

# PH20017/63 Condensed Matter Physics 1

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Lecture notes set 3 - Semiconductors

These are only summary notes – you should annotate, expand and supplement.

# Semiconductors

## 1. Electrons and holes in semiconductors

- Energy bands in semiconductors
- Holes
- Equations of motion

## 2. Intrinsic semiconductors

- Carrier concentrations
- Chemical potential
- Effective masses

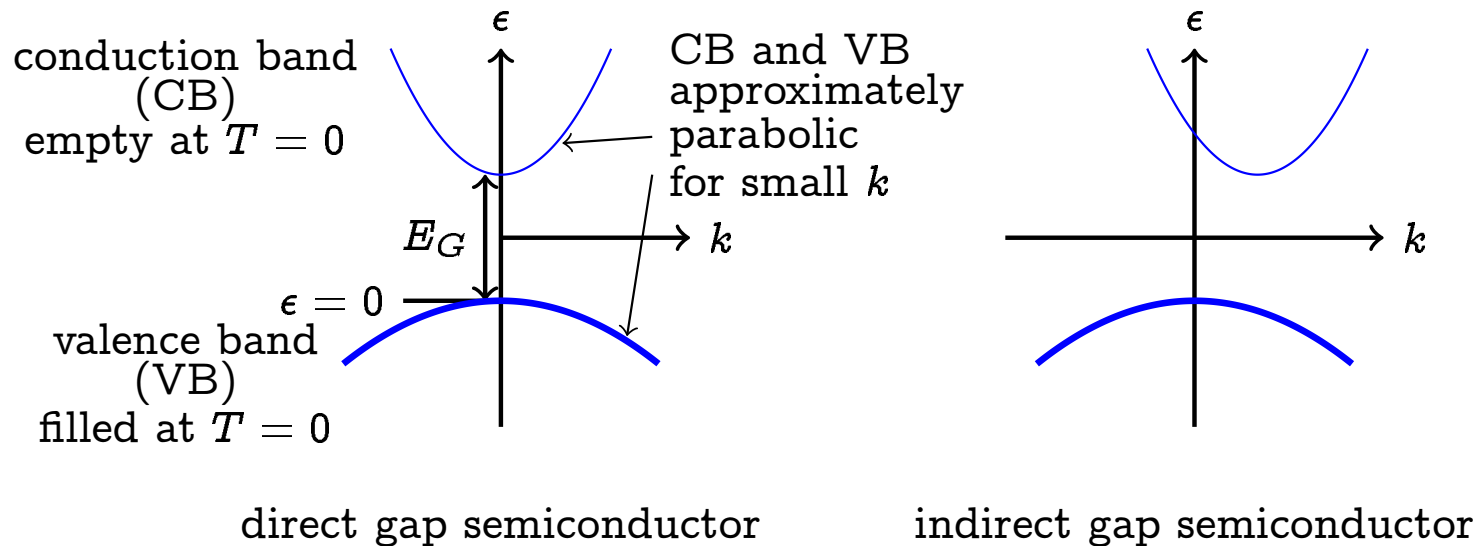
## 3. Extrinsic semiconductors

- H-atom model for  $n$ -type and  $p$ -type
- Carrier concentrations

# Semiconductors

In some materials an energy gap separates the occupied and unoccupied energy bands. If the gap is  $\sim 1$  eV, the material is called a semiconductor.

The highest occupied band is called the **valence band**, and the lowest unoccupied band is called the **conduction band**.

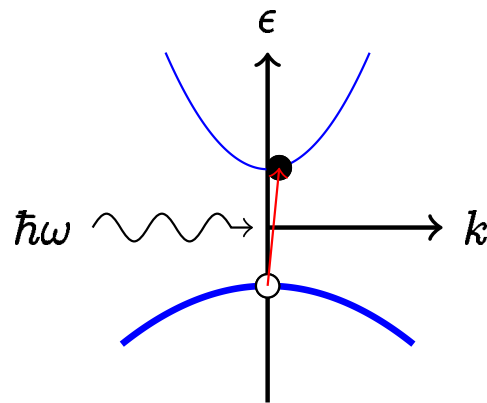


In a **direct band gap** semiconductor the CB minimum and VB maximum occur at the same wave vector  $\vec{k}$ .

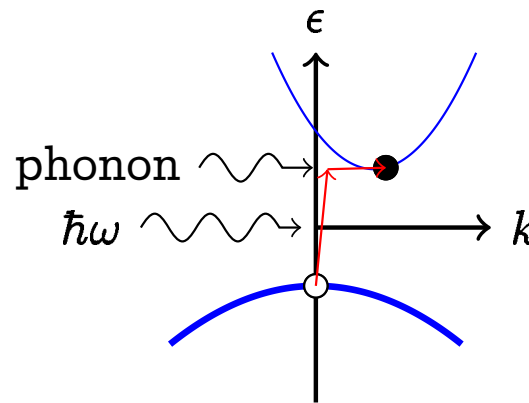
Otherwise, the semiconductor is an **indirect band gap** semiconductor.

# Direct vs indirect

Imagine an electron at the top of the valence band absorbing a photon with energy  $\hbar\omega$  and being excited into the bottom of the conduction band.



direct gap



indirect gap

Energy conservation:

$$\hbar\omega \simeq E_G$$

Momentum conservation:

$$\hbar\Delta k = \hbar\omega/c \text{ (photon mom.)}$$

$$\text{or } \Delta k = \omega/c$$

For photon energy  $\hbar\omega \sim 1 \text{ eV}$ ,  $\Delta k \sim 10^{-3} \text{ \AA}^{-1}$ , just a small fraction of the BZ ( $\sim 1 \text{ \AA}^{-1}$ ). This corresponds to a  $\sim$  vertical transition in the energy bands.

In an indirect band gap semiconductor, a **phonon** (lattice vibration) must also be involved to conserve both energy and momentum (lattice vibrations can have low energy, large momentum). This is an **indirect** absorption process.

In many semiconductors both the VB maximum and CB minimum lie at  $k = 0$ . We will assume this.

We measure energies from the top of the valence band ( $\epsilon = 0$ ).

The bottom of the conduction band is then  $E_G$ , the band gap.

We approximate the energy of an electron state in the conduction band as

$$\epsilon(\vec{k}) = E_G + \frac{\hbar^2 k^2}{2m_C^*} \quad m_C^* \text{ is positive.}$$

We approximate the energy of an electron state in the valence band as

$$\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m_V^*} \quad m_V^* \text{ is negative.}$$

If the energy gap  $E_G$  is of the order of 1 eV, then at room temperature a number of electrons will be thermally excited from the VB into the CB.

We will look at how many shortly. For Si at 300 K it is  $\sim 10^{10}/\text{cm}^3$  — far fewer than the number of conduction electrons in a metal.

# Energy gaps of some materials

Material	Gap	$E_G$ (eV)	
		0 K	300 K
Diamond	i	5.4	
Si	i	1.17	1.14
Ge	i	0.74	0.67
InSb	d	0.24	0.18
GaP	i	2.32	2.26
GaAs	d	1.52	1.43
CdS	d	2.58	2.42
CdSe	d	1.84	1.74
CdTe	d	1.61	1.45

after Kittel

d = direct gap, i = indirect gap

# Holes

In a thermally excited semiconductor the valence band is not full.

As a result the valence band is no longer inert. Instead, it contributes to the conduction properties.

If a relatively small number of electron states are empty, it is more efficient to describe the properties of the nearly full valence band in terms of the empty states.

$$\text{band of } N - n \text{ electrons} \equiv \underbrace{\text{full band of } N \text{ electrons}}_{\text{inert, no effect}} + n \text{ holes}$$

We will now develop this idea and see the holes behave like particles with

charge  $q_h = +e$

positive effective mass  $m_h^* > 0$

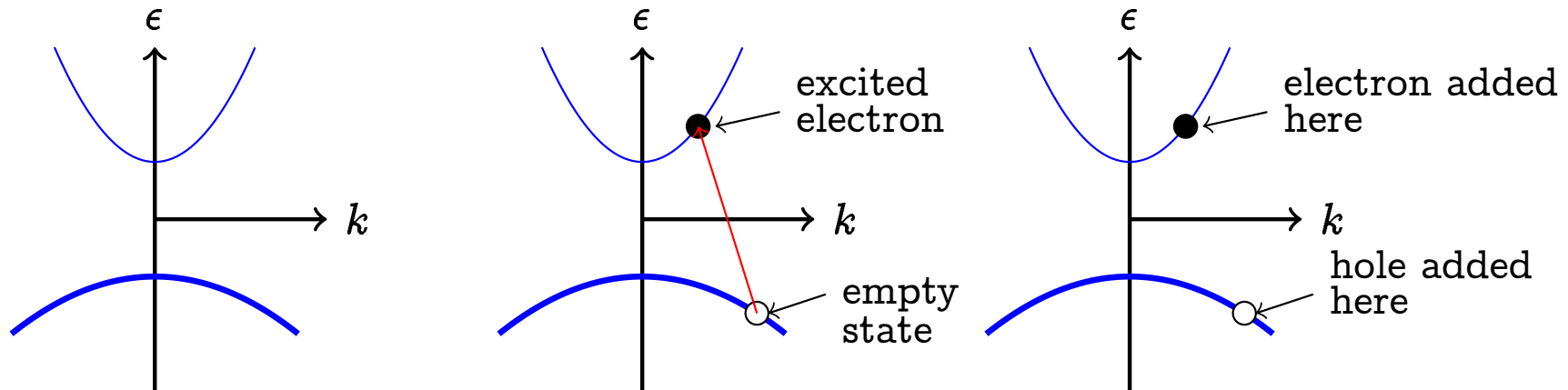
wave vector  $\vec{k}_h = -\vec{k}_e$

positive energy  $\frac{\hbar^2 k_h^2}{2m_h^*} > 0$

velocity  $\vec{v}_h = \vec{v}_e$

# Hole charge

Imagine a semiconductor at  $T = 0$ , with a completely filled valence band. The total charge of the semiconductor is zero.



We now excite one electron from the filled valence band into the empty conduction band. The total charge on the semiconductor does not change.

This is equivalent to placing an electron, charge  $q_e$  into the conduction band, and placing a hole, charge  $q_h$ , into the valence band.

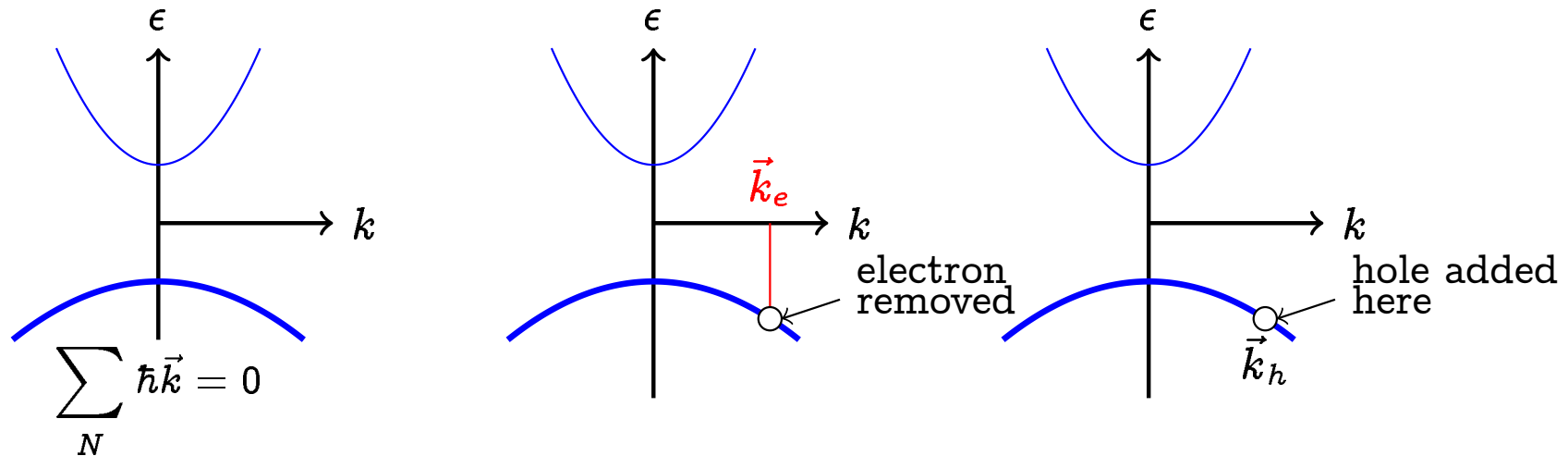
From charge conservation, initial charge = final charge. Therefore

$$0 = q_e + q_h \quad \Rightarrow \quad q_h = -q_e = +e. \quad \text{The hole carries a charge } +e.$$



# Hole wave vector

Imagine a semiconductor at  $T = 0$ , with a completely filled valence band. The total crystal momentum of the  $N$  electrons is zero.



Now remove an electron from a state with wave vector  $\vec{k}_e$ .

$$\text{Now total crystal momentum} = \sum_{N-1} \hbar \vec{k} = \sum_N \hbar \vec{k} - \hbar \vec{k}_e = 0 - \hbar \vec{k}_e = -\hbar \vec{k}_e.$$

The final state is equivalent to adding a hole with wave vector  $\vec{k}_h$ .

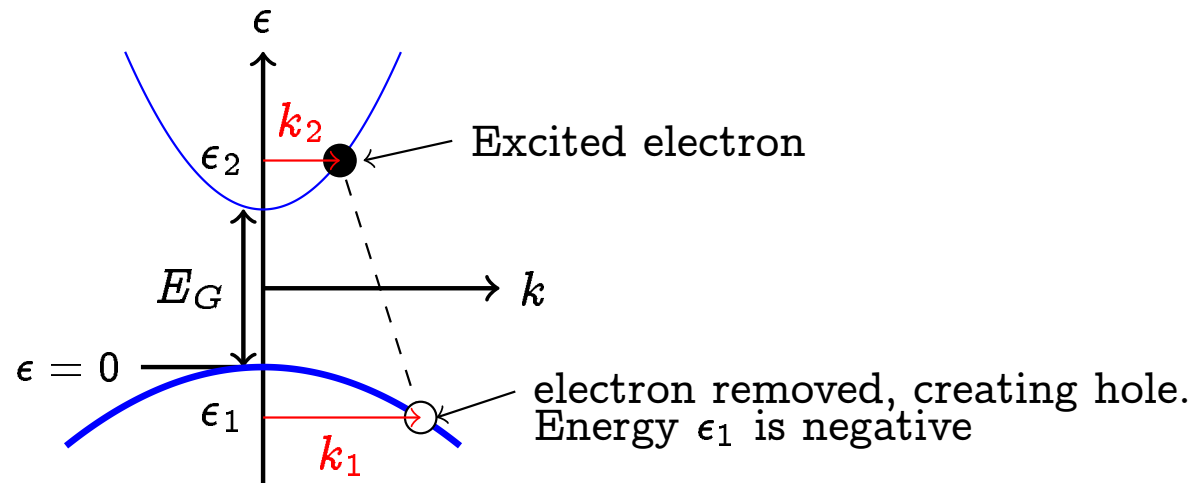
$$\text{To get the same total crystal momentum } -\hbar \vec{k}_e = \hbar \vec{k}_h + \sum_N \hbar \vec{k}_e = \hbar \vec{k}_h + 0.$$

The hole wave vector is  $\vec{k}_h = -\vec{k}_e$ .

# Hole energy and mass

We start from a semiconductor with a filled valence band.

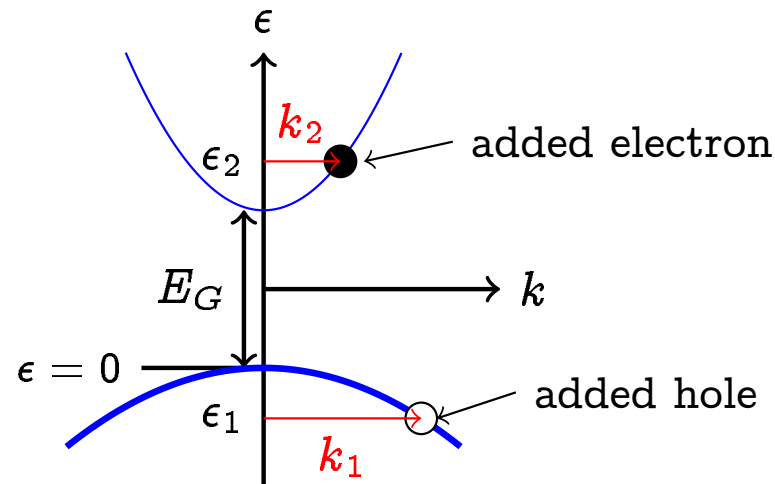
Now imagine thermally or optically exciting an electron from state  $\vec{k}_1$  with energy  $\epsilon_1$  in the full valence band, to state  $\vec{k}_2$  with energy  $\epsilon_2$  in an empty conduction band.



The energy input required for the transition is  $\Delta\epsilon = \epsilon_2 - \epsilon_1$ , or

$$\Delta\epsilon = \underbrace{\left[ E_G + \frac{\hbar^2 k_2^2}{2m_C^*} \right]}_{\epsilon_2} - \underbrace{\left[ \frac{\hbar^2 k_1^2}{2m_V^*} \right]}_{\epsilon_1}$$

We now create the same state of the system by starting with the full valence band, and then putting an electron in the conduction band, and **putting** a hole in the valence band. Since we start and end with the same configuration, the energy change must be the same:  $\Delta\epsilon = \epsilon_2 - \epsilon_1$ .



But in terms of the added particles,  $\Delta\epsilon = \epsilon_e + \epsilon_h$ , and the energy of the added electron is  $\epsilon_2$ . Therefore  $\epsilon_h = -\epsilon_1$ . Since  $\epsilon_1 < 0$ ,  $\epsilon_h > 0$ .

The effective mass of the valence band is negative:  $m_V^* < 0$ : we define  $m_h^* = -m_V^*$  — **positive hole mass**

Then **the hole energy**  $-\epsilon_1 = \epsilon_h = +\frac{\hbar^2 k_1^2}{2m_h^*}$  is positive.

# Hole velocity

Imagine a semiconductor at  $T = 0$ , with a completely filled valence band.

The current carried by the  $N$  electrons is zero:  $\vec{j} = -e \sum_{i=1}^N \vec{v}_i = 0$

Now remove an electron from a state with group velocity  $\vec{v}_e$ . Then

$$\vec{j}' = -e \sum_{i=1}^{N-1} \vec{v}_i = -e \sum_{i=1}^N \vec{v}_i - (-e\vec{v}_e) = 0 - (-e\vec{v}_e) = e\vec{v}_e.$$

Instead, we could add a hole to the full valence band of electrons. The resulting current should be the same.

$$\vec{j}' = -e \sum_{i=1}^N \vec{v}_i + q_h \vec{v}_h = 0 + (+e\vec{v}_h) = e\vec{v}_h$$

Comparing, the hole velocity is the same as that of the missing electron.

# Equations of motion

We can now write down the equations of motion.

We saw previously that

$$\hbar \frac{d\vec{k}}{dt} = -e \left( \vec{\mathcal{E}} + \vec{v}(\vec{k}) \times \vec{\mathcal{B}} \right), \quad \vec{v}(\vec{k}) = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} \epsilon(\vec{k}).$$

For parabolic bands,  $\epsilon(\vec{k}) = \epsilon(0) + \frac{\hbar^2 k^2}{2m^*}$ , so the group velocity is  $\vec{v}(\vec{k}) = \frac{\hbar \vec{k}}{m^*}$ .  
So  $\hbar \vec{k} = m^* \vec{v}$ .

Therefore, for electrons in the conduction band including the effects of scattering by impurities, defects and lattice vibrations

$$\underbrace{m_e^*}_{m_e^* = m_C^*} \frac{d\vec{v}_e}{dt} = -e \left( \vec{\mathcal{E}} + \vec{v}_e \times \vec{\mathcal{B}} \right) - m_e^* \frac{\vec{v}_e}{\tau_e}.$$

For holes in the valence band

$$\underbrace{m_h^*}_{m_h^* = -m_V^*} \frac{d\vec{v}_h}{dt} = +e \left( \vec{\mathcal{E}} + \vec{v}_h \times \vec{\mathcal{B}} \right) - m_h^* \frac{\vec{v}_h}{\tau_h}$$

# Current density

If there are  $n$  electrons per unit volume:

$$\vec{j}_e = n(-e)\vec{v}_e.$$

If there are  $p$  holes per unit volume:

$$\vec{j}_h = p(+e)\vec{v}_h.$$

If both types of carrier are present

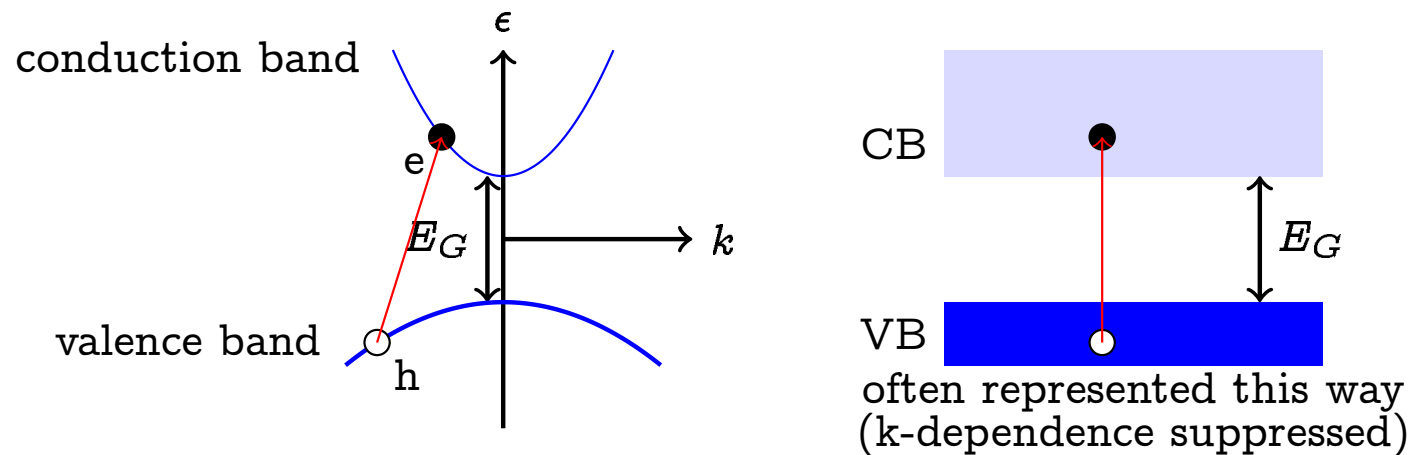
$$\vec{j}_{\text{total}} = \underbrace{\vec{j}_e}_{\text{in CB}} + \underbrace{\vec{j}_h}_{\text{in VB}}$$

For uniform flow, the current flowing through a semiconductor of cross section area  $A$  is  $I = j_{\text{total}}A$ .

# Intrinsic semiconductors

**Intrinsic** semiconductors are **pure** semiconductors.

In thermal equilibrium, the electrons in the conduction band are those excited across the energy gap from the valence band.



Each electron excited into the conduction band leaves behind a hole in the valence band.

Hence

$$\underbrace{n}_{\text{electron concentration}} = \underbrace{p}_{\text{hole concentration}} = \underbrace{n_i (= p_i)}_{\text{intrinsic concentrations}}$$

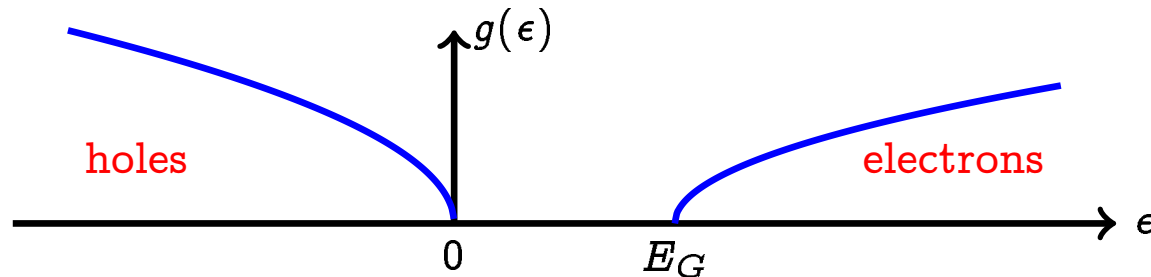
# Carrier concentrations in intrinsic semiconductors

How many electrons and holes are there at temperature  $T$ ?

We adapt previous results for the density of states:

	energy	density of states
free electrons	$\epsilon = \frac{\hbar^2 k^2}{2m}$	$g(\epsilon) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\epsilon}$
conduction electrons	$\epsilon - E_G = \frac{\hbar^2 k^2}{2m_e^*}$	$g_e(\epsilon) = \frac{V}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\epsilon - E_G}$
holes	$\epsilon = -\frac{\hbar^2 k^2}{2m_h^*}$	$g_h(\epsilon) = \frac{V}{2\pi^2} \left( \frac{2m_h^*}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{-\epsilon}$

(energies  $\epsilon$  measured upwards from top of VB.)

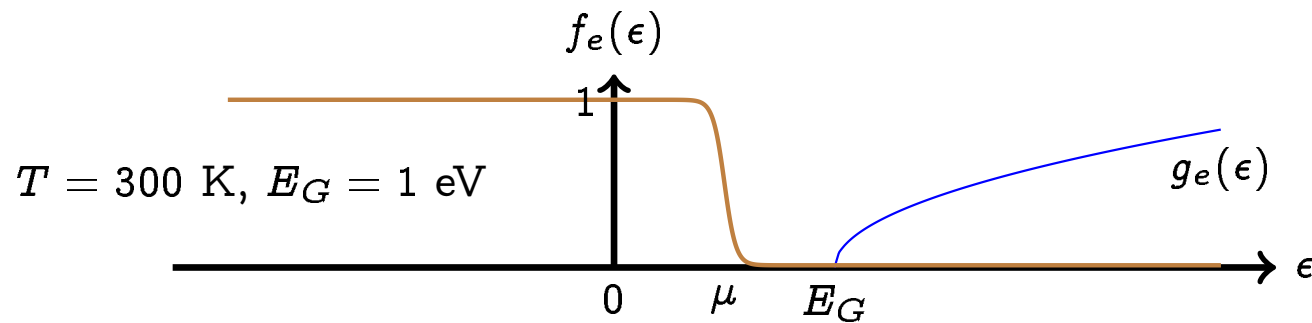




The density of **occupied** electron states in the CB is  $g_e(\epsilon)f_e(\epsilon)$ , where  $f_e$  is the Fermi-Dirac occupation function for electrons.

We assume the Fermi level  $\mu$  lies near the middle of the gap; at relevant  $T$  in the conduction band we then have  $\epsilon - \mu \gg k_B T$  ( $E_G \sim 1$  eV, 300 K  $\simeq 0.026$  eV).

The following is draw to scale:



Therefore for energies in the CB we can approximate the occupation function as

$$f_e(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} \simeq e^{(\mu-\epsilon)/k_B T}.$$

The **number** of conduction electrons is given by

$$N_e = \int_{E_G}^{\infty} g_e(\epsilon) f_e(\epsilon) d\epsilon$$

so the *concentration* of electrons in the conduction band  $n = \frac{N_e}{V}$  is

$$\begin{aligned} n &= \frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{\frac{3}{2}} e^{\mu/k_B T} \int_{E_G}^{\infty} \sqrt{\epsilon - E_G} e^{-\epsilon/k_B T} d\epsilon = \dots \\ &= 2 \left( \frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} e^{-(E_G - \mu)/k_B T}, \end{aligned}$$

or

$$n = N_C e^{-(E_G - \mu)/k_B T}$$

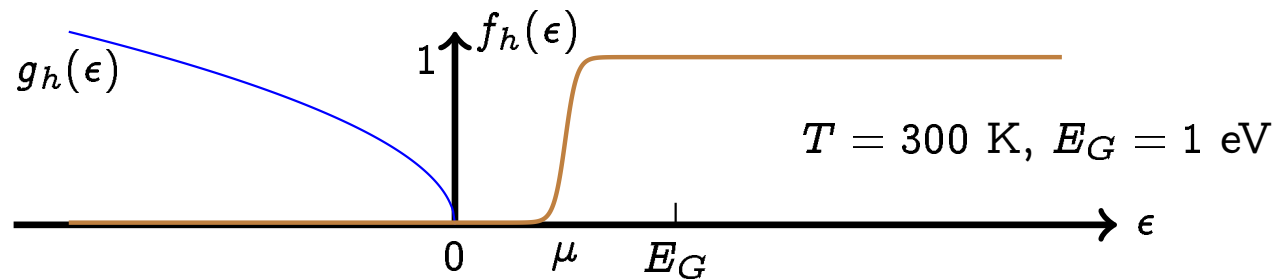
where  $N_C = 2 \left( \frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}}$  is sometimes called the *effective density of states* for the CB.

The density of **occupied hole** states in the VB is  $g_h(\epsilon)f_h(\epsilon)$ , where  $f_h$  is the distribution function for holes.

The distribution function  $f_h$  for holes is related to that for electrons  $f_e$  by  $f_h = 1 - f_e$  since a hole is the absence of an electron:

$$f_h = 1 - \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} = \frac{1}{e^{(\mu-\epsilon)/k_B T} + 1}$$

The following is draw to scale:



If  $\mu$  lies near the middle of the gap, then at relevant  $T$  and for energies in the valence band  $\mu - \epsilon \gg k_B T$ .

Therefore in the VB we can approximate the occupation function as

$$f_h(\epsilon) \simeq e^{(\epsilon-\mu)/k_B T}.$$

The **number** of holes is given by

$$N_h = \int_{-\infty}^0 g_h(\epsilon) f_h(\epsilon) d\epsilon$$

so the *concentration* of holes in the valence band  $p = \frac{N_h}{V}$  is

$$\begin{aligned} p &= \frac{1}{2\pi^2} \left( \frac{2m_h^*}{\hbar^2} \right)^{\frac{3}{2}} e^{-\mu/k_B T} \int_{-\infty}^0 \sqrt{-\epsilon} e^{\epsilon/k_B T} d\epsilon = \dots \\ &= 2 \left( \frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} e^{-\mu/k_B T}, \end{aligned}$$

or

$$p = N_V e^{-\mu/k_B T}$$

where  $N_V = 2 \left( \frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}}$  is the *effective density of states* for the VB.

# Carrier concentrations

$$\begin{array}{ll} n &= N_C e^{-(E_G - \mu)/k_B T} & N_C &= 2 \left( \frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2} \\ \text{So} & & & \\ p &= N_V e^{-\mu/k_B T} & N_V &= 2 \left( \frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{3/2} \end{array}$$

This leads to the following “law of mass action” for the intrinsic carrier concentrations in a semiconductor:

$$n \times p = n_i^2 = N_C N_V e^{-E_G/k_B T}$$

In an intrinsic semiconductor the number of conduction electrons equals the number of holes, and so

$$n = p = n_i = \sqrt{N_C N_V} e^{-E_G/2k_B T}$$

If  $E_G \sim 1$  eV, and  $T = 300$  K, then  $e^{-E_G/2k_B T} \simeq 10^{-9}$   
— the number of excited free electrons and holes is very small.

We will see how the number can be increased by **doping**.

# Determining gaps

Recalling  $N_C = 2 \left( \frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}}$  and  $N_V = 2 \left( \frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}}$ , then

$$n_i = \sqrt{N_C N_V} e^{-E_G/2k_B T} = A T^{3/2} e^{-E_G/2k_B T}$$

where  $A$  is a material constant. Then

$$\begin{aligned} \frac{n_i}{T^{3/2}} &= A e^{-E_G/2k_B T} \\ \ln \left( \frac{n_i}{T^{3/2}} \right) &= \ln A e^{-E_G/2k_B T} = \ln A + \ln e^{-E_G/2k_B T} = \ln A - \frac{E_G}{2k_B T} \\ \underbrace{\ln \left( \frac{n_i}{T^{3/2}} \right)}_y &= \underbrace{\ln A}_c - \underbrace{\frac{E_G}{2k_B}}_m \underbrace{\frac{1}{T}}_x \end{aligned}$$

This has the form  $y = c - mx$ , the equation of a straight line.

Plotting  $\ln n_i/T^{3/2}$  versus  $1/T$  yields a straight line with slope  $-E_G/2k_B$ , allowing  $E_G$  to be determined. (But how to get  $n_i$ ?)

# Fermi level of intrinsic semiconductors

We have seen  $n = N_C e^{-(E_G - \mu)/k_B T}$  and  $p = N_V e^{-\mu/k_B T}$ .

To know how many free charge carriers there are, we need to know the value of the Fermi level  $\mu$ .

For an intrinsic semiconductor  $n = p$  and so

$$\begin{aligned} N_C e^{-(E_G - \mu)/k_B T} &= N_V e^{-\mu/k_B T} \\ \text{rearrange} \quad e^{(2\mu - E_G)/k_B T} &= \frac{N_V}{N_C} \\ \text{take logs} \quad \frac{2\mu - E_G}{k_B T} &= \ln \left( \frac{N_V}{N_C} \right) \\ 2\mu - E_G &= k_B T \ln \left( \frac{N_V}{N_C} \right) \end{aligned}$$

Finally,

$$\mu = \frac{E_G}{2} + \frac{k_B T}{2} \ln \left( \frac{N_V}{N_C} \right) = \frac{E_G}{2} + \frac{3k_B T}{4} \ln \left( \frac{m_h^*}{m_e^*} \right)$$

If  $m_e^* = m_h^*$  then the effective densities of states  $N_V, N_C$  are the same, and since  $\ln 1 = 0$  we get  $\mu = \frac{1}{2} E_G$ . So the Fermi level lies mid-gap (as assumed).

Even if  $m_e^* \neq m_h^*$ , putting in numbers one finds  $\mu$  still lies close to mid-gap.

The probability of a level being occupied by an electron is  $f_e$ :

$$f_e(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}$$

When  $\epsilon = \mu$ ,  $f_e(\epsilon) = \frac{1}{2}$ . In general the Fermi level  $\mu$  is the energy at which the probability of occupation is one half.





# Measuring effective masses by cyclotron resonance

The effective masses of electrons  $m_e^*$  and holes  $m_h^*$  can be measured by **cyclotron resonance**.

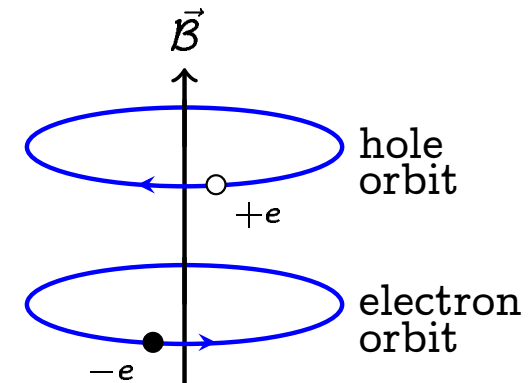
The equation of motion of a free charge carrier in a magnetic field  $\vec{B}$  is

$$m^* \frac{d\vec{v}}{dt} = q\vec{v} \times \vec{B}$$

The force is perpendicular to both  $\vec{B}$  and the direction of motion – the charge is accelerated into a circular orbit in the plane perpendicular to  $\vec{B}$ .

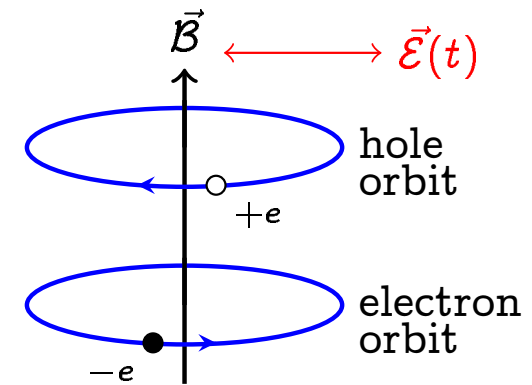
The charges orbit with angular frequency  $\omega_C = \frac{eB}{m^*}$

For small electron and hole energies in a semiconductor  $\epsilon - \epsilon_0 = \frac{\hbar^2 k^2}{2m^*}$  and this model can be used.



An oscillating electric field is now applied, perpendicular to the magnetic field.

Resonant absorption occurs when the frequency of the electric field  $\omega$  is the same as the cyclotron frequency  $\omega_C = e\mathcal{B}/m^*$ ; then the orbits are in phase with  $\vec{\mathcal{E}}$ .



In order for the resonance to be observed, the charges must complete at least one orbit before scattering. Therefore

$$\text{period of orbit, } \frac{2\pi}{\omega_C} < \tau_{\text{tot}}, \text{ scattering time}$$

Microwave frequencies  $\sim 100 \text{ GHz} = 10^{11} \text{ Hz}$  require  $\tau_{\text{tot}} > 10^{-11} \text{ s}$  (10 ps).

This generally requires pure samples and low temperatures (e.g. liquid helium temperatures, 4 K).

Experimentally, often easier to fix frequency of  $\vec{\mathcal{E}}(t)$ , and vary  $\vec{\mathcal{B}}$ .

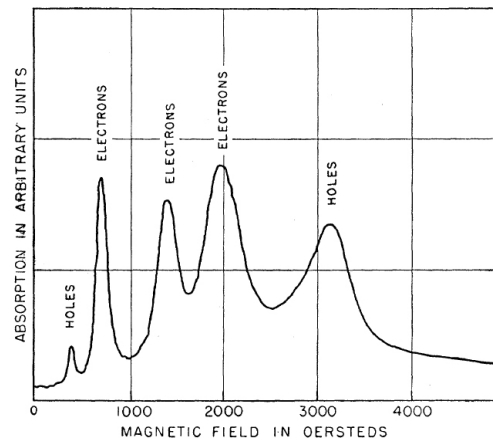


FIG. 2. Typical cyclotron resonance results in germanium near 24 000 Mc/sec and 4°K: direct copy from a recorder trace of power absorption vs static magnetic field in an orientation in a (110) plane at 60° from a [100] axis.

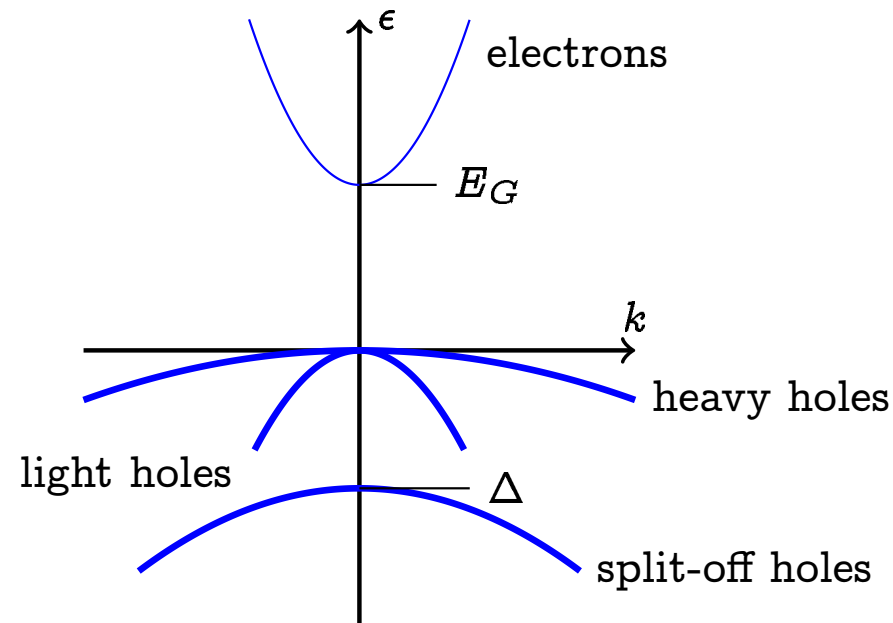
Note:  $10^4$  Oe = 1 Tesla (Fig. from Dresselhaus, Kip and Kittel).

Electron and hole resonances may be distinguished using circularly polarised light – only one or other orbit resonates.

For Ge (an indirect semiconductor) one observes several electron resonances. Conduction band minima occur along  $\langle 111 \rangle$  directions, and depending upon  $\hat{\vec{B}}$  up to 4 resonances occur.

Two hole resonances occur. There are two bands at the valence band maximum at  $\vec{k} = 0$ , called the light and heavy hole bands.

# Some effective masses in direct-gap semiconductors



Material	Electron $m_e^*/m$	Heavy hole $m_{hh}^*/m$	Light hole $m_{lh}^*/m$	Split-off hole $m_{soh}^*/m$	Spin orbit $\Delta$ (eV)
InSb	0.015	0.39	0.021	0.11	0.82
InAs	0.026	0.41	0.025	0.08	0.43
InP	0.073	0.4	0.078	0.15	0.11
GaSb	0.047	0.3	0.06	0.14	0.80
GaAs	0.07	0.68	0.12	0.20	0.34

after Kittel

# Carrier concentrations

The number of free carriers in an intrinsic semiconductor is low.

semiconductor	band gap	conduction electron concentration (300 K)
Si	1.1 eV	$\sim 10^{10} \text{ cm}^{-3}$
GaAs	1.4 eV	$\sim 10^6 \text{ cm}^{-3}$

For comparison, the atomic density in Si is (8 atoms in conventional unit cell, cube side 5.4 Å)  $\sim 10^{22} \text{ cm}^{-3}$ .

— there is only 1 conduction electron for every  $10^{12}$  Si atoms (!!!!!)

The electrical conductivity of a semiconductor is  $\sigma = \underbrace{\frac{ne^2\tau_e}{m_e^*}}_{\text{electrons}} + \underbrace{\frac{pe^2\tau_h}{m_h^*}}_{\text{holes}}.$

Experimentally, it is found that substituting 1 in  $10^5$  of the Si atoms with B (boron) increases the conductivity of Si by a factor 1000! How?

# Extrinsic semiconductors: $n$ -type

Extrinsic semiconductors are semiconductors to which impurities or **dopants** are deliberately introduced in order to modify their properties.

The dopant atoms *substitute* for the semiconductor atoms, taking their place in the crystal structure.

In  $n$ -type semiconductors the dopant atoms are electron **donors**, and called donor atoms. They increase the number of **negatively** charged carriers.

For example, consider Si (silicon), which is a group IV element in the periodic table. It has 4 electrons in its valence shell. Group V elements in the next column (e.g. P, phosphorus) have one extra electron in their valence shell, plus an extra proton in the nucleus.

► [Periodic table](#)

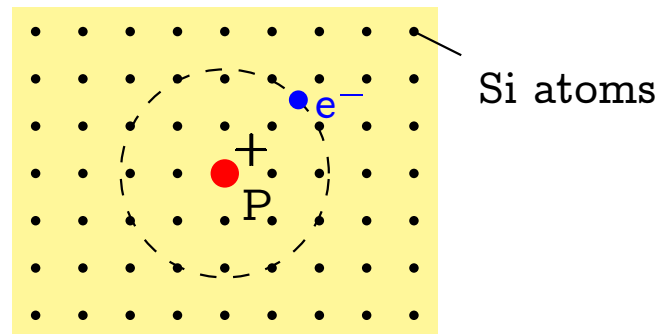
The extra electron is only **weakly bound to the donor atom**, so is easily thermally excited into the conduction band of the semiconductor leaving behind an ionised donor atom.

In this way, the electrical properties of the semiconductor may be modified.

# Hydrogen atom model of donors

Substituting a group V atom for a group IV semiconductor atom adds an extra electron and an extra proton to an otherwise periodic crystal.

The extra electron will orbit the donor atom in the semiconductor under the influence of the extra proton.



We see that the problem of an electron orbiting a positively charged donor atom is analogous to the hydrogen atom. However, there are important differences.

# Adapting the H-model to dopants

- The extra electron orbits in the crystal, not free space, and so its mass is the effective mass  $m_e^*$  and not the free electron mass  $m$

$$m \rightarrow m_e^*$$

- The space between the electron and the extra proton is not vacuum, but contains other charges from the semiconductor atoms, a medium of high permittivity

in vacuum, electric permittivity  $\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$

in semiconductor, electric permittivity  $\epsilon_r \epsilon_0$  with  $\epsilon_r$  typically  $\sim 10$

$$\epsilon_0 \rightarrow \epsilon_r \epsilon_0$$

With these replacements, we can use the hydrogen atom model to model dopants in semiconductors.



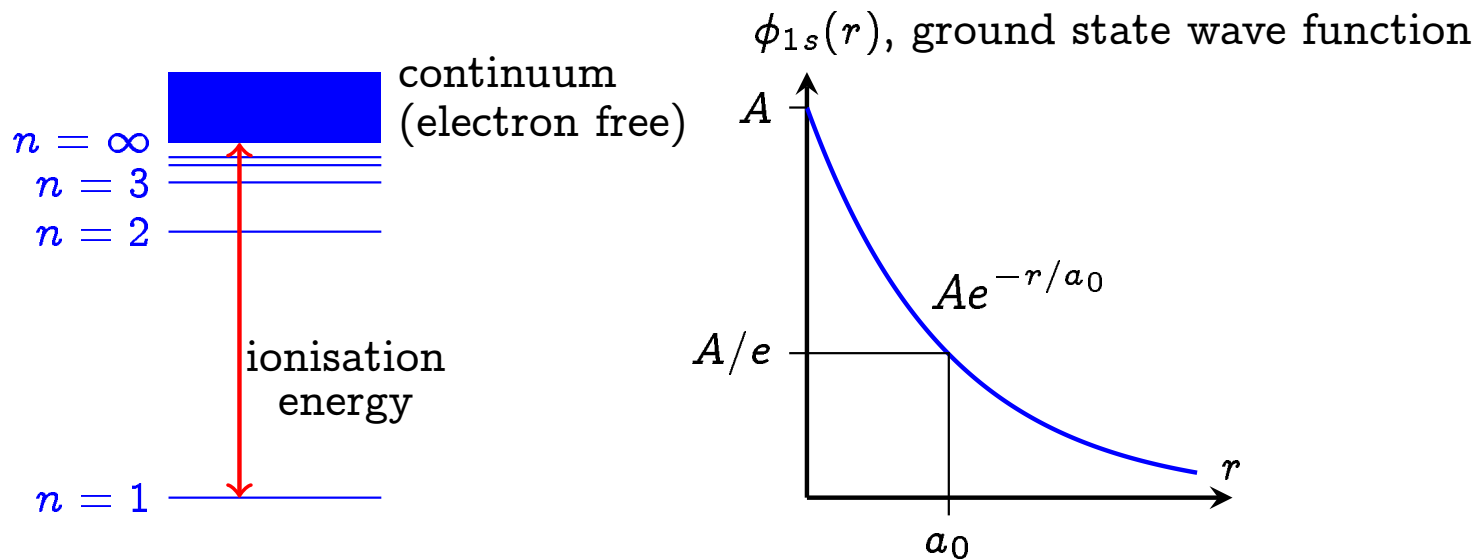
# From Quantum & Atomic course

The energy levels of an electron in a hydrogen atom are

$$\epsilon_n^H = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \times \frac{1}{n^2} = -\frac{13.6}{n^2} \text{ eV}, \quad n = 1, 2, 3, \dots$$

The “radius” of the electron in the ground state ( $n = 1$ ) level is

$$a_0 = \frac{(4\pi\epsilon_0)\hbar^2}{me^2} = 0.529 \text{ \AA} \quad (\text{the Bohr radius})$$



# Extending hydrogen atom results to donors

We now replace  $m$  by  $m_e^*$ , and  $\epsilon_0$  by  $\epsilon_r \epsilon_0$ .

The energy levels become

$$\epsilon_n^D = -\frac{m_e^* e^4}{2(4\pi\epsilon_r\epsilon_0)^2 \hbar^2} \times \frac{1}{n^2} = -\frac{1}{\epsilon_r^2} \left( \frac{m_e^*}{m} \right) \times \frac{13.6}{n^2} \text{ eV}$$

The donor Bohr radius is

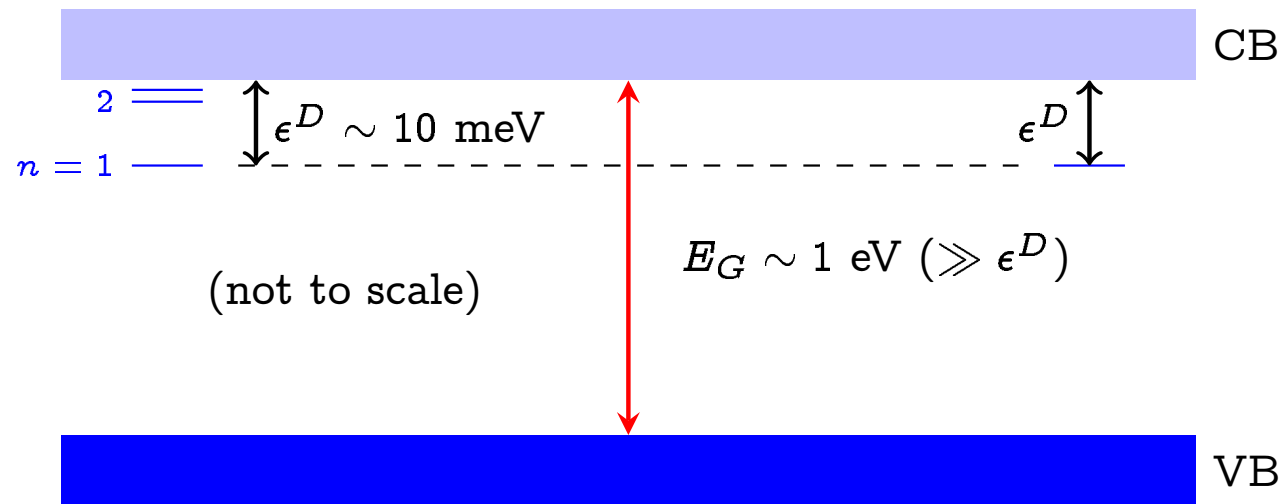
$$a_D = \frac{(4\pi\epsilon_r\epsilon_0)\hbar^2}{m_e^* e^2} = \epsilon_r \left( \frac{m}{m_e^*} \right) \times 0.529 \text{ \AA}$$

Typically,  $m_e^* \sim 0.1m$ , and  $\epsilon_r \sim 10$ . Then [note the units]

$$\epsilon_n^D \sim -\frac{13.6}{n^2} \text{ meV} \quad \text{and} \quad a_D \sim 5 \text{ nm}$$

We see  $a_D$  is much larger than the lattice spacing — validating our use of a continuum medium approximation ( $\epsilon_r$ ).

The  $n = \infty$  limit corresponds to the electron escaping from the donor — this energy must therefore correspond to the bottom of the conduction band.



For clarity, usually only the  $n = 1$  level is indicated (right, above)

When the electron orbits the donor atom, the donor is said to be **neutral**.

When the electron is removed, the donor is said to be **ionised** (charge  $+e$ ).

The ionisation energy of the donor is  $\epsilon^D = -\epsilon_1^D$ , and typically  $\epsilon^D \sim 10 \text{ meV}$ .

# Extrinsic semiconductors: *p*-type

In *p*-type semiconductors the dopant atoms are electron **acceptors**. They increase the number of **p**ositively charged carriers.

For example, for a group IV element like Si, group III elements such as Al (aluminium) have one fewer electron in their valence shell, and one fewer proton in the nucleus.

► [Periodic table](#)

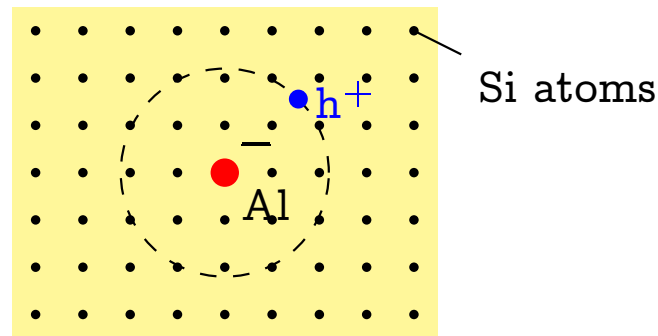
Replacing a Si atom with an Al atom, the missing electron acts like a hole ( $q_h = +e$ ) which orbits the “missing proton” ( $q = -e$ ).

The problem is similar to that of the donor case, but the signs of the charges are reversed. Also (i) the hole has a different effective mass to that of the electron, and (ii) hole energies are positive in the opposite sense (increasing as one moves further into the VB).

# Hydrogen atom model of acceptors

Substituting a group III atom for a group IV semiconductor atom has the effect of adding an extra hole and removing a proton from an otherwise periodic crystal.

The extra hole will orbit the acceptor atom in the semiconductor under the influence of the **missing**  $+e$  charge.

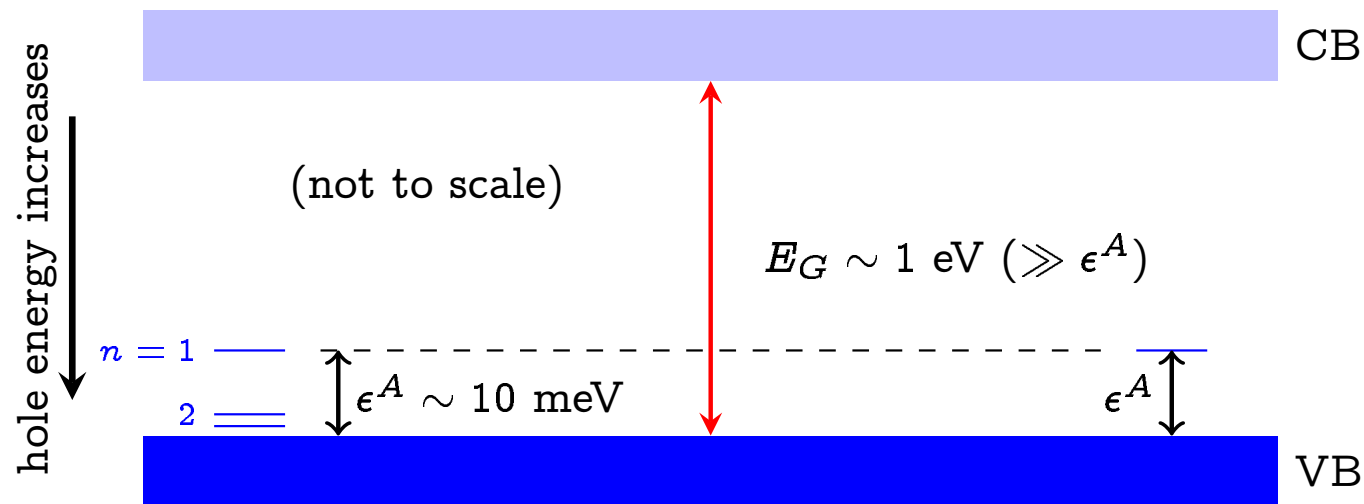


The problem of a hole orbiting a negatively charged acceptor atom can again be modelled by analogy with the hydrogen atom, and we can immediately write down the results.

# Extending hydrogen atom results to acceptors

$$\epsilon_n^A = -\frac{1}{\epsilon_r^2} \left( \frac{m_h^*}{m} \right) \times \frac{13.6}{n^2} \text{ eV}, \quad a_A = \epsilon_r \left( \frac{m}{m_h^*} \right) a_0$$

The  $n = \infty$  limit corresponds to the hole just escaping from the acceptor — this energy must therefore correspond to the top of the valence band.



When the hole moves away from the acceptor atom, it becomes **negatively ionised** (charge  $-e$ ).

# Some common dopants

Group IV semiconductors Si, Ge:

*n*-type: replace Si, Ge by group V atoms N, P, As

*p*-type: replace Si, Ge by group III atoms B, Al

III-V semiconductors e.g. GaAs

*n*-type: replace group III Ga atoms by group IV Si atoms

*p*-type: replace group III Ga atoms by group II Be atoms

If a compound semiconductor (eg. GaAs) is non-stoichiometric (e.g. Ga-rich), the “extra” atoms also act as impurities that affect carrier concentrations.

Impurities that do not ionise do not affect carrier concentrations.

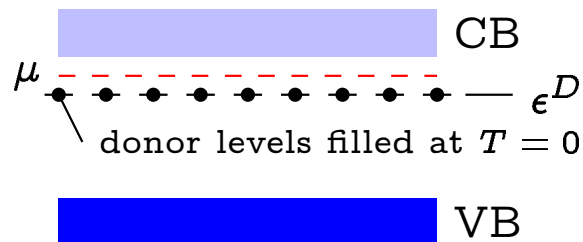
Even the purest semiconductors contain significant numbers of impurities ( $> 10^{10}/\text{cm}^3$ ).

# Fermi level in extrinsic semiconductors

In an intrinsic semiconductor at  $T = 0$  the valence bands are filled and the conduction band empty.

***n*-type:** Doping with donor atoms adds electrons into donor levels just below the CB. At low  $T$  the Fermi level lies within the donor levels.

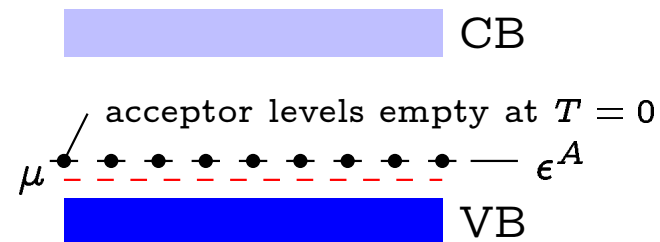
At higher  $T$  the Fermi level drops to a value between the donor level  $\epsilon^D$  and the middle of the gap. The precise value needs a non-trivial calculation.



At 300 K,  $k_B T \simeq 25 \text{ meV} > \epsilon^D$ , so at room temp. most donors will be ionised.

***p*-type:** Doping with acceptor atoms adds holes to acceptor levels just above the VB. At low  $T$  the Fermi level lies within the acceptor levels.

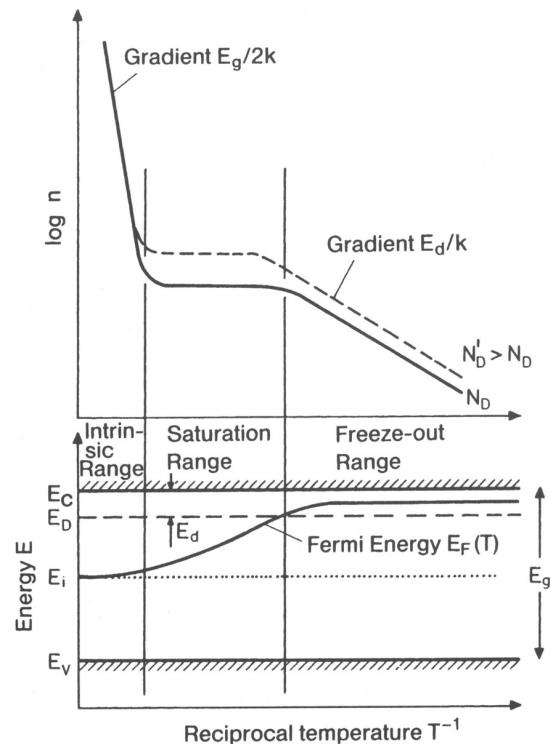
At higher  $T$  the Fermi level rises to a value between the acceptor level  $\epsilon^A$  and the middle of the gap. The precise value needs a non-trivial calculation.



At 300 K,  $k_B T \simeq 25 \text{ meV} > \epsilon^A$ , so at room temp. most acceptors will be ionised (filled with electrons).



# Carrier concentrations in *n*-type semiconductors



For Si, plateau at  $N_D \sim 10^{15}/\text{cm}^3$  extends between  $150\text{K} < T < 500\text{K}$ .

From previous lecture  $n = N_C e^{-(E_G - \mu)/k_B T}$ .

At low  $T$ :  $k_B T < \epsilon^D$  electrons occupy the bound states of the donor atoms – **carrier freeze out**. The Fermi level lies at the donor level,  $\mu = E_G - \epsilon^D$ :

$$n \simeq N_D e^{-\epsilon^D/k_B T} \quad k_B T \ll \epsilon^D$$

Around room  $T$ :  $k_B T \simeq 25 \text{ meV}$ , which is  $> \epsilon^D \sim 10 \text{ meV}$ . The donors will be ionised. The effective conduction band density of states  $N_C \sim 10^{19}/\text{cm}^3 \gg N_D \sim 10^{14-18}/\text{cm}^3$ . The probability of excitation will be large:

$$n \simeq N_D \quad \text{- saturation}$$

At high  $T$ : donor atoms will be ionised, donating their electrons to the CB. Direct excitation across the gap also possible, and dominates – **intrinsic behaviour**.

$$n \simeq n_i \propto T^{3/2} e^{-E_G/2k_B T}$$

# Carrier concentrations in $p$ -type semiconductors

Arguments mirror those of  $n$ -type semiconductors.

Graph of  $\ln p$  vs  $1/T$  is similar to that for  $n$ -type semiconductor.

At low temperatures ( $k_B T \ll \epsilon^A$ ) holes freeze out:

$$p \sim N_A e^{-\epsilon^A / k_B T}$$

At room temperature acceptors ionised:

$$p \simeq N_A$$

At high temperatures intrinsic carriers dominate:

$$p_i \simeq \sqrt{N_C N_V} e^{-E_G / 2k_B T}$$

# Suggested further reading

For alternative descriptions and explanations, often at a different level, plus further problems, see

Hook and Hall (2nd Ed.)

Ch 5; p131–160

Myers\*

Ch 9; p298–306. Ch 10; 309–328

Kittel (5th ed.)

Ch 8; p205–237

Ibach & Lüth (3rd Ed.)

Ch 12; p391–409, 464–466

Ashcroft & Mermin

Chs 28; p562–587.