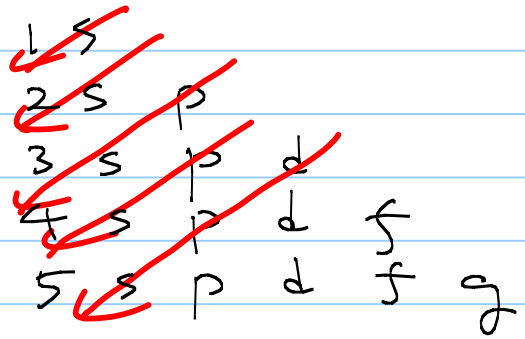
Atoms II + Solids

Note Title

Electronic configurations of an atom can be written as

$$(1s)^2(2s)^2(2p)^6(3s)^2 \ldots$$

The filling order is as discussed in the last class,



When we fill the orbitals, the total angular momentum values are important in atomic physics.

All filled orbitals have net zero angular momentum values, and the partially filled top most orbital determines the total angular momentum values written as $^{2S+1}L_J$.

We use numbers for S and J, but symbols for L such that

$0 \Rightarrow S$, $1 \Rightarrow P$, $2 \Rightarrow D$, $3 \Rightarrow F$

We use so-called "Hund's rules" to fill the highest orbital and determine the angular momentum values for the ground state of the atom.

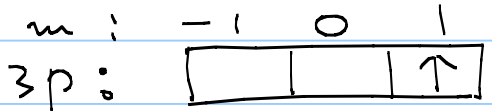
① Hund's first rule
Maximize S (the spin)

② Hund's 2nd rule
Maximize L (the orbital)

③ Hund's 3rd rule
The grand total J is either
$|L-S|$ if no more than half-filled
$L+S$ if more than half-filled

Ex.

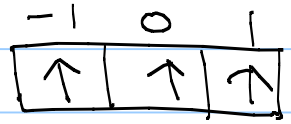
① Al ($Z=13$): $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^1$



$\Rightarrow S=\frac{1}{2},\ L=1,\ J=|L-S|=\frac{1}{2}$

$\Rightarrow {}^{2\times\frac{1}{2}+1}P_{\frac{1}{2}} = {}^{2}P_{\frac{1}{2}}$

② P ($Z=15$) $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^3$



$\Rightarrow S=\frac{3}{2}$

$L=1+0+(-1)=0$

$\Leftarrow J=S=\frac{3}{2}$

${}^{4}S_{\frac{3}{2}}$

③ $Cl\ (Z=17)$ $(1s)^2 \cdots (3p)^5$

$3p$: $\boxed{\uparrow \mid \uparrow\downarrow \mid \uparrow\downarrow}$ (−1, 0, 1) $\Rightarrow S = \frac{1}{2} + 0 + 0 = \frac{1}{2}$

$\Rightarrow L = -1 \times 1 + 0 \times 2 + 1 \times 2 = 1$

$J = S + L = \frac{1}{2} + 1 = \frac{3}{2}$

$\Rightarrow \quad ^{2\times\frac{1}{2}+1}P_{\frac{3}{2}} = {}^2P_{\frac{3}{2}}$

④ $Tz\ (Z=22)$

$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^2$

$3d$: $\boxed{\ \mid\ \mid\ \mid\ \mid \uparrow \mid \uparrow\ }$ (−2, −1, 0, 1, 2)

$\Rightarrow S = \frac{1}{2} + \frac{1}{2} = 1, \quad L = 1 + 2 = 3$

$J = |L - S| = 2 \Rightarrow {}^3F_2$

Solid I : Free-electron gas

* Electrons in metals are very well approximated by the free electron gas,

Consider a 3D - infinite cubical well

$$V(x,y,z) = \begin{cases} 0, & \text{if } 0 < x,y,z < a \\ \infty, & \text{else} \end{cases}$$

This problem was done in the previous homework problem (prob. 4.2).

The Schrödinger equation can be solved by separation of variables in cartesian coordinates. If we use the result from the HW problem,

$$\psi_{n_x n_y n_z}(x,y,z) = \left(\frac{2}{a}\right)^{\frac{3}{2}} \sin\left(\frac{n_x \pi}{a} x\right) \times \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right)$$

, with the eigenenergies of

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$= \frac{\hbar^2 k^2}{2m}$$

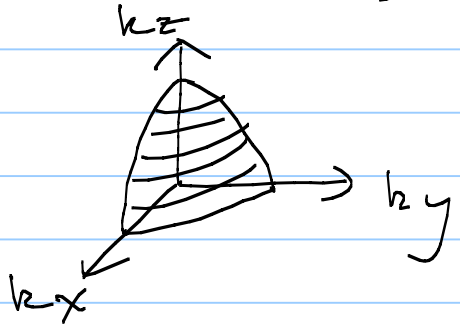
, with $\vec{k} = \frac{\pi}{a}(n_x, n_y, n_z)$

, where $n_x, n_y, n_z = 1, 2, 3, \ldots$. positive integers.

If we approximate a cubical solid metal of a side length of "a", which is a macroscopic length, the number of electrons in this metal, "N" will be a huge number of the order of Avogadro's number.

We fill these electronic states from the lowest energy state

$k_{111} = \frac{\pi}{a}(1,1,1)$ to higher energy states, with each state occupied by two electrons : spin up and down.



Each state in $\vec{n}$ space has a volume of $\Delta n = 1 \times 1 \times 1 = 1$, and so each state in k-space has a volume of

$$\Delta k = \left(\frac{\pi}{a}\right)^3 \cdot \Delta n = \left(\frac{\pi}{a}\right)^3 = \frac{\pi^3}{V}$$

If we call the maximum k value by k_F

Total # of electrons (N)

$= 2 \times$ total # of states

$= 2 \times \dfrac{\text{Volume in k-space}}{\Delta k}$

$$= 2 \times \frac{\frac{1}{8} \times \frac{4}{3}\pi (k_F)^3}{\Delta k}$$

$$= \frac{\pi}{3} \frac{k_F^3}{\frac{\pi^3}{V}} = V \cdot \frac{k_F^3}{3\pi^2}$$

$$\Rightarrow N = V \frac{k_F^3}{3\pi^2} \Rightarrow k_F = (3\pi^2 \rho)^{\frac{1}{3}}$$

, $\rho \equiv \frac{N}{V}$; density of electrons

The maximum energy of electrons in the ground state of a metal is called Fermi energy (E_F)

$$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{\frac{2}{3}}.$$

If we plug in the electron density we find for common metals

metal	$\rho (10^{28}/m^3)$	E_F (eV)
Cu	8.47	7.00
Ag	5.86	5.49
Au	5.90	5.53

* Compare this with the room temperature $\Rightarrow kT(300K) \simeq 25\,meV$.

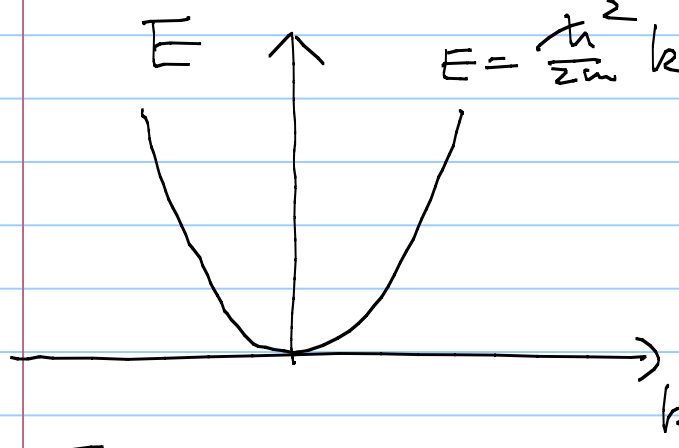
Solid II: Band Structure

We can improve the free-electron model of a solid by introducing the periodicity of atoms.

This periodicity alone induces so-called band-gap.

See Griffiths to see how to solve the Schrödinger Equation.

Here I will just mention the main result.



dispersion relation for a free-electron gas model

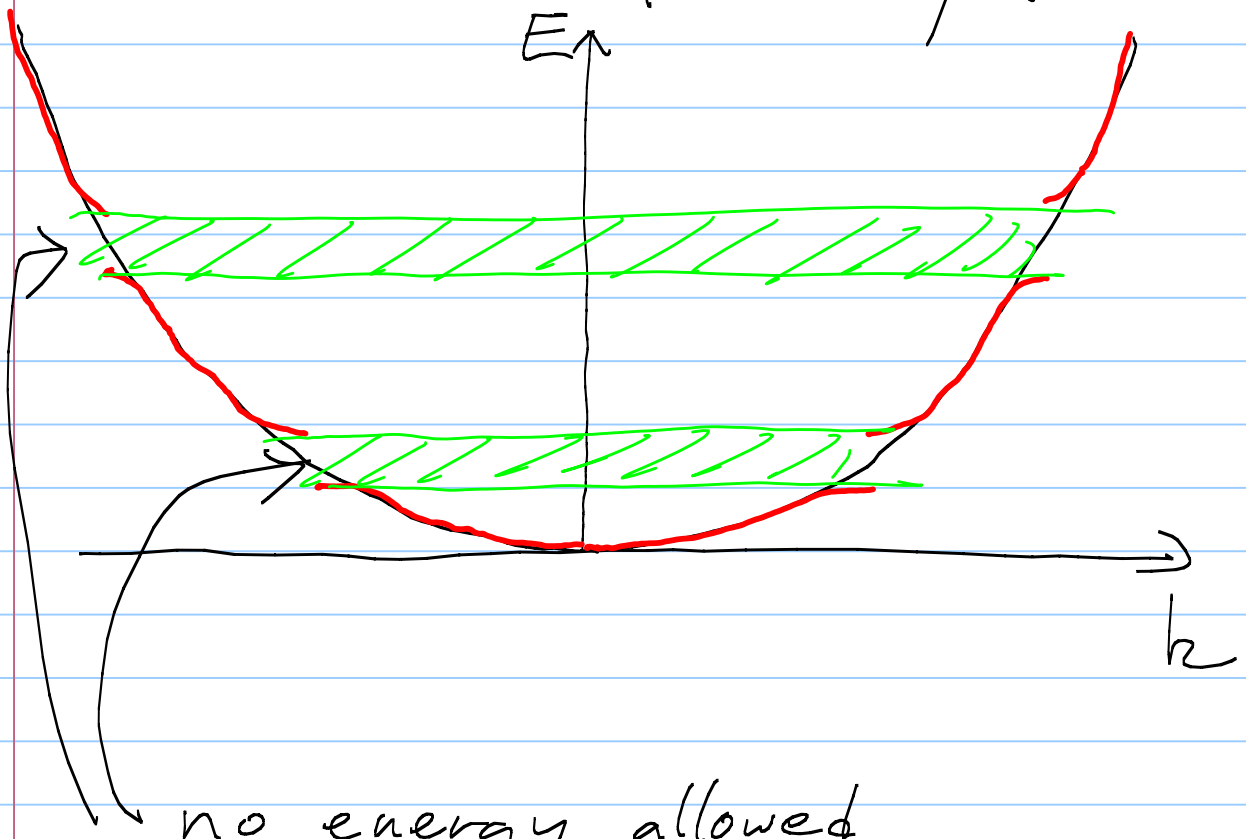
* Refresh your memory: we discussed dispersion relation previously in the context of the group velocity

$$v_{group} = \frac{\partial \omega}{\partial k} = \frac{1}{\hbar}\frac{\partial E}{\partial k} = \frac{\hbar k}{m} = \frac{p}{m}$$

$$v_{phase} = \frac{\omega}{k} = \frac{1}{\hbar}\frac{E}{k} = \frac{\hbar k}{2m}$$

$$v_{phase} = \frac{v_{group}}{2} = \frac{v_{classical}}{2}$$

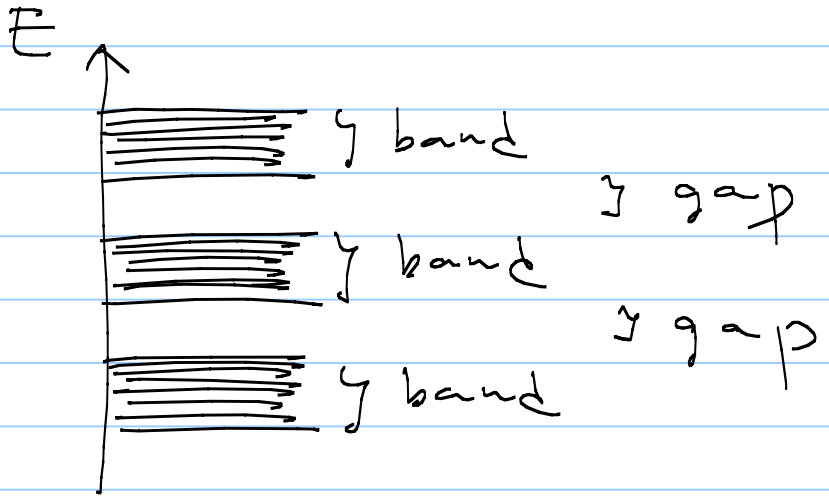
If we introduce periodicity of atoms



no energy allowed

These energy gaps are called band-gap.

They play very important roles in the electronic property of solids



If bands are partially filled, the solid is a metal (conductor).

If bands are completely filled, it is an insulator.

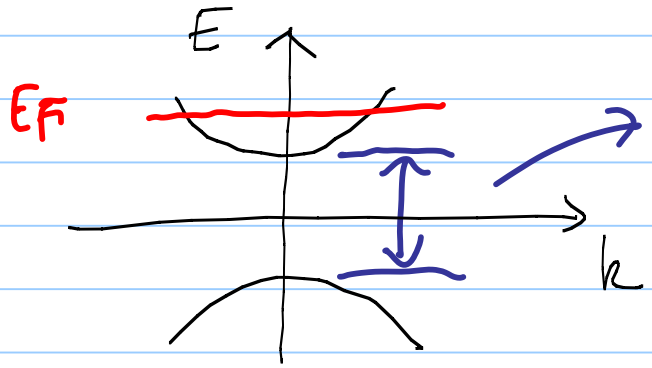
If the insulator can be made conducting by introducing impurities, it is called a semiconductor.

* Recently a new class of materials has been discovered, which does not belong to any of the above classification. It is called "Topological Insulators"

In topological insulators, the bulk is an insulator. However, the surface is a metal

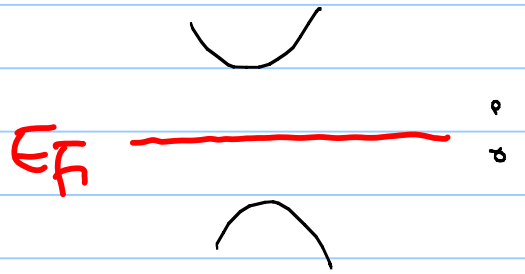
If we compare different class of materials

① Metal



Band gap (E_g)

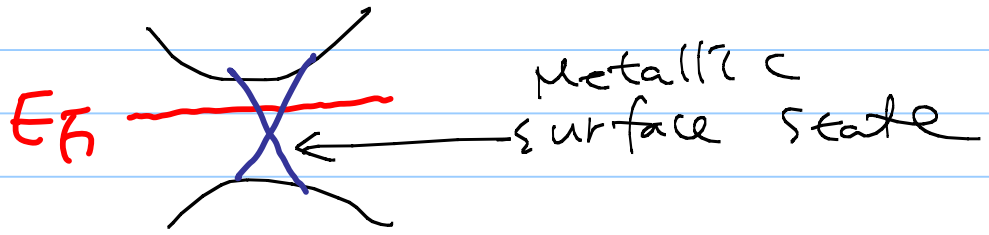
②



$E_g < 4eV$; Semiconductor

$E_g > 4eV$; Insulator

③



Topological Insulator