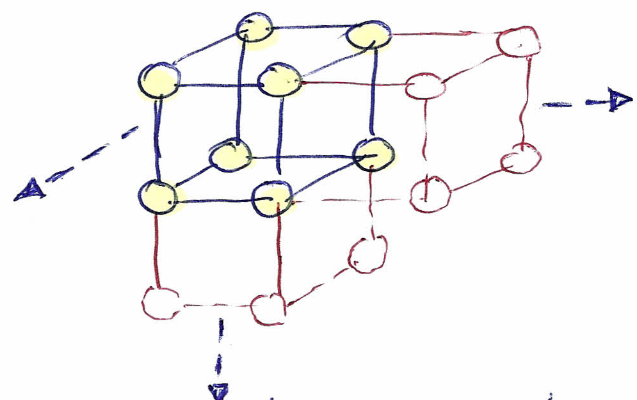
FROM ATOM TO SOLID STATE

It is interesting to consider not only the atom alone but also more complex systems:

→ molecules :  → diatomic molecule

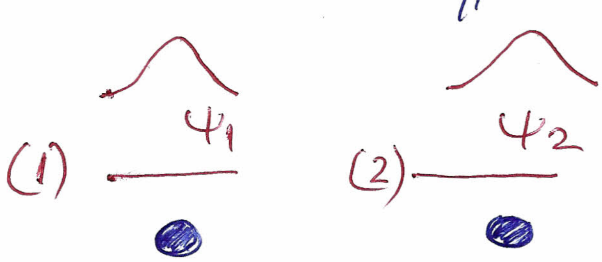
→ atoms in crystals = periodic arrangements of atoms in x, y, z



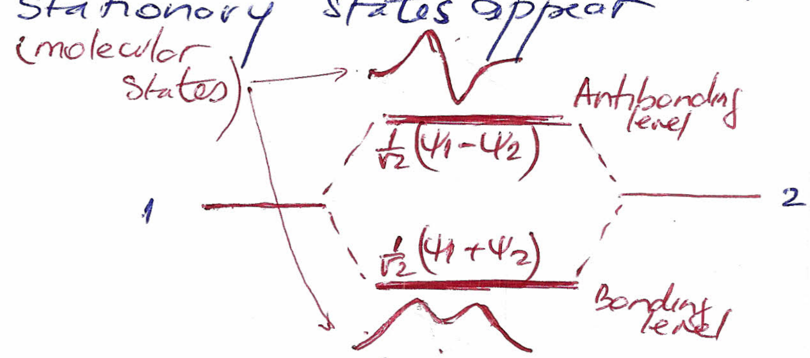
In quantum mechanics the wave functions and the corresponding energy levels will be calculated by solving the Schrödinger equation by taking into account the corresponding potential $U(\vec{r})$ in each configuration.

(1) MOLECULES (diatomic molecule)

If the two atoms (for simplifying, identical) are far apart, they do not interact and their electronic energy levels can be considered to be those of isolated atoms. When they are brought closer the interaction appears ⟺ individual wave function overlap and new different stationary states appear



far apart
no interaction
atomic levels



close atoms ⇒
overlap ⇒
interaction
molecular levels

This can be quantum mechanically demonstrated.

<u>see:</u> C. Tiusan & al, Mecanica cuantică prin aplicatii
UTPRESS, Cluj Napoca 2013
pg. 135

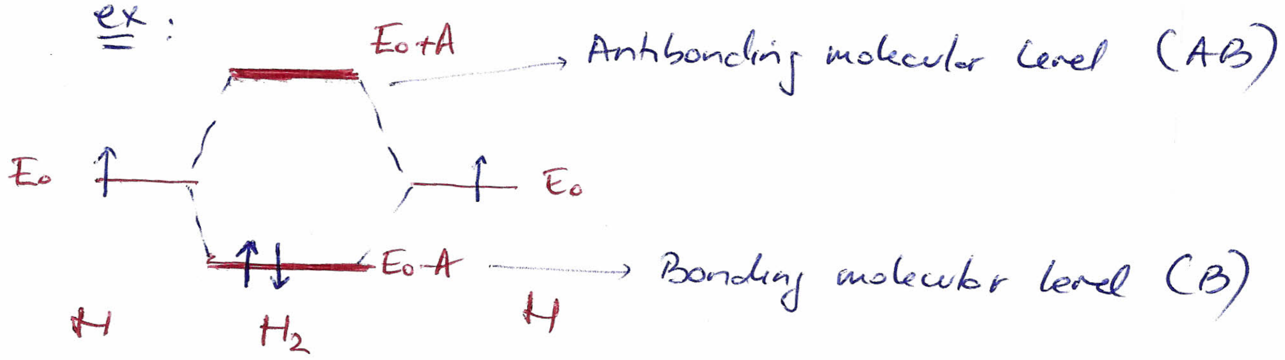
One can also demonstrate that an electron is fluctuating sinusoidally (periodically) in time between the atoms (1) and (2) with a frequency:

$$\boxed{\omega = \frac{2A}{\hbar}}$$ ~~flip-flop frequency~~ A = interaction energy

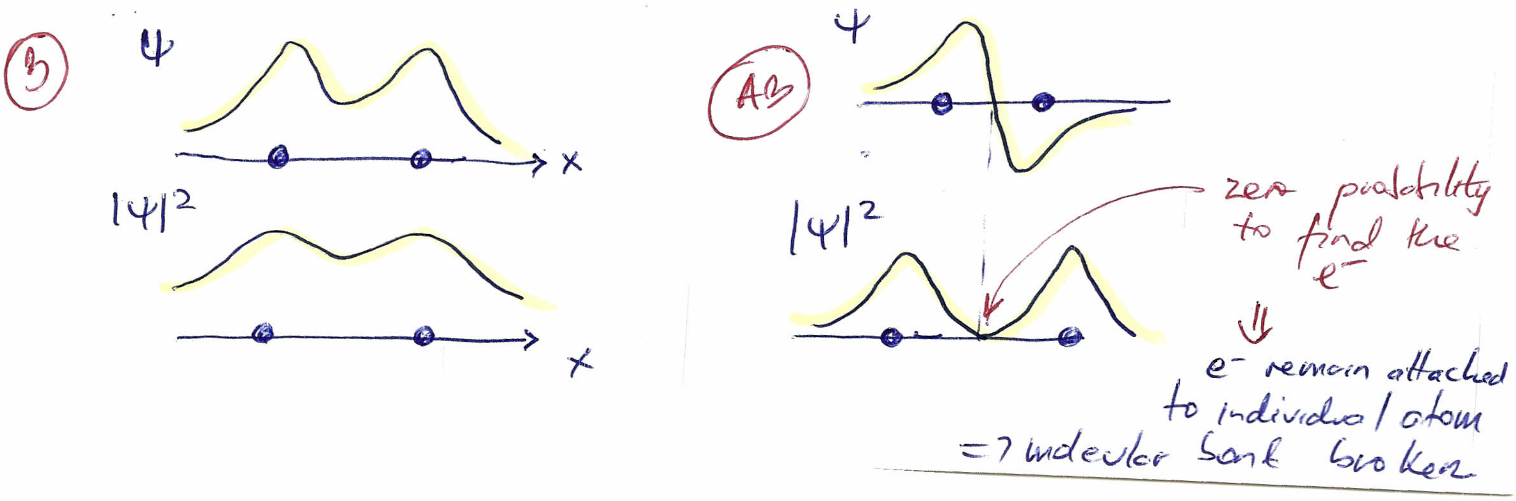
⇒ the e^- is "shared" between the atoms (1) and (2) which explain the covalent bonding in the molecule.

<u>Obs:</u> (1) The molecular levels are populated with the electrons accordingly to the Pauli exclusion principle

<u>ex:</u>

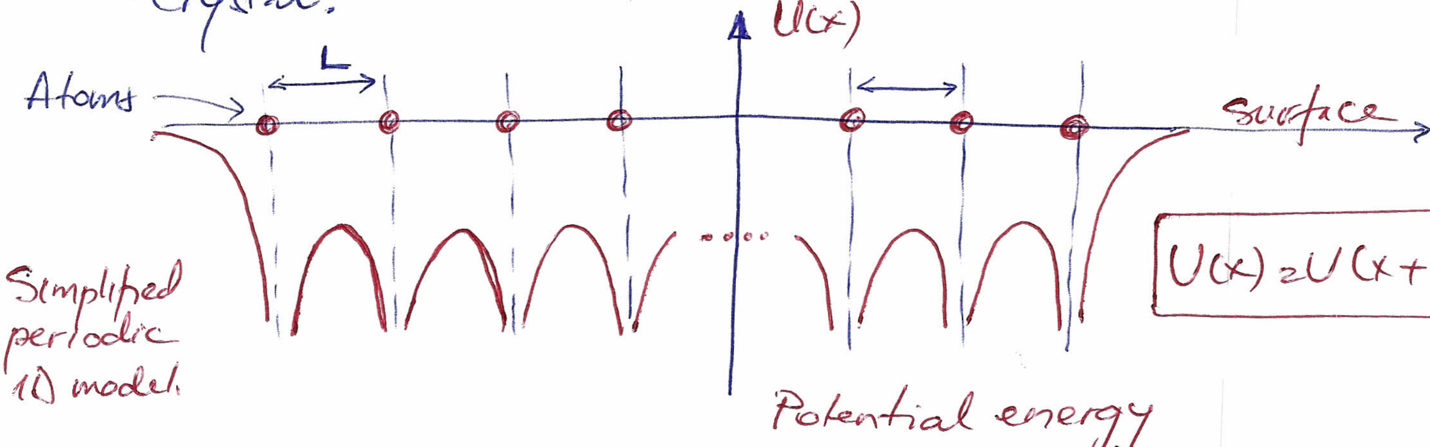


(2) When the e^- are brought to the AB level (e.g. by energy absorbtion) the molecular bound is broken



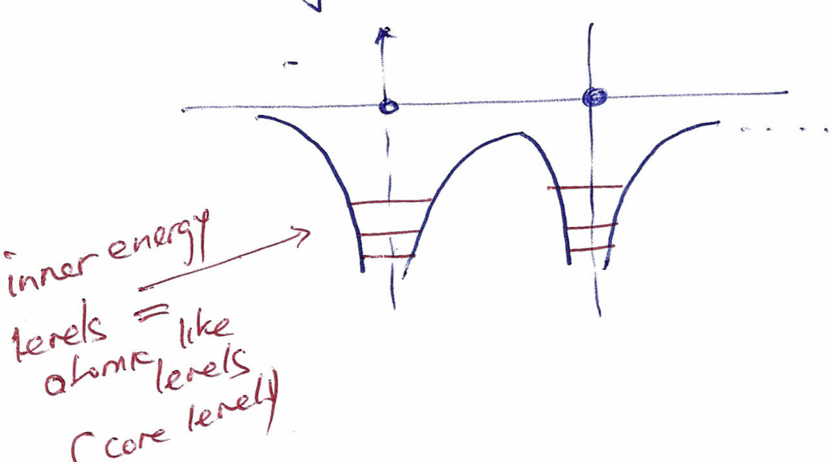
② Band theory of solids

Cristalline solids represent periodic arrangements of atoms. The electrons of these atoms will "see" therefore a periodical potential, with exactly the periodicity and the symmetry properties of the crystal.



$$U(x) = U(x+L)$$

The most electrons will remain attached to the nuclea, only the electrons of the external shells will be able to pass from one atom to the other by tunneling =>



Only the outer levels are affected by the neighbouring with other atoms.

The Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\psi = E\,\psi \qquad U(x) = U(x+L)$$

will have a general solution:

$$\psi(x) = u(x)\,e^{ikx} \qquad \text{with } u(x) = u(x+L)$$

$u(x)$: function having the crystal periodicity; e^{ikx}: plane wave

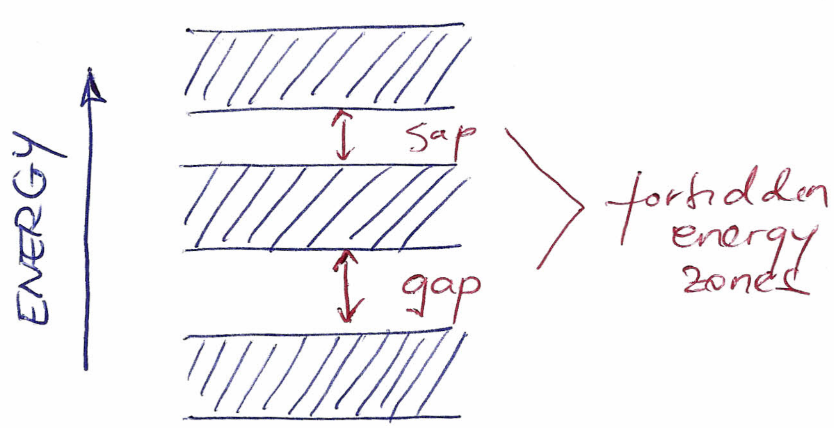
For a 3D model:

$$\boxed{\psi(\vec{r}) = U_{nk}(\vec{r})\, e^{i\vec{k}\vec{r}}}$$

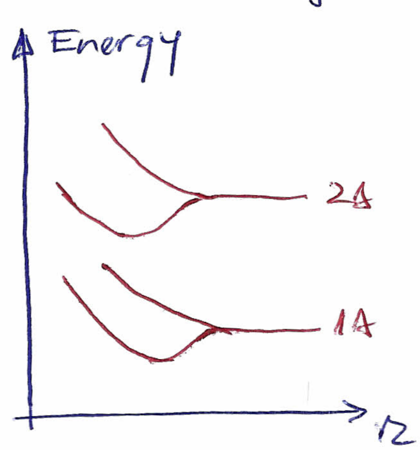
$\hookrightarrow$ $U_{nk}(\vec{r}) = U_{nk}(\vec{r}+\vec{R})$

where $\vec{R}$ is an elementary translation vector of the crystal (periodicity)

Solving the Schrödinger eq. and taking into account the periodical limit condition provide the <u>band structure of solids</u>. One find that in solids, the electrons energy levels are grouped in energy bands separated by forbidden zones called <u>band-gaps</u>.

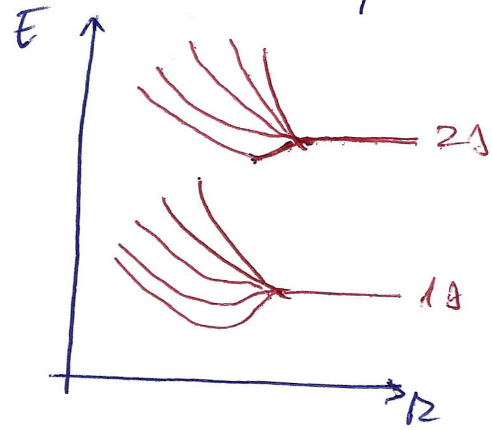


The origin of bands can be qualitatively understood going from atoms, through molecules, to multiple atoms periodical arrangements.

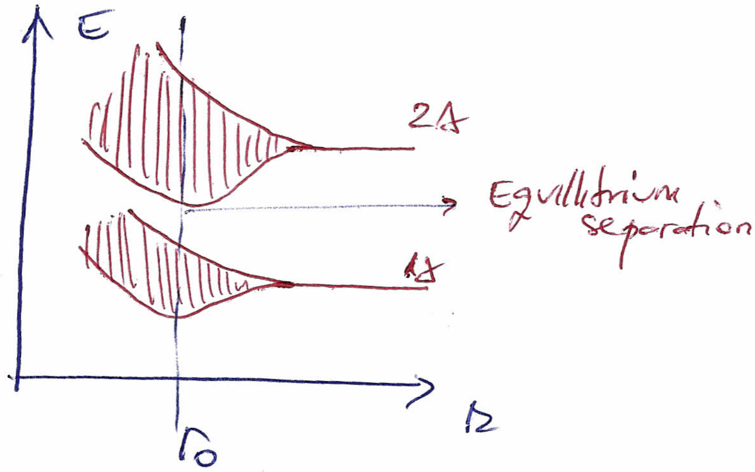


when two atoms are brought together, the 1A and 2A levels (and so on..) split into two components.

When 5 atoms are brought together, the 1s, 2s, ... levels split into five component.



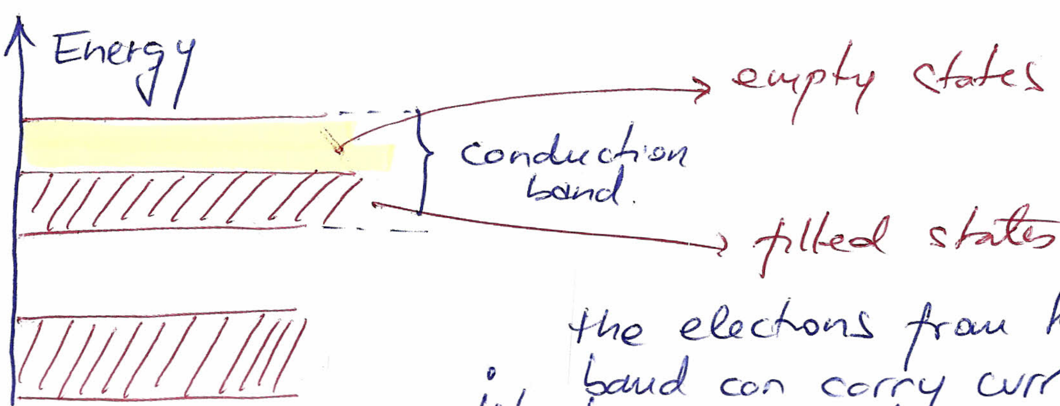
When a large number of atoms are brought together, the 1s, 2s, ... levels spread into energy bands.



Band theory allows us to build simple models to understand the behavior of conductors, insulators, semiconductors. The energy bands allow to explain the conduction. Two distinct situations appear:

METALS

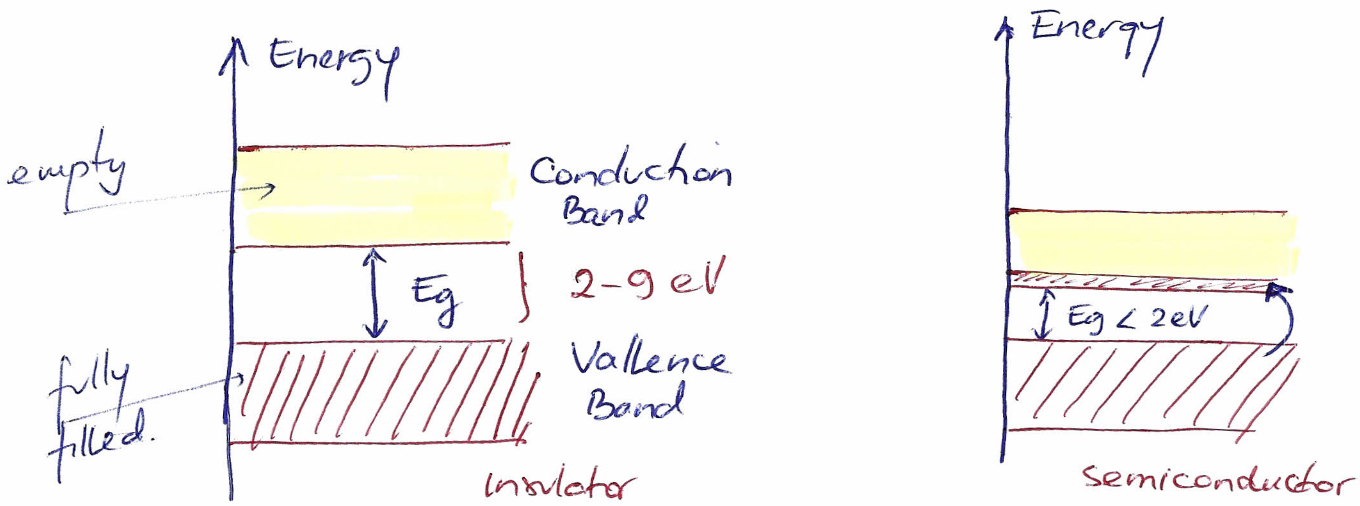
(1) the last band (higher energy) is not fully filled by electrons. (partially filled)
This band is called CONDUCTION BAND.



the electrons from the conduction band can carry currents. This is the case of METALS

INSULATORS

(2) The conduction band is fully empty. Bellow, separated by a long gap we find a fully filled band called the VALENCE BAND. Because the conduction band is empty, the electric conduction is not possible and we call the material insulator.



(3) SEMICONDUCTORS

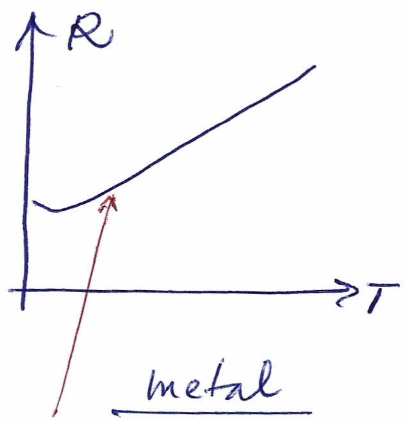
The band structure resembles to the one of an insulator but the gap between the vallence and the conduction band is much smaller than in case of insulators. The small energy gap allows electrons from the valence band to be thermally excited to the conduction band (the electron energy is $k_B T$.

$$k_B = \text{Boltzmann constant} = \frac{R}{N_A}$$

$$\boxed{k_B = 1{,}38 \cdot 10^{-23}\ J K^{-1}}$$

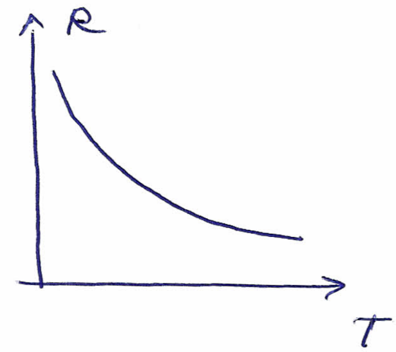
$T = 300\ K$ $\boxed{k_B T = 25{,}6\ meV}$

The band structure of a semiconductor explains the exponential increase of its conductance (exponential decrease of resistance) with increasing the temperature.



metal

R increases with T due to increasing collisions with lattice vibrations (see phenomenological microscopic model of conduction) ⇔ decrease of the mean free path



semiconductor

R decreases because the density of carriers on the conduction band increases due to thermal excitation

$$n = n_0 e^{-E_g/2k_BT}$$

Energy gap values for

Insulators: ex. MgO
$E_g = 7.8\,eV$

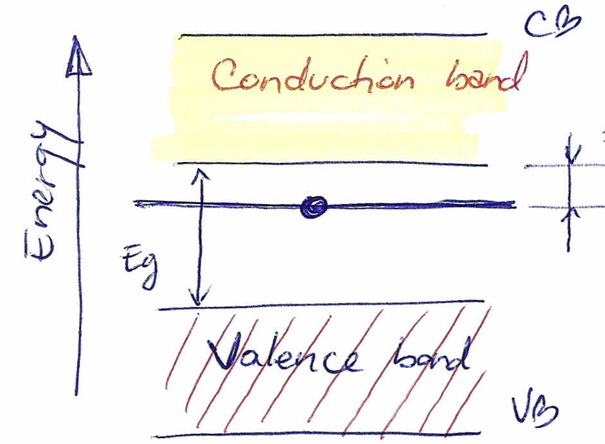
semiconductors

Crystal	Eg(300K) [eV]
Si	1,14
Ge	0,67
GaAs	1,42

A semiconductor can be pure ⇒ intrinsic or
dopped → with electron accepting impurities
→ with electron donor impurities

This impurities will lead to localized energy levels within the energy gap of the semiconductor.

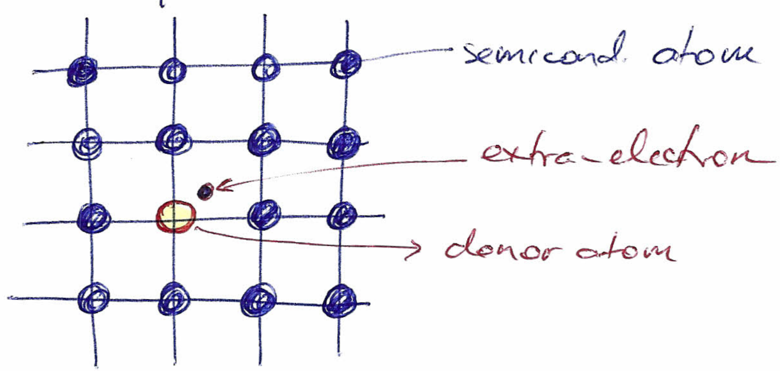
(1) n-type semiconductors



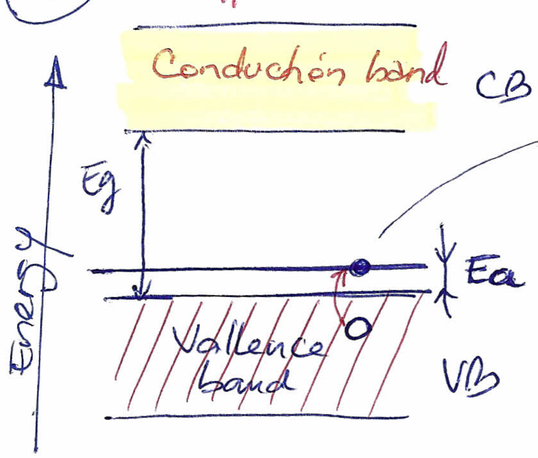
A small amount of energy is required to excite the electrons from the donor level to the conduction band

=> **n-type semiconductors**
↳ conduction by electrons excited in the conduction band.

Obs: On the crystalline structure the donor atom of impurity replaces the host atom locally and provides an extra-electron



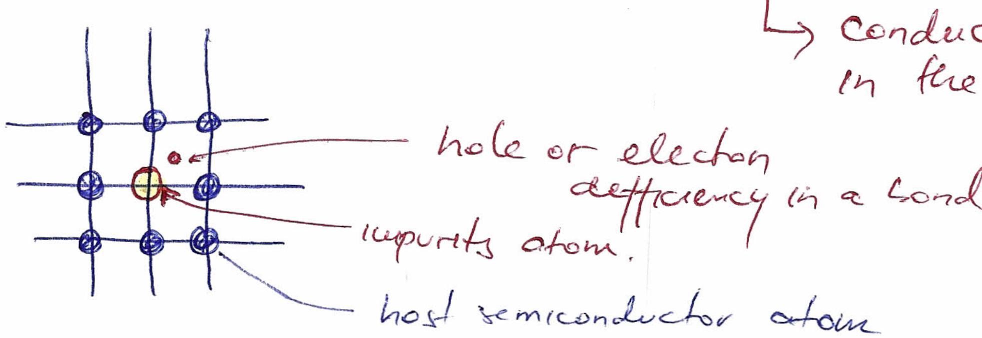
(2) p-type semiconductors



A small amount of energy is required to excite an e⁻ from the vallence band to the accepting impurity level => empty space in VB

<=> hole (<=> of positive charge)

=> **p-type semiconductors**
↳ conduction by holes in the vallence band.



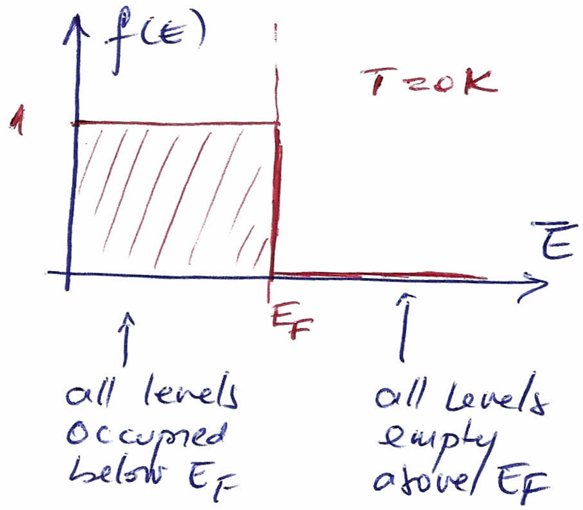
Fermi energy

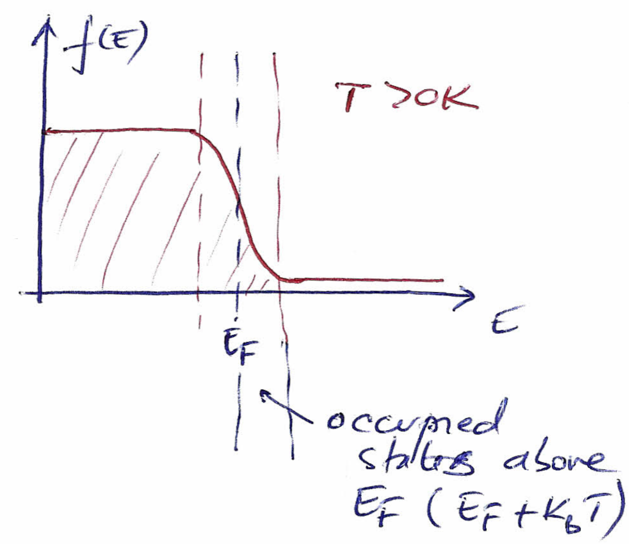
In a metal, the last energy level occupied by electrons is called the FERMI LEVEL. Statistical physics shows that the probability of a particular state of energy E to be occupied of the electrons in solids is described by:

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

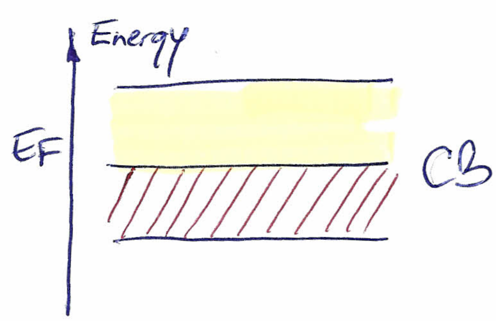
the Fermi-Dirac distribution function

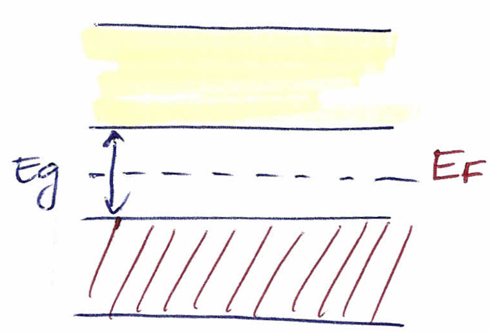
with E_F = energy of the Fermi level





For a metal: and a semiconductor/insulator





The Fermi level is taken into the gap (for intrinsic pure semiconductor or insulator in the middle of the gap

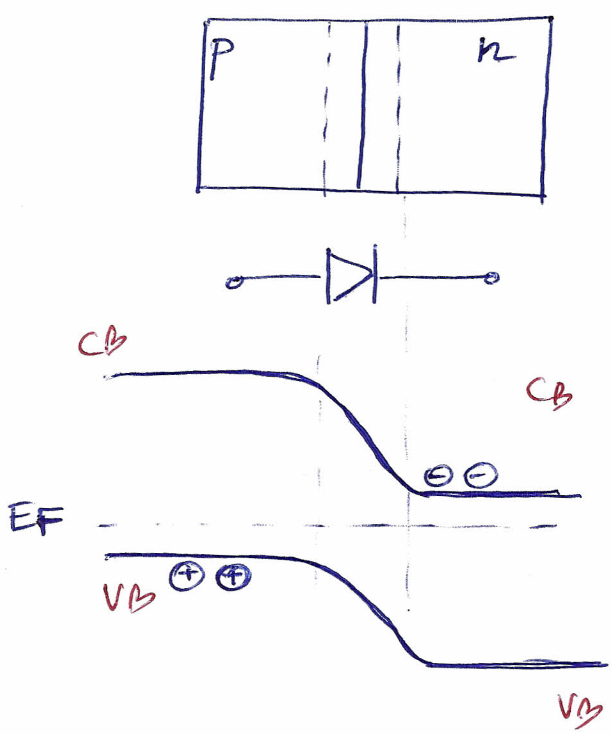
Semiconductor devices

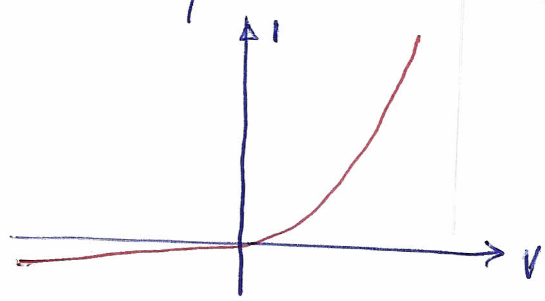
Based on different types of semiconductors one can built complex semiconductor devices

Junction diode (p-n junction)

→ obtained at the junction between a p-type and an n-type semiconductor

⇒ rectifying characteristic (assymmetric in voltage)





Transistors npn, pnp junctions

The transistor was invented in 1948 and lead to a shift away from vacuum tubes and served as a future basis of electronic devices developed afterwards. From transistors to modern complex integrated circuits electronics undergo 70 years of continuous developement. The basic principle of electronics consist in manipulating the electron charge in complex band structure architectures obtained by alternating semiconductor materials (as in case of junctions, transistors, etc).

Spin Electronics

However, we learned that, beyond of the electrical charge, the electron has also a spin. The manipulation of both CHARGE and SPIN in an electronic device opened a newer field of electronics called SPIN ELECTRONICS or SPINTRONICS. This relativelly new research and technology area started in 1988 with the discovery of the Giant Magnetorezistance Effect by Albert FERT and Peter Grunberg in magnetic multilayers (rewarded in 2007 by Nobel Prize in Physics).

Spintronics revolutioned the sensors and data-storage technologies and has tremendous fields off application from the high-density-hard disk drivers and read heads, magnetic field sensors, microwave generation, high-frequency oscillators to many other future generation devices currently under research in academic and industrial laboratories.