$\sum_{\mathbf{k}} \lambda_{\mathbf{k}} \cdot \mathbf{c}(\mathbf{k}) \cdot \mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}} + \sum_{\mathbf{G}} \mathbf{V}_{\mathbf{G}} \sum_{\mathbf{k}} \mathbf{c}(\mathbf{k}) \cdot \mathbf{e}^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} = \mathbf{E} \cdot \sum_{\mathbf{k}} \mathbf{c}(\mathbf{k}) \cdot \mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}}$ , where the sums run over the  $\mathbf{k}$  values ( $n,m,l = 0,1,2,3,\dots$ ) and over the reciprocal space vectors  $\mathbf{G}$ . The lengths of the smallest  $\mathbf{k}$  and  $\mathbf{G}$  vectors are very different:  $k_x = 2\pi n/L_x$ , with  $L_x = \text{cm}$ ,  $G = 2\pi h/a_x$ , with  $a_x = \text{angstroms}$ . Since the  $\mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}}$  are orthogonal functions, we can multiply the equation by  $\mathbf{e}^{-i\mathbf{k}' \cdot \mathbf{r}}$  and integrate. The result is zero unless  $\mathbf{k}' = \mathbf{k}$

So, we get (using  $\mathbf{k}$  instead of  $\mathbf{k}'$ ):

$$\lambda_{\mathbf{k}} \cdot \mathbf{c}(\mathbf{k}) + \sum_{\mathbf{G}} \mathbf{V}_{\mathbf{G}} \cdot \mathbf{c}(\mathbf{k} - \mathbf{G}) = \mathbf{E} \cdot \mathbf{c}(\mathbf{k}), \text{ or } (\lambda_{\mathbf{k}} - \mathbf{E}) \cdot \mathbf{c}(\mathbf{k}) + \sum_{\mathbf{G}} \mathbf{V}_{\mathbf{G}} \cdot \mathbf{c}(\mathbf{k} - \mathbf{G}) = 0$$

This is a very important set of linear equations whose solution will give us the  $\mathbf{c}(\mathbf{k})$ 's and from that we can build  $\psi(\mathbf{r})$ , and the energy eigenvalue  $\mathbf{E}$ . It is called the **central equation**.

A fundamental result is that the solution for  $\mathbf{c}(\mathbf{k})$  contains only values of  $\mathbf{k}$  separated by vectors  $\mathbf{G}$  of the reciprocal lattice. In other words:

$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \mathbf{c}(\mathbf{k} - \mathbf{G}) \cdot \mathbf{e}^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{r}}$  For every  $\mathbf{k}$  in the list of  $k_x = 2\pi n/L_x$ ,  $n = \text{integer } (0, +1, +2, \dots, -1, -2, \dots)$  there is a solution of the Schroedinger equation that contains the original plane wave  $\mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}}$ , combined with other plane waves  $\mathbf{e}^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{r}}$  with weighs  $\mathbf{c}(\mathbf{k}-\mathbf{G})$ .

**The Bloch theorem:**

Another way to express this result is rewriting  $\psi_{\mathbf{k}}(\mathbf{r})$  as:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \cdot \sum_{\mathbf{G}} \mathbf{c}(\mathbf{k} - \mathbf{G}) \cdot e^{-i\mathbf{G}\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} \cdot \mathbf{u}_{\mathbf{k}}(\mathbf{r})$$

where  $u_{\mathbf{k}}(\mathbf{r})$  is a periodic function of the lattice. This is the Bloch theorem.

**Solutions of the central equation:**

We can see that the central equation:  $(\lambda_{\mathbf{k}} - E) \cdot \mathbf{c}(\mathbf{k}) + \sum_{\mathbf{G}} \mathbf{V}_{\mathbf{G}} \cdot \mathbf{c}(\mathbf{k} - \mathbf{G}) = 0$

is an infinite set of linear equations with infinite unknowns. For every  $\mathbf{k}$  we will find many different values of E or  $E_n$ , which from now on we will label it as  $E_n(\mathbf{k})$ . To facilitate understanding lets assume that  $V(\mathbf{r})$  has only two components  $V_{\mathbf{G}}$  and  $V_{-\mathbf{G}} = V_o$ .

$$\begin{aligned} (\lambda_{\mathbf{k}} - E) \cdot \mathbf{c}(\mathbf{k}) + V_o \cdot \mathbf{c}(\mathbf{k} - \mathbf{G}) + V_o \cdot \mathbf{c}(\mathbf{k} + \mathbf{G}) &= 0 \\ (\lambda_{\mathbf{k}+\mathbf{G}} - E) \cdot \mathbf{c}(\mathbf{k} + \mathbf{G}) + V_o \cdot \mathbf{c}(\mathbf{k}) + V_o \cdot \mathbf{c}(\mathbf{k} + 2\mathbf{G}) &= 0 \\ (\lambda_{\mathbf{k}-\mathbf{G}} - E) \cdot \mathbf{c}(\mathbf{k} - \mathbf{G}) + V_o \cdot \mathbf{c}(\mathbf{k}) + V_o \cdot \mathbf{c}(\mathbf{k} - 2\mathbf{G}) &= 0 \\ (\lambda_{\mathbf{k}+2\mathbf{G}} - E) \cdot \mathbf{c}(\mathbf{k} + 2\mathbf{G}) + V_o \cdot \mathbf{c}(\mathbf{k} + \mathbf{G}) + V_o \cdot \mathbf{c}(\mathbf{k} + 3\mathbf{G}) &= 0 \\ (\lambda_{\mathbf{k}-2\mathbf{G}} - E) \cdot \mathbf{c}(\mathbf{k} - 2\mathbf{G}) + V_o \cdot \mathbf{c}(\mathbf{k} - 3\mathbf{G}) + V_o \cdot \mathbf{c}(\mathbf{k} - \mathbf{G}) &= 0 \\ \text{etc} \quad \text{etc} \end{aligned}$$

The rows and columns of the determinant  $\Delta$  of the system are shown in the table:

$\Delta$	-3	-2	-1	0	1	2	3
-3	.....						
-2	$V_o$	$\lambda_{\mathbf{k}-2\mathbf{G}}-E$	$V_o$	0	0	0	0
-1	0	$V_o$	$\lambda_{\mathbf{k}-\mathbf{G}}-E$	$V_o$	0	0	0
0	0	0	$V_o$	$\lambda_{\mathbf{k}}-E$	$V_o$	0	0
+1	0	0	0	$V_o$	$\lambda_{\mathbf{k}+\mathbf{G}}-E$	$V_o$	0
+2	0	0	0	0	$V_o$	$\lambda_{\mathbf{k}+2\mathbf{G}}-E$	$V_o$
	.....						

To have a solution we must have  $\det[\Delta] = 0$ . If we limit the number of coefficients  $c(\mathbf{k})$  to  $n$ , this gives a polynomial of n-th degree giving  $n$  different values of E for each  $\mathbf{k} \rightarrow E_n(\mathbf{k})$ . These functions are the energy dispersion bands.

As we see, even with only 1 component of  $V$  ( $V_o$ ), we have an infinite set of equations. So to solve the problem algebraically we need more approximations. We have already seen that when  $k_x = 1/2 |\mathbf{G}|$  only two plane waves are important: the incident  $e^{i\mathbf{k}\cdot\mathbf{r}}$  and the reflected  $e^{-i\mathbf{k}\cdot\mathbf{r}}$ . For weak potentials, the central equation tells us that:

$$c(\mathbf{k}) = -\frac{\sum_{\mathbf{G}} V_{\mathbf{G}} \cdot c(\mathbf{k} - \mathbf{G})}{\lambda_{\mathbf{k}} - E}$$

So that only when  $\lambda_{\mathbf{k}} = E$  or close to it, will  $c(\mathbf{k})$  be large. In general for any  $\mathbf{k}$  value that does not satisfy the Laue condition only the  $\mathbf{G} = 0$  term in the sum is important and the wave is almost a plane wave. If however the Laue condition is satisfied, then  $\mathbf{k}' = \mathbf{k} - \mathbf{G}$ , so that two coefficients will be large:  $c(\mathbf{k})$  and  $c(\mathbf{k} - \mathbf{G})$ . That means, for  $\mathbf{G}$  in the  $x$ -direction,  $k_x = \frac{1}{2} G$  and  $k'_x = -1/2G$ . This  $\mathbf{k}$  is near the Brillouin zone boundary.

### Solutions near the Brillouin zone boundary

The determinant can be simplified to only two rows and columns:

$$\begin{vmatrix} \lambda_{\mathbf{k}'} - E & V_0 \\ V_0 & \lambda_{\mathbf{k}} - E \end{vmatrix} = 0, \quad \text{with } \mathbf{k}' = \mathbf{k} - \mathbf{G}$$

Along the  $G$ -axis and exactly at the zone boundary  $\mathbf{k}' = \mathbf{k} = G/2$

$$\text{And the energy is } (\lambda - E)^2 = V_0^2 \rightarrow E = \lambda \pm |V_0| = \hbar^2 k^2 / 2m \pm |V_0|$$

This indicates the existence of an energy gap  $E_g = 2|V_0|$

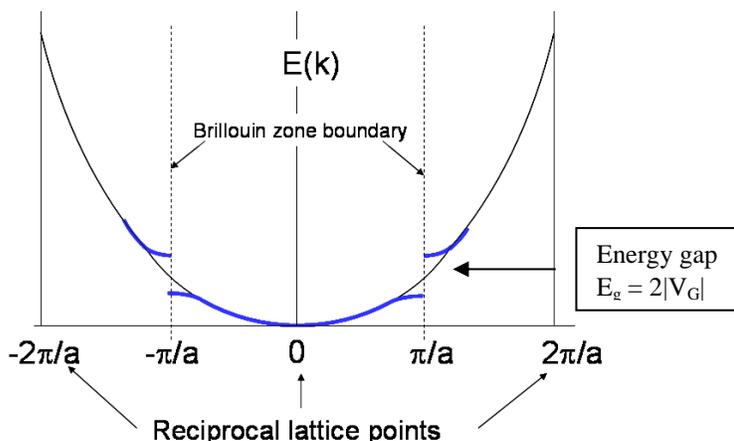
This is an extremely important result. It tells us that there is a range of energies, between  $\hbar^2 k^2 / 2m - |V_0|$  and  $\hbar^2 k^2 / 2m + |V_0|$  where no solutions of the Schrodinger equation exist, i.e, no orbitals are possible.

$$(\lambda_{\mathbf{k}'} - E)c(\mathbf{k} - \mathbf{G}) + V_0 \cdot c(\mathbf{k}) = 0; \text{ or } c(\mathbf{k} - \mathbf{G})/c(\mathbf{k}) = \pm 1$$

If we are not exactly at the boundary:  $(\lambda_{\mathbf{k}'} - E) \cdot (\lambda_{\mathbf{k}} - E) - V_0^2 = 0$

The solution of this 2<sup>nd</sup> degree equation is:

$$E(\mathbf{k}) = \frac{\lambda_{\mathbf{k}-\mathbf{G}} + \lambda_{\mathbf{k}}}{2} \pm \sqrt{1/4 \cdot (\lambda_{\mathbf{k}-\mathbf{G}} - \lambda_{\mathbf{k}})^2 + V_0^2}$$



this gives the blue lines in the figure of  $E(k)$ , showing the gap at  $\pm\pi/a$ . This representation of the Energy dispersion is called “the extended zone scheme”.

We have seen that the coefficients  $c(\mathbf{k})$  at the zone Boundary are equal to each

other in absolute value but with + or - sign. With the + we get:

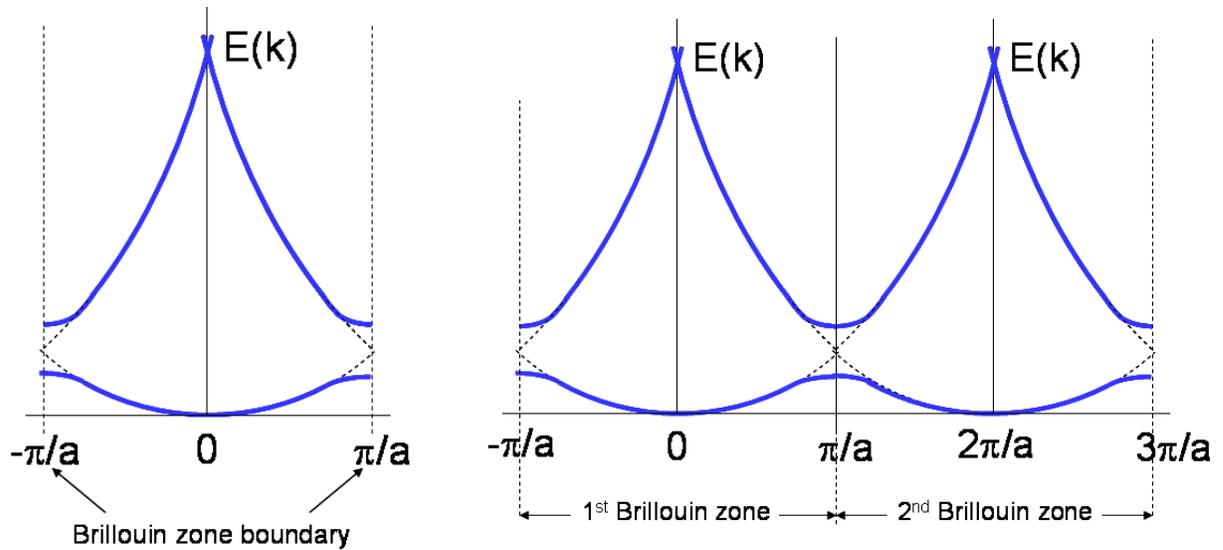
$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \text{ and since } \mathbf{k}-\mathbf{G} = -\mathbf{k}, \quad \psi_{\mathbf{k}}^+(\mathbf{r}) = 2\cos(kr)$$

Similarly for the - sign,  $\psi_{\mathbf{k}}^-(\mathbf{r}) = 2i\sin(kr)$

### Reduced and periodic zone schemes

Since  $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \cdot \sum_{\mathbf{G}} \mathbf{c}(\mathbf{k}-\mathbf{G}) \cdot e^{-i\mathbf{G}\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} \cdot \mathbf{u}_{\mathbf{k}}(\mathbf{r})$  we can always make sure that the plane wave  $e^{i\mathbf{k}\cdot\mathbf{r}}$  has  $\mathbf{k}$  within the first Brillouin zone. If not we pick a  $\mathbf{G}$  in the sum such that  $\mathbf{k}-\mathbf{G}$  is inside the 1<sup>st</sup> zone. This is the reduced zone scheme. There is no new information to be gained outside of the 1<sup>st</sup> zone representation.

The names reduced, extended and periodic zone schemes are found in the literature.



The reduced scheme is obtained by folding into the 1<sup>st</sup> Brillouin zone the branches of the  $E(k)$  function by translation of a suitable  $\mathbf{G}$  vector, as in the left figure. The periodic zone scheme is obtained by repeating the reduced zone scheme and emphasizes the periodic nature of  $E(k)$ .

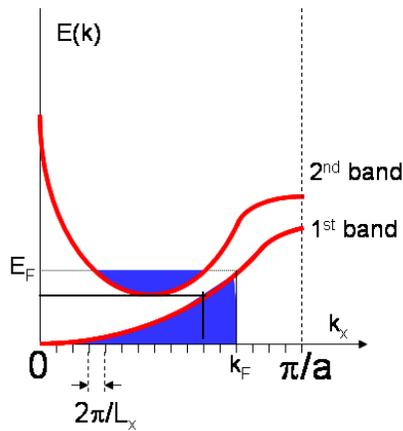
### Metals, insulators and semiconductors

If the material is made of a divalent element, with 2 valence electrons per atom, as in Be, Mg, Ca, in one dimension it would be an insulator.

The reason is that the number of orbitals or  $k$ -states inside the 1<sup>st</sup> Brillouin zone is:

$$\frac{2\pi/a}{2\pi/L} = \frac{L}{a} = \text{Number of atoms (in one dimension)}$$

Since each orbital or  $k$ -value can accommodate 2 electrons (with up and down spin), the divalent atom will have the band completely full. Applying an electric field will not accelerate the electrons since the  $k$  value cannot increase with all orbitals occupied.



If the atoms are monovalent (alkalis, noble metals) they contribute one electron each and the band is only half full, i.e., the Fermi wave vector  $k_F$  is located near the middle of the zone, around  $\pm\pi/2a$ . The electrons near the Fermi level can easily increase their  $k$  vector and contribute to the conductivity (accelerate), and to the heat capacity. This explains the existence of insulators and conductors.

Because solids have 3 dimensions, it could be that for a divalent metal the bands might overlap in one or in two different directions, so that only part or the first band is filled, and part of the second. This then produces a metal. In other words, while an odd number of valence electrons guarantees that the element is a metal, an element with an even number is not always an insulator, as this requires that there is no overlap between bands in several directions of  $k$ -space. In the example of the figure, the states of the first band are filled up to the  $k$  value with energy equal to the bottom of the second band. After that and up to  $k_F$  the second band is also being filled, so that after entering the  $2N$  electrons neither is full.

An exceedingly important class of materials is the so called semiconductors. These materials have energy gaps that are of the order of 1 eV, so that by thermal excitation a number of electrons (Fermi distribution) can jump from the fully occupied band (at 0 Kelvin) to the bottom of the second band. The electrical conductivity of these materials increases with temperature, the opposite as in metals, where thermal agitation of the ions increases their scattering cross section and thus increases the *resistivity*. We will come back to these materials later.

### **Band gap states**

We have seen that there are no states in the solid that are solutions of the Schrödinger equations with energy in the gap region. This is because we assumed an infinite, periodic solid, which requires solutions to be of the Bloch form: a plane wave multiplied by a periodic function. These represent propagating states in the form of plane waves or combination of plane waves.

However, when this infinite periodicity assumption is not valid, we can find states with energy in the band gap. This occurs at the surface of the materials, and in defects or impurities that break the translational symmetry.

To find values of  $k$  at the zone boundary, with energies in the band gap we write  $k$  as a complex number:

$k = G/2 + i\kappa$ , and we insert this value into the energy function found before:

$$\mathbf{E}(\mathbf{k}) = \frac{\lambda_{\mathbf{k}-\mathbf{G}} + \lambda_{\mathbf{k}}}{2} \pm \sqrt{1/4 \cdot (\lambda_{\mathbf{k}-\mathbf{G}} - \lambda_{\mathbf{k}})^2 + \mathbf{V}_0^2}$$

$$k^2 = (G/2 + i\kappa)^2; (k-G)^2 = (-G/2 + i\kappa)^2, \text{ so that}$$

$$\mathbf{E}(\kappa) = \frac{\mathbf{G}^2}{4} - \kappa^2 \pm \sqrt{-\mathbf{G}^2 \cdot \kappa^2 + \mathbf{V}_G^2}, \text{ where to simplify writing we put } \hbar^2/2m = 1$$

From here we get the value of  $\kappa$ : 
$$\kappa^2 = \sqrt{\mathbf{E} \cdot \mathbf{G}^2 + \mathbf{V}_G^2} - \left(\mathbf{E} + \frac{\mathbf{G}^2}{4}\right)$$

It is easy to verify that at the edges of the band gap:  $E = G^2/4 - V_G$  and  $E = G^2/4 + V_G$  the value of  $\kappa = 0$ , as expected.

The wave function for values of  $E$  between these two limits is:

$$\psi(z) = c_{G/2} \cdot e^{i(G/2+i\kappa)z} + c_{(-G/2)} \cdot e^{i(-G/2+i\kappa)z} = e^{-\kappa z} \cdot (c_{G/2} \cdot e^{i(G/2)z} + c_{(-G/2)} \cdot e^{i(-G/2)z})$$

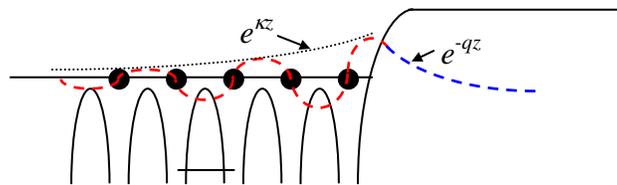
defining:  $\sigma = E - G^2/4$

$$\frac{c_{-G/2}}{c_{G/2}} = \frac{\kappa^2 + \sigma - iG\kappa}{V_G} \approx \frac{\sigma}{V_G} - i \sqrt{1 - \left(\frac{\sigma}{V_G}\right)^2} = e^{-i2\delta} \quad (21)$$

So the wavefunction takes the form:

$$\psi(z) = 2 \cdot c_{G/2} \cdot e^{\kappa z} \cdot e^{-i\delta} \cdot \cos\left(\frac{\pi z}{a} + \delta\right) \quad (22)$$

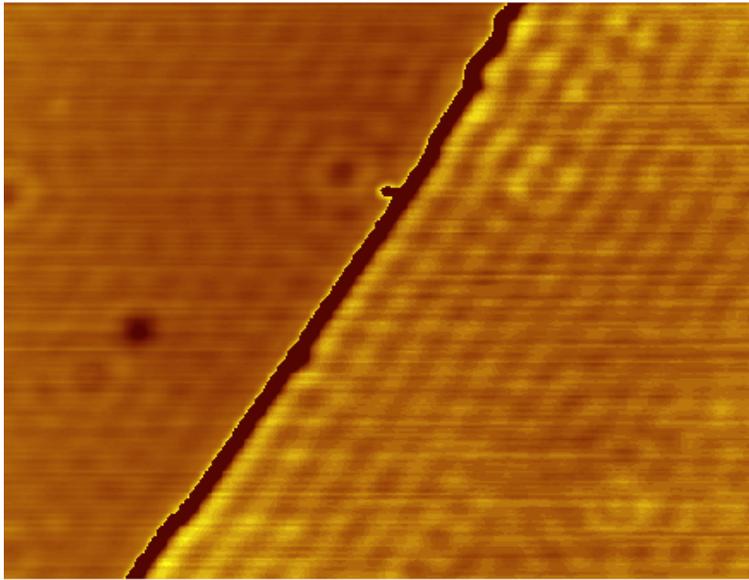
where we have used  $G = 2\pi/a$ . We recognize an oscillatory function with periodicity  $2a$  and exponentially decaying amplitude into the bulk. This wave function should be



matched (continuity of the logarithmic derivative) with the solution outside the crystal, which is  $\sim e^{-qz}$ , with  $q = (V_0 - E)^{1/2}$ . This requires that  $\delta$  have a specific value. If a solution can be found we have a so-called Shockley surface state. These states are observed in several metal surfaces, where a gap exists in the direction perpendicular to the surface (of course this is not an absolute gap, since in other directions there are no gaps at the corresponding energy). The electrons in these states are localized at the surface and form waves that are beautifully imaged in STM images. The component of the wvector

parallel to the surface does not need to be in a gap, so that the above wavefunction represents only the part normal to the surface. It should be multiplied by a surface propagating plane wave:  $e^{i\mathbf{k}\cdot\mathbf{R}}$ .

Example: Below are STM images of Cu(111) at 4K obtained by Aitor Mugarza and Tomoko Shimizu in my laboratory. Cu has a band gap along the [111] direction.

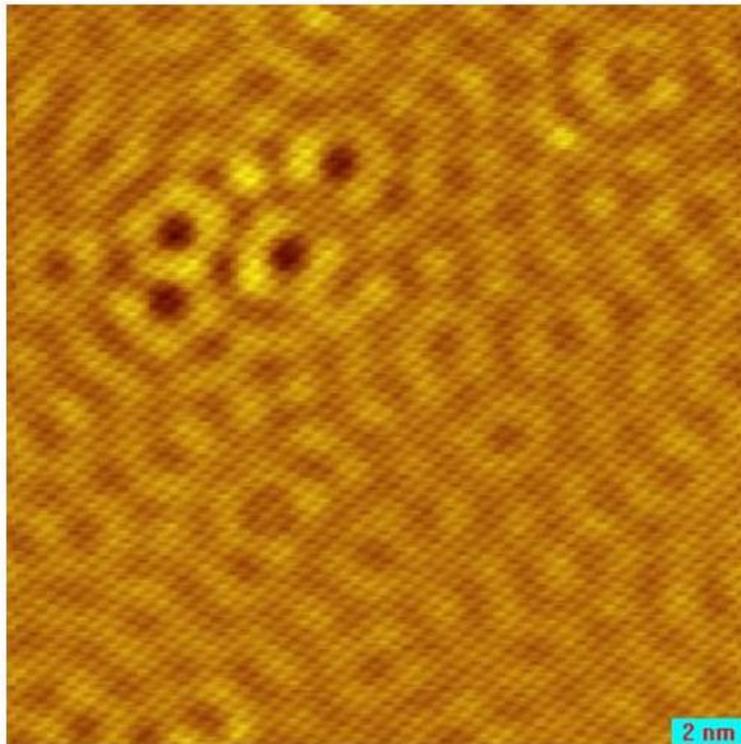


The top image shows the standing waves created by the electrons in the surface states of the Cu(111) surface.

The standing waves originate from the reflections on the two parallel steps (only one visible).

The second image shows an expanded view, with waves forming rings around impurities. The Cu atoms are visible forming a compact hexagonal network in the background.

5 nm



2 nm

### *The tight binding approximation*

In the preceding sections we have constructed solutions of the Schrödinger equation using plane waves as a basis. In the absence of the periodic potential of the positive nuclei this is an exact solution. When we introduced a periodic potential  $V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \cdot e^{i\mathbf{G} \cdot \mathbf{r}}$ , the plane wave basis is still good with only waves that fulfill the periodic boundary conditions needed. Only a few plane waves are needed, mostly near Brillouin zone boundaries, when the  $V_{\mathbf{G}}$  coefficients are small. This is the nearly free electron approximation. Another way to express the solution of the Schrödinger equation is to use atomic wave functions instead of plane waves as a basis. We choose the atomic orbitals of the isolated atoms. This is also called LCAO = linear combination of atomic orbitals.

The wave function we seek is now expressed as:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{j}} c_{\mathbf{k},\mathbf{j}} \cdot \phi(\mathbf{r} - \mathbf{r}_{\mathbf{j}}), \text{ k is the wave vector}$$

Where the  $\phi(\mathbf{r} - \mathbf{r}_{\mathbf{j}})$  are atomic orbitals (s, p, d, etc.) centered at the Bravais lattice points  $\mathbf{r}_{\mathbf{j}}$ ,  $\mathbf{j} = 1, 2, \dots$ , and the  $c_{\mathbf{k},\mathbf{j}}$  are coefficients with the property

$$c_{\mathbf{k},\mathbf{j}} = N^{-1/2} \cdot e^{i\mathbf{k} \cdot \mathbf{r}_{\mathbf{j}}}, \text{ with } N = \text{number of atoms, for normalization purposes}$$

This ensures that  $\psi_{\mathbf{k}}$  satisfies the Bloch theorem, i.e., it is invariant except for a phase factor of modulus 1 when subjected to periodic translations of the lattice:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = N^{-1/2} \cdot \sum_{\mathbf{j}} e^{i\mathbf{k} \cdot \mathbf{r}_{\mathbf{j}}} \cdot \phi(\mathbf{r} + \mathbf{R} - \mathbf{r}_{\mathbf{j}}) = N^{-1/2} \cdot e^{i\mathbf{k} \cdot \mathbf{R}} \cdot \sum_{\mathbf{j}} e^{i\mathbf{k} \cdot (\mathbf{r}_{\mathbf{j}} - \mathbf{R})} \cdot \phi(\mathbf{r} - (\mathbf{r}_{\mathbf{j}} - \mathbf{R})) = e^{i\mathbf{k} \cdot \mathbf{R}} \cdot \psi_{\mathbf{k}}(\mathbf{r})$$

since  $\mathbf{r}_{\mathbf{j}} - \mathbf{R}$  is a Bravais lattice vector, the sum is identically the same since as  $\mathbf{j}$  varies all the lattice points are counted.

In the same manner as the nearly free electron approx. with plane waves is a good approximation for small  $V_{\mathbf{G}}$  values, the LCAO works best when the system is made of tightly bound electrons that, even in the solid form, conserve their atomic character.

Since the atomic orbital functions  $\phi(\mathbf{r} - \mathbf{r}_{\mathbf{j}})$  are non-zero only close to the atom located at  $\mathbf{r}_{\mathbf{j}}$ , the energy of a given state is:

$$\mathbf{E}(\mathbf{k}) = \langle \psi_{\mathbf{k}} | \mathbf{H} | \psi_{\mathbf{k}} \rangle = N^{-1} \cdot \sum_{\mathbf{j},\mathbf{m}} e^{i\mathbf{k} \cdot (\mathbf{r}_{\mathbf{j}} - \mathbf{r}_{\mathbf{m}})} \cdot \int \phi(\mathbf{r} - \mathbf{r}_{\mathbf{j}}) \cdot \mathbf{H} \phi(\mathbf{r} - \mathbf{r}_{\mathbf{m}}) \cdot d\mathbf{V}$$

$\mathbf{H}$  is the Hamiltonian. Since the atomic orbital wavefunction  $\phi$  decays very rapidly, only when  $\mathbf{j} - \mathbf{m} = 0$  or  $1$ , will the overlap between  $\phi(\mathbf{r} - \mathbf{r}_{\mathbf{j}})$  and  $\phi(\mathbf{r} - \mathbf{r}_{\mathbf{m}})$  be non-negligible.

We write  $\langle \phi(\mathbf{r} - \mathbf{r}_{\mathbf{j}}) | \mathbf{H} | \phi(\mathbf{r} - \mathbf{r}_{\mathbf{j}}) \rangle = -\alpha$

This is the Coulomb energy integral, with  $\alpha = \text{energy of the atomic orbital } \phi(\mathbf{r} - \mathbf{r}_j)$ , which is the same for all  $j$ 's since the atoms are all the same.

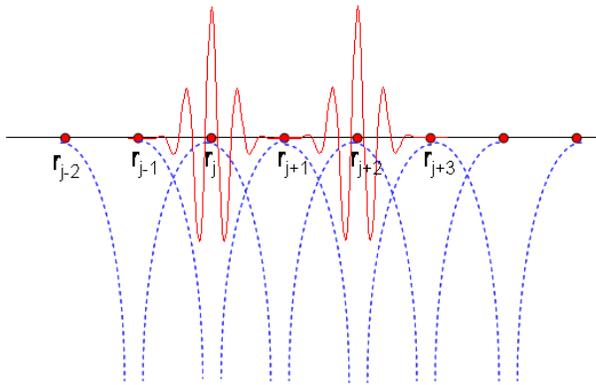
The overlap between nearest neighbors gives another integral, the so called exchange or resonance integral:

$$\langle \phi(\mathbf{r} - \mathbf{r}_j) | \mathbf{H} | \phi(\mathbf{r} - \mathbf{r}_m) \rangle = -\gamma, \quad \gamma \text{ is the same for } j-m = \pm 1$$

Therefore we have: 
$$\mathbf{E}(\mathbf{k}) = \mathbf{N}^{-1} \cdot [-\mathbf{N} \cdot \alpha - \mathbf{N} \cdot \gamma \cdot \sum_m \mathbf{e}^{-i\mathbf{k} \cdot \rho_m}] = -\alpha - \gamma \cdot \sum_m \mathbf{e}^{-i\mathbf{k} \cdot \rho_m},$$

where the vector  $\rho_m$  connects one lattice point with each of its  $m$ -nearest neighbors.

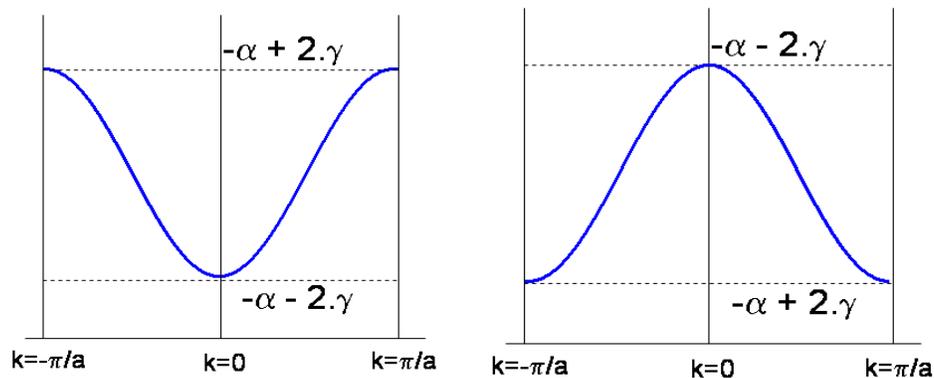
Example: In a linear chain of atoms separated by a distance  $a$ , like that shown



schematically in the figure below, we have drawn the Coulomb atomic potentials centered on each atom and two hypothetical atomic orbitals at positions  $r_j$  and  $r_{j+2}$ . The overlap is nearly zero. Only for nearest neighbors is the overlap not negligible. For this chain  $\rho_m = +a, -a$ , corresponding to  $m=1$  and  $m=-1$

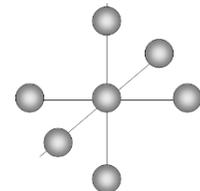
Substituting we obtain for a line of atoms: 
$$E(k) = -\alpha - 2\gamma \cos(ka)$$

The energy band in the reduced zone scheme therefore looks like:



The width of the band is  $4\gamma$ . If  $\gamma$  were negative, then the curve is upside down, as in the right hand side drawing.

For a simple cubic system: There are 6 vectors  $\rho_m = \pm (100); \pm (010); \pm (001)$ , and therefore:



$E(k) = -\alpha - 6\gamma \cos(k.a)$  which has a band width of  $12\gamma$ .

Other systems (bcc, fcc, diamond, etc) can be easily calculated and are left as an exercise.

### The effective mass

An interesting and important concept is that of the effective mass. This arises from the fact that near the center of the Brillouin zone ( $k = 0$ ) the  $\cos(k.a)$  shaped band can be approximated by a parabola, like in the free electron case where:

$$E(k) = \hbar^2 k^2 / 2m$$

The cosine function can be expanded as  $\cos(x) \approx 1 - x^2/2 + \dots$ . Therefore:

$$E(k) = -\alpha - 2\gamma \cos(k.a) \approx -\alpha - 2\gamma + \gamma k^2 a^2 = E_0 + \hbar^2 k^2 / 2m^*, \text{ with } m^* = \hbar^2 / (2\gamma a^2).$$

As we can see, the “flatter” the band, i.e., the smaller the value of  $\gamma$ , the larger is the effective mass  $m^*$ . Heavy electrons (or holes) are characteristic of narrow localized bands, like those made of d orbitals for example.

Exercise: draw the wavefunctions near the band center ( $k=0$ ) and near the Brillouin zone  $k = \pi/a$  for the band derived from:

- s-like orbitals
- $p_z$  orbitals and with the  $k$  direction in the  $y$  axis
- Same for  $p_x$  orbitals with  $k$  along the same  $x$  axis.
- Are the functions bonding or antibonding in character? Do the bands look like a parabola pointing up or down?

