

Bonding in Solids

Ionic Model

- electrostatic forces between ions

Band Theory

- molecular orbital theory

Ionic Model

Recap

Two aspects

- Structure prediction
 - hard elastic spheres
 - moderate success
- Calculation of properties
 - lattice energy
 - considerable usefulness

Energetics and Properties of Ionic Crystals

Internuclear distance determined by:

- electrostatic forces between the ions

Coulomb's Law

$$F = \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r^2}$$

- repulsive force

Uncertainty principle

$$F = b \exp\left(-\frac{r}{\rho}\right)$$

Lattice energy given by

$$U_L = -\frac{AZ_A Z_B e^2 N_A}{4\pi\epsilon_0 r_0} \left(1 - \frac{\rho}{r_0}\right)$$

A = Madelung constant (geometry of the lattice)

Theoretical (NaCl) = -757 kJmol⁻¹

Experimental (NaCl) = -770 kJmol⁻¹

Molecular Orbital Theory

Construct molecular orbitals from atomic orbitals

Usual model

- linear combination of atomic orbitals (LCAO)

Mathematically

$$\psi_j = \sum_i c_{ij} \phi_i$$

Sum is over

all the atomic orbitals

all independent combinations

Large c_{ij} means large electron density of the atom.

Two atomic orbitals can give just two molecular orbitals

$$\psi_1 = \phi_1 + \phi_2$$

$$\psi_2 = \phi_1 - \phi_2$$

The coefficients are the same for the same type of atomic orbital.

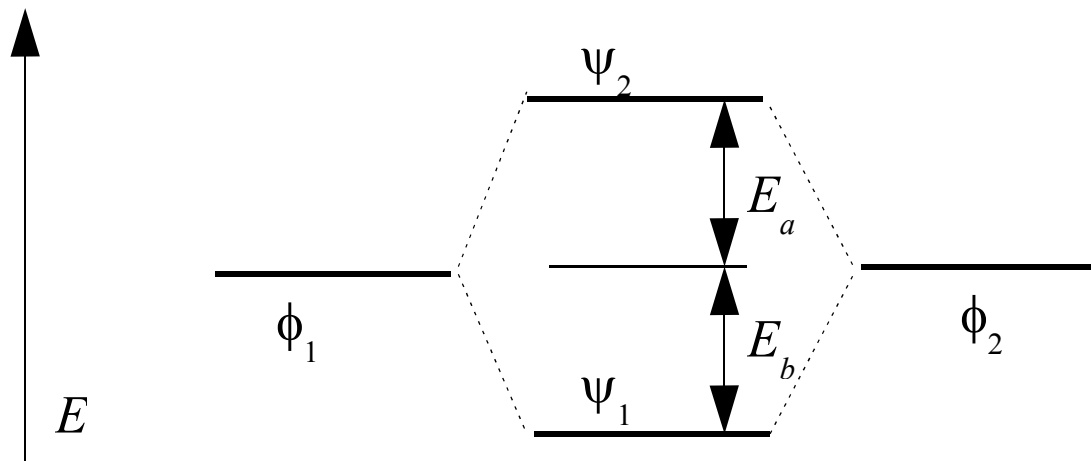
These we know as the

- bonding orbital
- antibonding orbital

Look at the electron distributions

1. Bonding - constructive overlap in between the nuclei
2. Anti bonding - destructive overlap

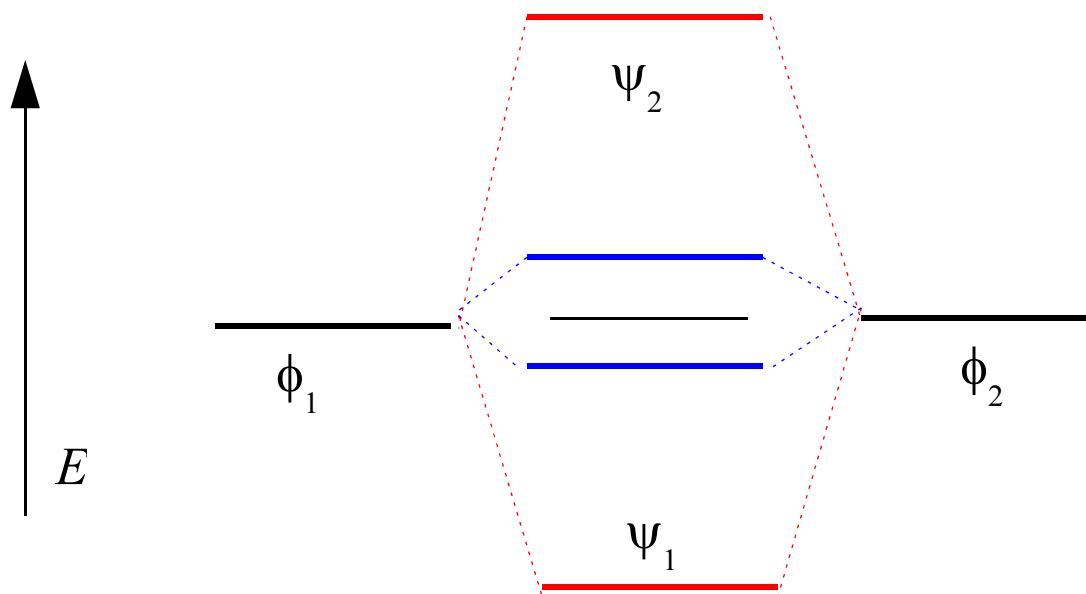
Can represent the molecular orbital formation using a diagram



$$E_a > E_b$$

E_b large for strong interactions between the atomic orbitals

Large E_b means a strong bond, electron is stabilised in the molecular orbital



Red - strong interaction between the atomic orbitals

Blue - weak interaction between the atomic orbitals

Fill the molecular orbitals using the same Aufbau Principle

- lowest energy first
- spin pair (Pauli principle)

Type of molecular orbital depends on the symmetry with respect to the internuclear axis

σ - sigma: symmetric about axis
(no angular momentum)

π - pi: antisymmetric about axis
(one unit of angular momentum)

Atomic s-orbitals will always give σ bonds

Atomic p-orbitals can give both σ and π bonds

Three atomic orbitals will give three molecular orbitals

$$\psi_1 = \phi_1 + \phi_2 + \phi_3$$

$$\psi_2 = \phi_1 - \phi_3$$

$$\psi_3 = \phi_1 - \phi_2 + \phi_3$$

These we can see as

- bonding
- non-bonding
- antibonding

Again look at the electron distributions.

In general then:

N atomic orbitals will give **N** molecular orbitals

N large for an extended solid

Molecular orbitals

Factors to consider

- overlap
- symmetry
- relative energy

Overlap

The strength of the interaction between atomic orbitals depends on their overlap

Poor overlap = poor interaction
= small stabilisation energy

Poor overlap if atomic orbitals contracted

- High effective nuclear charge, Z_{eff}
e.g. 1s orbitals for heavy elements

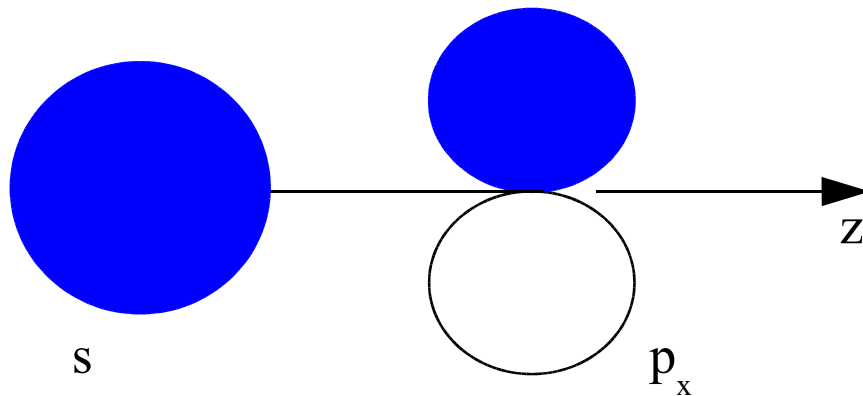
Can ignore inner core electrons when forming molecular orbitals

Symmetry

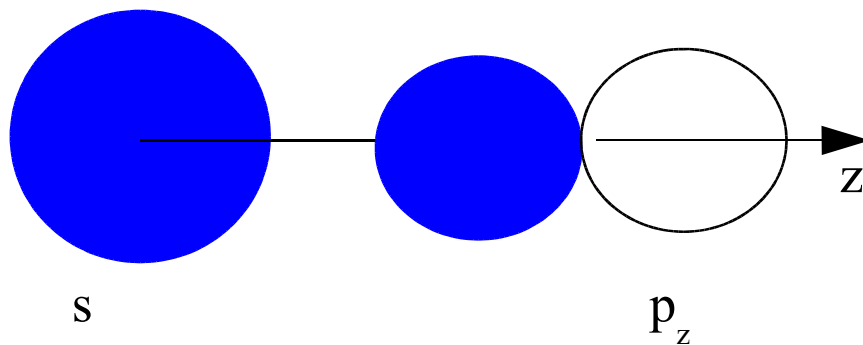
Orbitals of unlike symmetry will give zero overlap

- overlap from positive and negative lobes cancel

Example



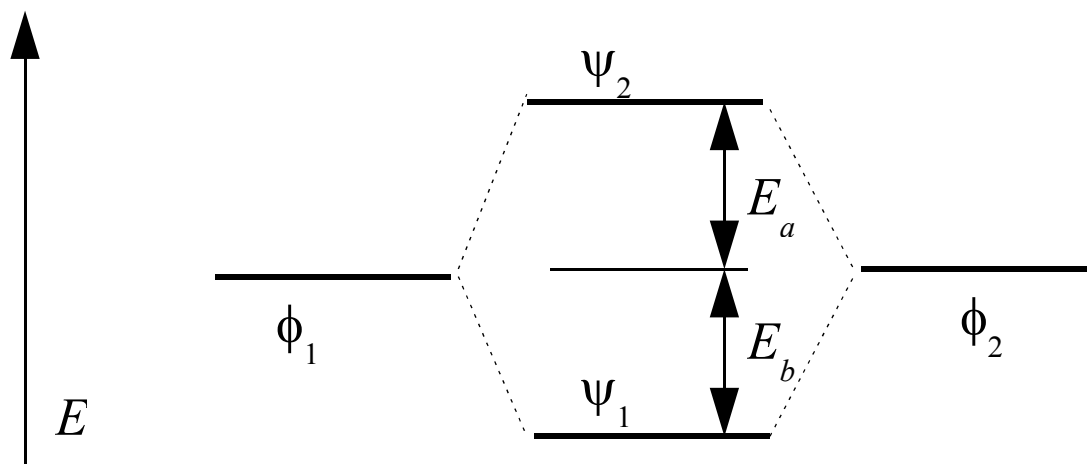
contrast with the p_z



Energy

Atomic orbitals must be of similar energy to get a strong interaction

The resulting molecular orbital will then have similar contributions from both atomic orbitals.



For the molecular orbitals we have

$$\psi_1 = \phi_1 + \phi_2$$

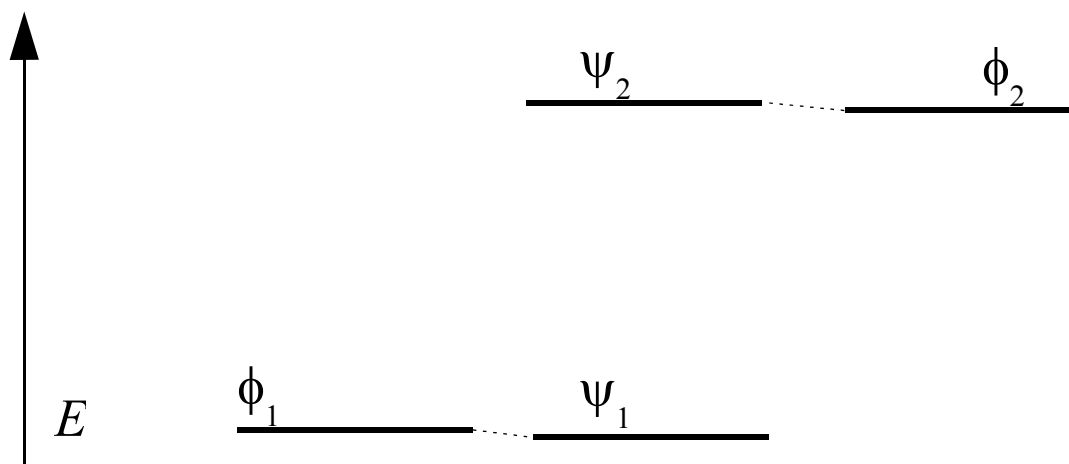
$$\psi_2 = \phi_1 - \phi_2$$

The coefficients of the atomic orbitals are the same

- the electron spends as much time on each atom

When the energies are widely different

- weak interaction
- molecular orbitals are principally atomic in character
- coefficients reflect how much time an electron spends on an atom (eg electronegative, F⁻)



Now we have

$$\psi_1 \approx \phi_1$$

$$\psi_2 \approx \phi_2$$

The molecular orbital ψ_1 is essentially the same as the atomic orbital ϕ_1

Molecular orbital ψ_2 is essentially the same as atomic orbital ϕ_2 .

Example for a molecule: N_2 :

N is $1s^2, 2s^2 2p^3$:

5 occupied atomic orbitals $1s, 2s, 2p_{x,y,z}$ on each
10 atomic orbitals on each

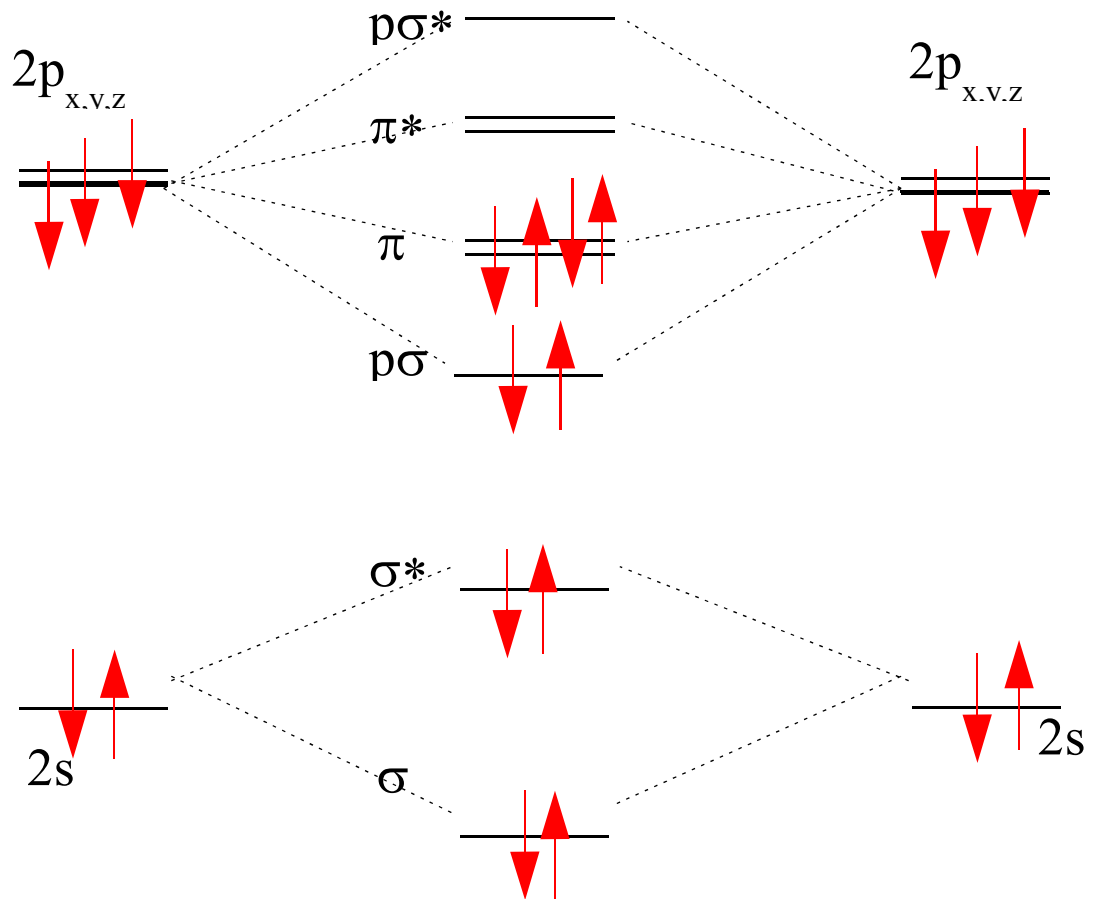
Do not include unoccupied orbitals of higher energy

Assume only orbitals of similar energy overlap
 $1s - 1s : 2s - 2s : 2p - 2p$

(In any case by symmetry $2s$ can only give non-zero overlap with $2p_z$)

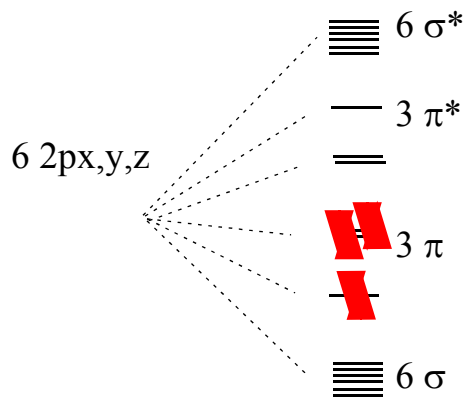
Ignore $1s-1s$ overlap,

Molecular orbital diagram for N₂



What happens for a large molecule?

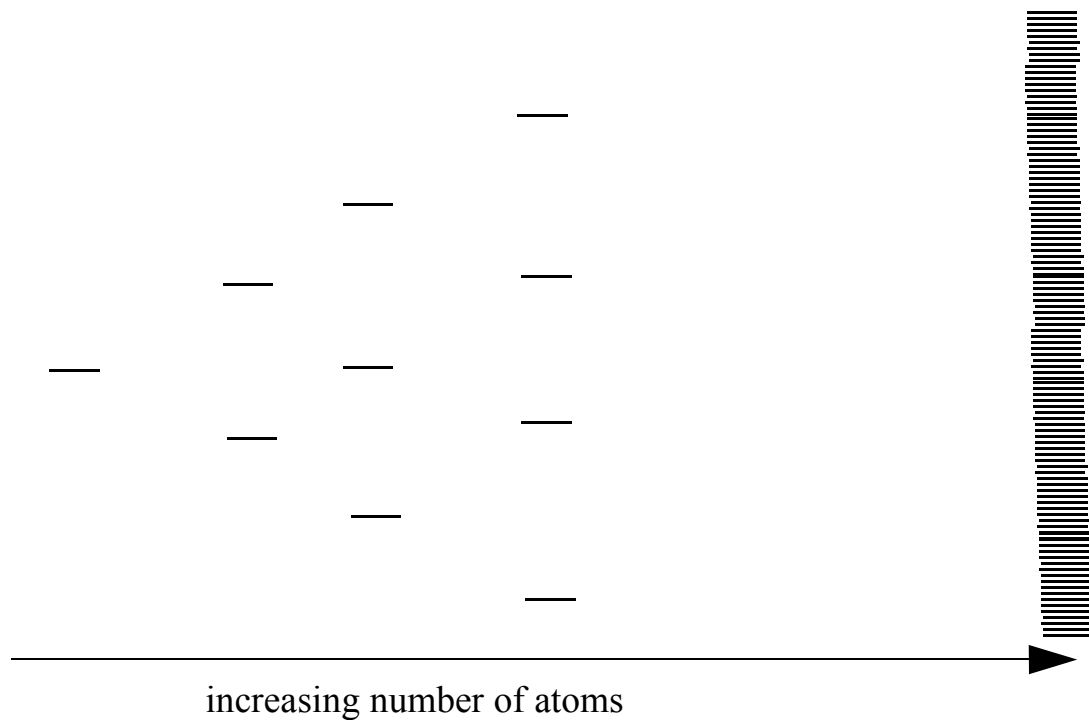
For the benzene framework (that is neglecting the hydrogens) we have:



Now as more atoms join the chain so the energy levels get closer together.

Also the difference in energy between the bonding and antibonding orbitals decrease.

In the limit of a large number of atoms, such as in a solid with 10^{20} atoms, the discrete orbitals have formed a continuous band of energies. The difference in energy between the bonding and antibonding set depends on the number of atoms, their separation and the orbital overlap.



Note still discontinuous energy, N orbitals, NOT a continuous energy

NB Although the number of orbitals increase
The maximum energy separation is limited:

$$E_N - E_1 \rightarrow 4\beta$$

where β is the resonance integral.

The energy of an electron found in two atomic orbitals A and B

Free electron theory

Sommerfeld

Metal is regarded as a potential well (box)

Valence electrons are free to move

Particle in a box.

In the simplest form - potential from the nuclei omitted.

Energy levels are quantised, and as the box gets bigger so the levels get closer together

Electron fill the levels two at a time (spin-paired)

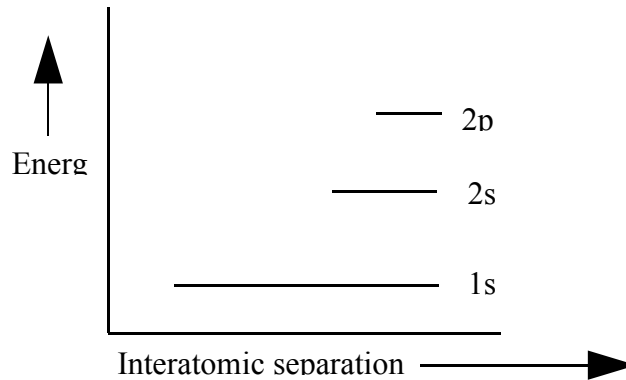
Highest filled level at absolute zero known as the *Fermi* level

corresponding energy is the *Fermi* energy, E_F

Work function, ϕ , the energy required to remove the uppermost valence electrons from the potential well

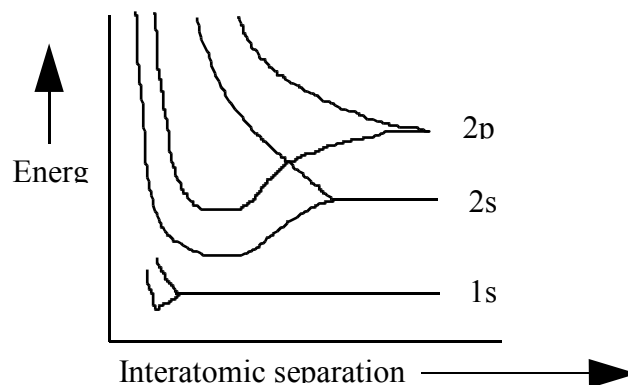
Here band gaps arise because of the effect of destructive interference between the electron waves and the lattice points which provide a periodic potential.

Take a set of atoms on lattice points
- far enough apart for the orbitals to be atomic like.



Now, bring the atoms closer together. Orbitals interact and broaden.

First, more radially diffuse, high energy, orbitals
Gradually as the atoms get closer so lower energy interact.



For H_2 , at a pressure of $> 10^6$ atm the atoms will have been forced close enough together for the orbital overlap to broaden the 1s into a band and give metallic character.

How many orbitals have particular energies?

Must look at number of combinations.

Completely bonding or antibonding orbitals = 1 way



For others we have to remember it doesn't matter what order we take them in.

I.e.



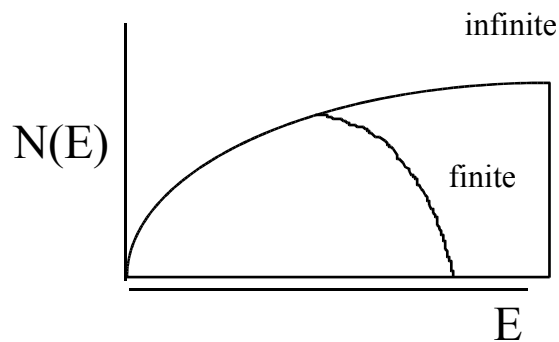
is the same as



Thus we need the binomial coefficient (in this simple case) ${}^7C_1 = 7$: For two⁺ ${}^7C_2 = 21$ and so on:

Draw stick diagram 1:7:21:35:35:21:7:1

Number of equivalent energy levels at any one energy is called the 'density of states' $N(E)$. In practise rather more complex than this picture but the general shape is as shown, the shape for an infinite number of atoms is parabolic:



Sometimes on the other way with E as the y axis

The actual shape of the density of states function is of great importance in the theory of metal structures.

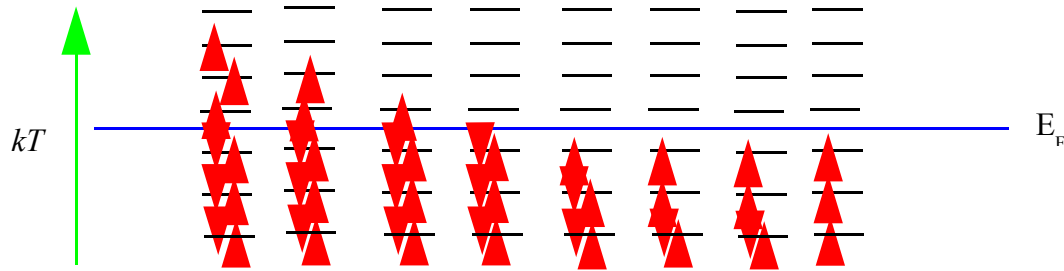
Energy levels within a band close ,effectively form a continuum

- still discrete
- Pauli principle is observed when feeding electrons into them.

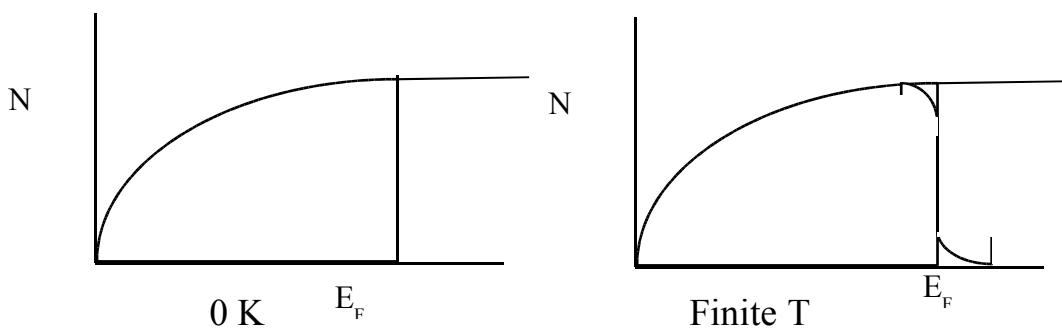
The energy corresponding to the highest filled level at absolute zero , the HOMO, in a partly filled band is called Fermi Level at the Fermi energy, E_F .

Unlike small molecules the energy difference between the electronic orbitals making up the band is very small of the order or less than the thermal energy available.

Sketch the Fermi Level :



Thus at the Fermi level there will be some electrons in orbitals of slightly higher energy, with the population determined by the Boltzmann distribution. This can be drawn using the band diagrams as below;



Two features:-

- electrons can move to orbitals of equivalent energy, hence we have electrical conductivity
- some unpaired electrons at the Fermi level. This will give paramagnetism. However, only a small fraction of the total number of electrons in a metal so the effect will be small. Since the population is temperature dependent so too will the paramagnetism.

