Band filling: metals, insulators, semiconductors

Tight binding model in second quantization

We consider lattice with sites R_i.

Operators (Fermionic)

$c^+_{i,s}$ creates an electron of spin s on site R_i

$c_{i,s}$ annihilate an electron of spin s on site R_i

Then the tight binding Hamiltonian is

$$H = \sum_{i,s} \varepsilon_0 c^+_{i,s} c_{i,s} - \sum_{ij} t_{ij} c^+_{i,s} c_{j,s}$$

with $t_{ij} = t_{ji}$ being real numbers.

The first term describes atomic states with energy ε_0. The second one describes annihilation of an electron on site R_i and creation on site R_j, so the motion of electron from R_i to R_j. The coefficients t_{ij} are called hopping matrix elements.

Consider simple cubic lattice with only nearest neighbor hopping. We can diagonalize our Hamiltonian by going to the Fourier space.

$$c^{+}_{i,s} = \frac{1}{\sqrt{N}} \sum_{k} a^{+}_{ks} e^{-i\vec{k}\cdot\vec{R}_i}, \quad c^{}_{i,s} = \frac{1}{\sqrt{N}} \sum_{k} a_{ks} e^{i\vec{k}\cdot\vec{R}_i}$$

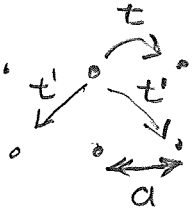
These a^{+-}_{ks} and a_{ks} create and annihilate an electron in the Bloch state with pseudo-momentum $\hbar k$. N is total number of sites. Substituting we get

$$H = \sum_{k,k',s} \left\{ \frac{1}{N} \sum_{i} \varepsilon_0 e^{i(k-k')\cdot R_i} - \frac{1}{N} \sum_{i,j} t_{ij} e^{ik\vec{R}_i - ik'R_j} \right\} a^{+}_{k's} a_{ks} =$$

$$= \varepsilon_0 - 2t\left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right] a^{+}_{ks} a_{ks} \Rightarrow$$

$$\varepsilon_k = -2t\left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right]$$

Extending it to next nearest neighbor hopping (diagonal)



we obtain

$$\varepsilon_k = -2t\left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right] +$$

$$- 4t'\left[\cos(k_x a)\cos(k_y a) + \cos(k_y a)\cos(k_z a) + \cos(k_x a)\cos(k_z a)\right]$$

For small k, $ka \to 0$ we get isotropic spectrum

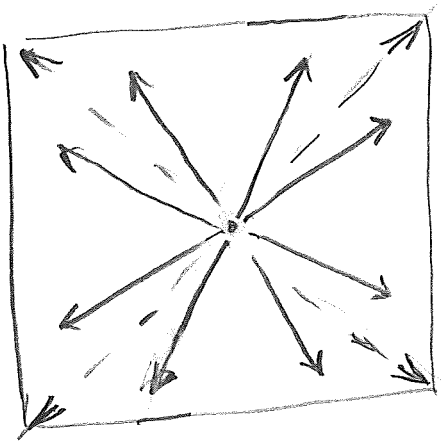
$$\varepsilon_k = -6t - 12t' + \frac{\hbar^2}{2m^*} k^2 + \dots$$

with $$\frac{1}{m^*} = \frac{2a^2}{\hbar^2}(t + 4t')$$

Away from the bottom of the band we have not spherical but cubic symmetry. This is general case that the energy function in the Brillouin zone has the full point group symmetry of the crystal.

There is a star like structure of equivalent points $g\vec{k}$ with the same band energy for each $\vec{k}$

g is the point group operation



Star of k-points with the same energy.

$$\varepsilon_k = \varepsilon_{gk}$$

Band filling and material properties

Number of orbitals in a band

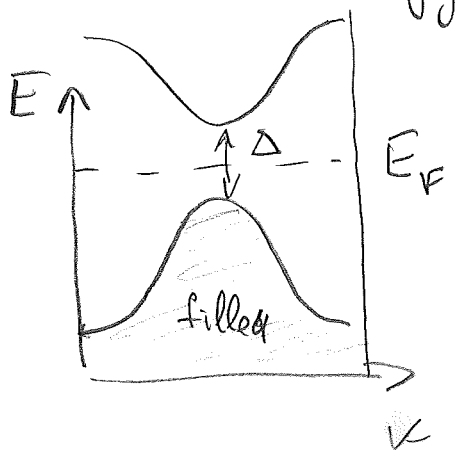
Consider a 1d crystal of an even number N of primitive cells of lattice constant a. Let us assume periodic boundary conditions, $\psi(r+L) = \psi(r)$, $L = Na$. The allowed values of the electron wave-vector k are $k_n = \frac{2\pi}{L} n = \frac{2\pi}{a} \frac{n}{N}$ where n is integer. Within the first Brillouin zone $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$ =>

$$n = -\frac{N}{2}+1, -\frac{N}{2}+2, \ldots, -1, 0, 1, 2 \ldots \frac{N}{2}$$

We excluded $n = -\frac{N}{2}$ since it is equivalent to $n = \frac{N}{2}$ $\left(\pm \frac{\pi}{a} \right)$. Altogether we have N possible values for k_n. Taking spin into account we get $2N$ states. The same is true in three dimensions. The total number of independent k states is equal to total number of atomic orbitals $2N$

Metals, insulators, semiconductors

If Fermi energy lies inside the gap



($T = 0$)

then the lower band is filled

It is called the <u>valence band</u>

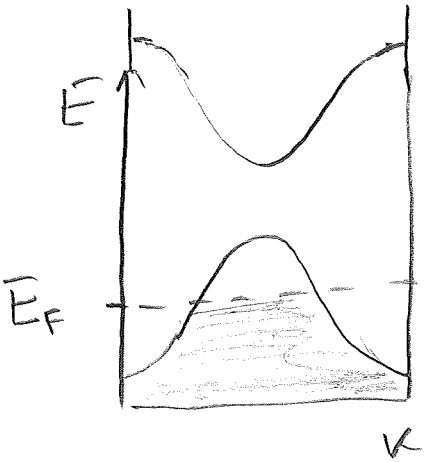
The upper, <u>conduction band</u> is empty

To produce current we need to excite the electron above the gap. This will cost energy Δ.

For low temperatures it is unprobable, current will be zero. It is called <u>band insulator</u>. The large gap insulators are usually transparent, because electromagnetic energy in the visible range $\hbar\omega \sim 1.5 - 3.5\,eV$ can not be absorbed by the electrons.

Insulators with rather small gap are called <u>semiconductors</u>. In this situation at not too low temperatures conductivity $\sigma \propto e^{(-\frac{\Delta}{T})}$ can be quite considerable.

Another situation occurs if Fermi level is inside the band. Then electrons can move,

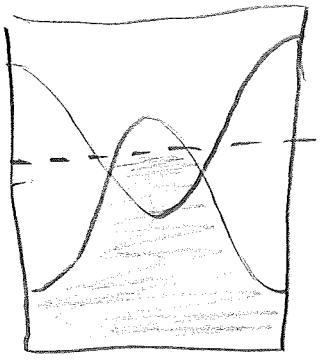


excitations with arbitrary low energy are possible. Then the system is a <u>metal</u>

The number of states in the band is 2 × number of unit cells. Then if we have odd number of electrons per unit cell we will have metals. This is the case for the first column of the periodic table Alkali metals Li, Na, K, Rb, Cs, all of them have one mobile electron per ion. The same is true for nobel metals, Cu, Ag, Au... Al, Ga, In, Tl have 3 electrons per cell thus also metals.

If a crystal has even number of electrons per primitive cell and the bands do not overlap it is insulator, Examples are C as diamond and semiconductors Si and Ge.

If the energy bands overlap then materials with the even number of electrons per cell may be metal as well. In this case it may be energetically advantages to leave the lower band unfilled and let some of the electrons go into the upper band. Example is



Pb belonging to the same Group IV as C, Si, Ge. If overlap is small at the Fermi energy we get <u>semi-metals</u>. A good periodic table description one finds in Ziman textbook.

Semiclassical dynamics

Bloch waves with fixed k are useless for discussing transport since coordinate is completely uncertain. To describe electron motion between the collisions we introduce wave packet of the form

$$\psi_k(r,t) = \sum_{k'} g_k(k')\, e^{i\vec{k}'\cdot\vec{r} - i\varepsilon_{k'}t}$$

where k' is around some k within a width $\Delta k \ll k \sim \frac{1}{a}$. Since from uncertainty principle $\Delta k\, \Delta x > 1$ then $\Delta x \gg a$, thus the electron is spread over many unit cells. In this case the pseudo momentum $\vec{k}$ is well defined. The equation of motion for such packet is

$$\frac{dr}{dt} = v(k) = \frac{\partial \varepsilon_k}{\partial \hbar k}$$

$$\hbar\dot{\vec{k}} = -e\vec{E}(r,t) - \frac{e}{c}\vec{v}(k) \times \vec{H}(r,t)$$

Bloch oscillations

Note that $\vec{k}$ is pseudo - rather than momentum of the electron. It is restricted to the Brillouin zone. Or one can say that ε_k is periodic function of k. This may lead to a strange oscillations. Consider 1-d tight binding model with $\varepsilon_k = -2\cos ka$. Then we have

$$\hbar \dot{k} = -eE \Rightarrow k = -eEt$$

$$\dot{x} = \frac{\partial \varepsilon_k}{\partial \hbar k} = 2a \sin ka = -\frac{2a}{\hbar} \sin\left(\frac{eEat}{\hbar}\right)$$

Then position of the electron oscillates

$$x(t) = \frac{2}{eE} \cos\left(\frac{eEat}{\hbar}\right)$$

This behavior is called Bloch oscillation. Instead of moving in the direction of field electron oscillates around its initial position. This behavior is never realized in real solids because any scattering will destroy it. But it was observed for called atoms on optical lattice

Current densities electrons and holes

The band electrons obbey Fermi statistics and have Fermi distribution function

$$n(k) = \frac{1}{\exp[(\varepsilon(k) - \mu)/T] + 1}$$

The current density is then

$$j = -2e \int_{BZ} \frac{d^3k}{(2\pi)^3} v(k) n(k) = -2e \int_{BZ} (d^3k)\, n(k) \frac{\partial \varepsilon_k}{\partial \hbar k}$$

For a completely filled band $j = 0$ since with $n(k) = 1$ $j \propto \int_{BZ} d^3k \frac{\partial \varepsilon_k}{\partial k}$

but ε_k is periodic $\varepsilon_{k+G} = \varepsilon_k$ thus the integral is zero. Using this we can rewrite current as

$$j = -2e \int_{BZ} (d^3k)\, n(k) v(k) = +2e \int d^3k [1 - n(k)] v(k)$$

Thus we can sum either over filled (electron) states (with charge $-e$) or over empty states (holes) (with charge $+e$). Holes, give useful description for almost filled band.