Engineering Physics (2025)
Course code 25PY101
Module 2 Unit 1: Quantum theories of solids

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Unit 2 Plan

1. Quantum Free Electron Theory
2. Fermi-Dirac distribution
3. Electronic specific heat of solids
4. Density of states (qualitative)
5. Success and Failures of quantum free electron theory of solids
6. E-k diagram
7. Classification of materials based on bands in solids
8. Fermi level in semiconductors- intrinsic and extrinsic

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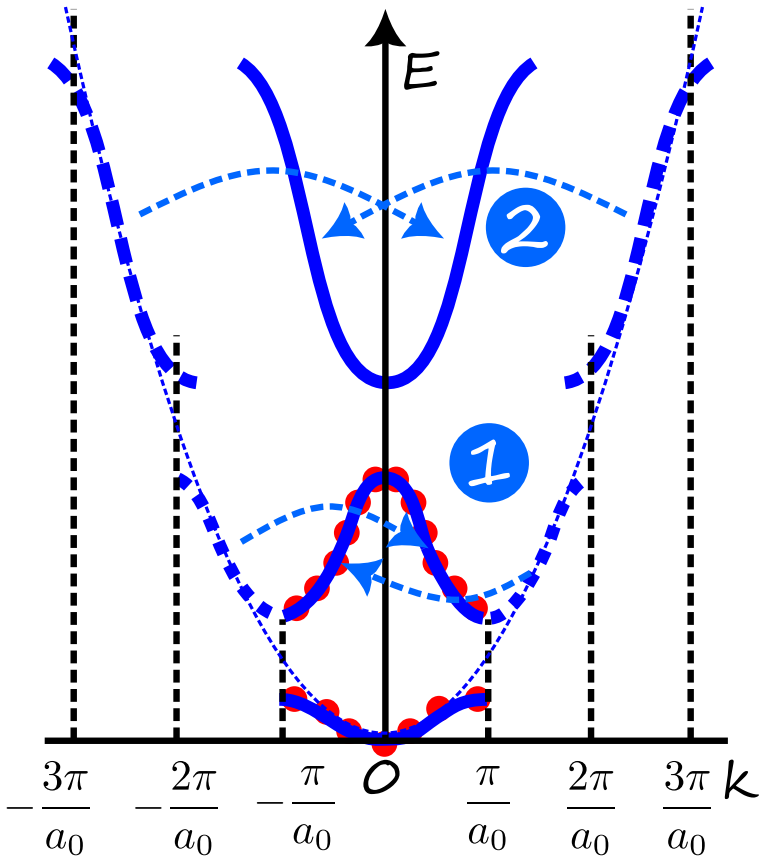
Intrinsic semiconductor

Reduced band dispersion – Band structure

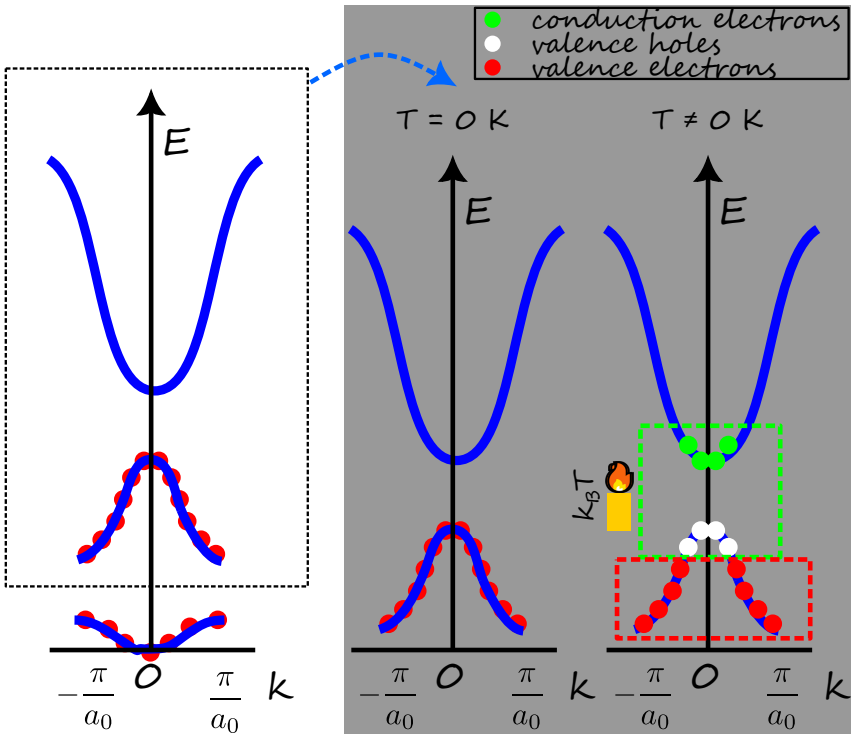


- Due to the periodicity of lattice, the band dispersion can be analyzed within the **zone** from $k = -\frac{\pi}{a_0}$ to $k = +\frac{\pi}{a_0}$.
- The original band dispersion can be reduced to the zone by folding the "arms" of the parabola resulting in the reduced band dispersion. This process is called **zone folding**.
- The reduced band dispersion is called the **band structure** of the material and it is the signature of the material.

Key Insight

Bandstructure is the fingerprint or "DNA" of a crystalline solid.

Band structure – Concept of hole

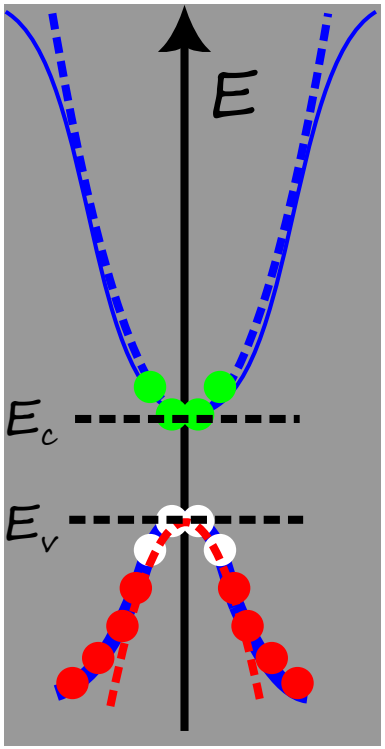


- For a semiconductor, due to the presence of energy band gap, there are no free electrons at $T = 0\,\mathrm{K}$.
- At $T \neq 0\,\mathrm{K}$, the electrons near the valence band maximum thermalize and jump to the levels near the conduction band minimum. This results in quantum vacancy in the valence band. This is called **hole**.
- Conduction electron and valence hole contribute to conduction.

Key Insight

- Hole is the absence of electron in the valence band.
- Hole is not a physical reality.

Parabolic approximation – Concept of effective mass



- For the conduction band, the dispersion relation can be approximated with an upward facing parabola given by

$$E = E_c + \frac{\hbar^2 k^2}{2m_n^*}$$

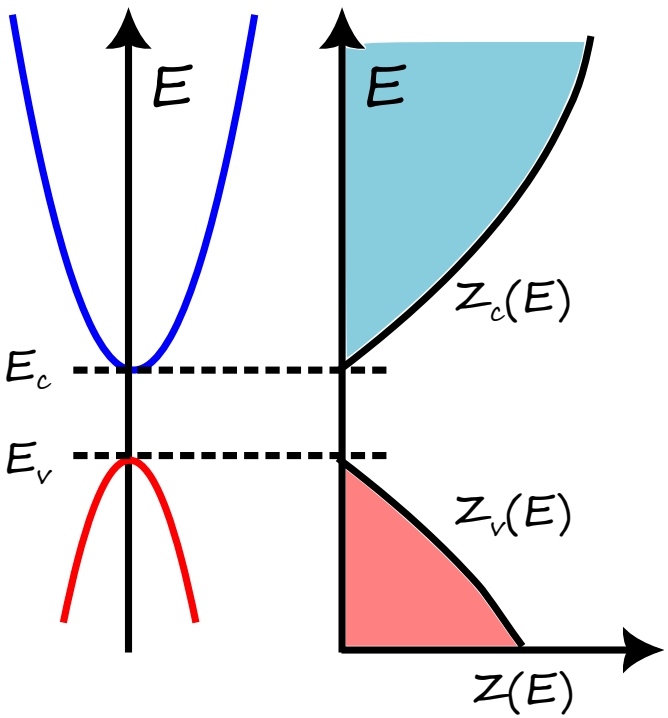
where m_n^* is the **effective electron mass** and E_c is the minimum of conduction band.

- Similarly, for the valence band, the dispersion relation can be approximated with a downward facing parabola given by

$$E = E_v - \frac{\hbar^2 k^2}{2m_p^*}$$

where m_p^* is the **effective hole mass** and E_v is the maximum of valence band.

Density of states in conduction band



- For the conduction band, dispersion relation can be written as

$$E - E_c = \frac{\hbar^2 k^2}{2m_n^*}$$

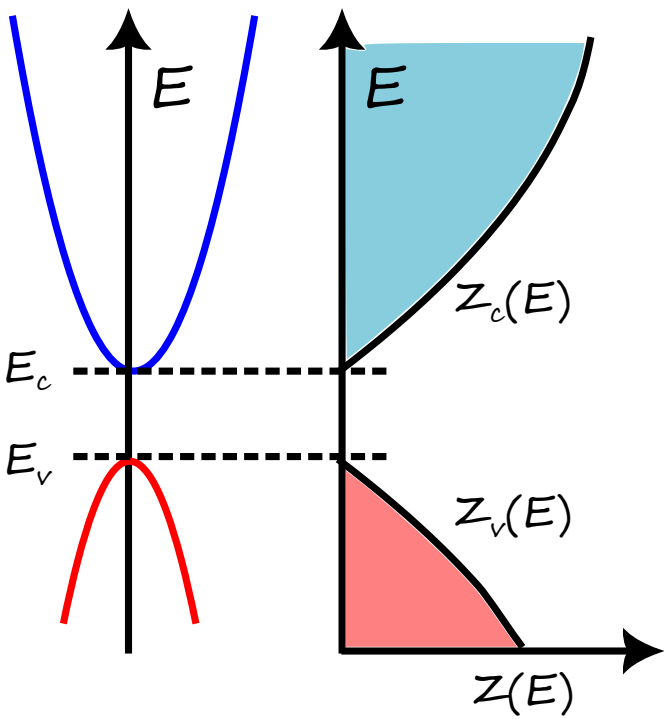
so that the form is similar to the free electron dispersion relation. Thus, the density of states in the conduction band $Z_c(E)$ is given by

$$Z_c(E) = \alpha^* \sqrt{E - E_c}$$

where α^* is a constant with expression that contains universal constants and m_n^* [a].

[a] From QFET slides, we can infer $\alpha^* = 4\pi \left(\frac{2m_n^*}{h^2}\right)^{3/2}$.

Density of states in valence band



- Similarly for the valence band, dispersion relation can be written as

$$E_v - E = \frac{\hbar^2 k^2}{2m_p^*}$$

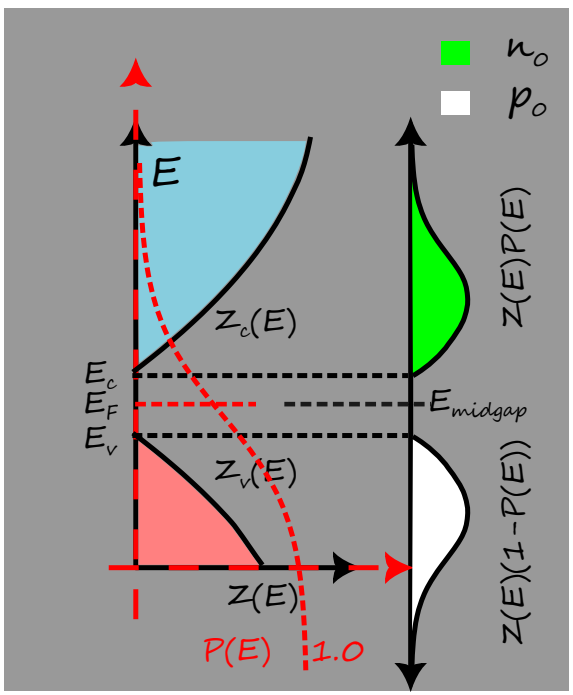
so that the density of states in the valence band $Z_v(E)$ is given by

$$Z_v(E) = \beta^* \sqrt{E_v - E}$$

where β^* is a constant with expression that contains universal constants and m_p^* [a].

[a] From QFET slides, we can infer $\beta^* = 4\pi \left(\frac{2m_p^*}{h^2}\right)^{3/2}$.

Electron carrier concentration



- The conduction electron density n_0 is given by

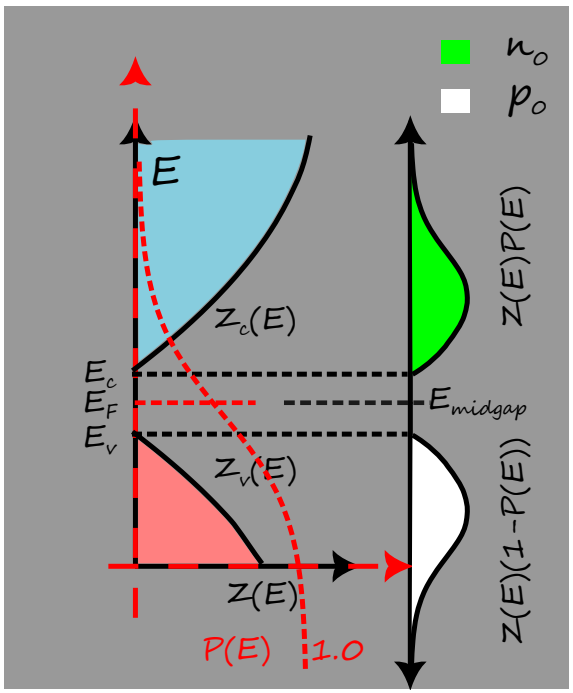
$$n_0 = \int_{E_c}^{\infty} Z_c(E)P(E)\,\mathrm{d}E$$
$$= \int_{E_c}^{\infty} \frac{\alpha^* \sqrt{E - E_c}}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}\,\mathrm{d}E$$

- By applying Boltzmann approximation and the exact expression for α^*, it can be shown that

$$\boxed{n_0 = N_c \exp\left(-\frac{E_c - E_F}{k_B T}\right)}$$

where N_c is the **effective density of states** in the conduction band.

Hole carrier concentration



- Similarly the valence hole density p_0 is given by

$$p_0 = \int_{E_c}^{\infty} Z_c(E)\,(1 - P(E))\,\mathrm{d}E$$

$$= \int_{0}^{E_v} \beta^* \sqrt{E_v - E}\left(1 - \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}\right)\,\mathrm{d}E$$

- By applying **Boltzmann approximation** and the exact expression for β^*, it can be shown that

$$\boxed{p_0 = N_v \exp\left(-\frac{E_F - E_v}{k_B T}\right)}$$

where N_v is the **effective density of states** in the valence band.

Intrinsic carrier concentration – $n_0 p_0$ product

- For an intrinsic semiconductor, electron-hole pairs are generated at $T \neq 0\,\mathrm{K}$. So the conduction electron density is equal to valence hole density

$$n_0 = p_0 = n_i$$

  where n_i is defined as the intrinsic carrier concentration.

- The intrinsic carrier concentration is given by the product of electron and hole concentrations

$$\begin{aligned} n_0 p_0 = n_i^2 &= N_c \exp\left(-\frac{E_c - E_F}{k_B T}\right) \cdot N_v \exp\left(-\frac{E_F - E_v}{k_B T}\right) \\ &= N_c N_v \exp\left(-\frac{E_c - E_F + E_F - E_v}{k_B T}\right) \\ n_i^2 &= N_c N_v \exp\left(-\frac{E_c - E_v}{k_B T}\right) \end{aligned}$$

Intrinsic carrier concentration

- Therefore, the $n_0 p_0$ is independent of Fermi energy level and is given in terms of the material properties and temperature.

$$\boxed{n_0 p_0 = n_i^2}$$

where n_i is given by

$$\begin{aligned} n_i &= \sqrt{N_c N_v \exp\left(-\frac{E_c - E_v}{k_B T}\right)} \\ &= \sqrt{N_c N_v} \exp\left(-\frac{E_c - E_v}{2k_B T}\right) \\ &= \sqrt{N_c N_v} \exp\left(-\frac{E_g}{2k_B T}\right) \end{aligned}$$

where E_g is the energy band gap and is given by

$$E_g = E_c - E_v$$

$$\boxed{\therefore n_i = \sqrt{N_c N_v} \exp\left(-\frac{E_g}{2k_B T}\right)}$$

Fermi level of intrinsic semiconductor

- Since the electron and hole exist in pairs in an intrinsic semiconductor

$$n_0 = p_0$$

$$\Rightarrow N_c \exp\left(-\frac{E_c - E_F}{k_B T}\right) = N_v \exp\left(-\frac{E_F - E_v}{k_B T}\right)$$

- Taking logarithm on both sides of the equation, we have

$$\ln N_c + \ln\left[\exp\left(-\frac{E_c - E_F}{k_B T}\right)\right] = \ln N_v \ln\left[\exp\left(-\frac{E_F - E_v}{k_B T}\right)\right]$$

$$\Rightarrow \ln N_c - \frac{E_c - E_F}{k_B T} = \ln N_v - \frac{E_F - E_v}{k_B T}$$

$$\Rightarrow \frac{2E_F}{k_B T} = \frac{E_c + E_v}{k_B T} + \ln N_v - \ln N_c$$

$$\Rightarrow E_F = \frac{E_c + E_v}{2} + \frac{k_B T}{2} \ln \frac{N_v}{N_c}$$

- If we substitute the expressions for N_c and N_v, in the ratio of N_c over N_v all the terms cancel out except the effective masses of electron and hole.

Fermi level of intrinsic semiconductor

- The expressions for effective density of states are

$$N_c = 2\left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2}, \qquad N_v = 2\left(\frac{2\pi m_p^* k_B T}{h^2}\right)^{3/2}$$

- Therefore, the Fermi level in terms of effective masses of charge carriers is given by

$$\begin{aligned} E_F &= \frac{E_c + E_v}{2} + \frac{k_B T}{2} \ln\left(\frac{m_p^*}{m_n^*}\right)^{3/2} \\ &= E_{\text{midgap}} + \frac{3k_B T}{4} \ln \frac{m_p^*}{m_n^*} \end{aligned}$$

where E_{midgap} is defined as the midgap energy level that is in the midpoint of conduction band minimum and valence band maximum and is given by

$$E_{\text{midgap}} := \frac{E_c + E_v}{2}$$

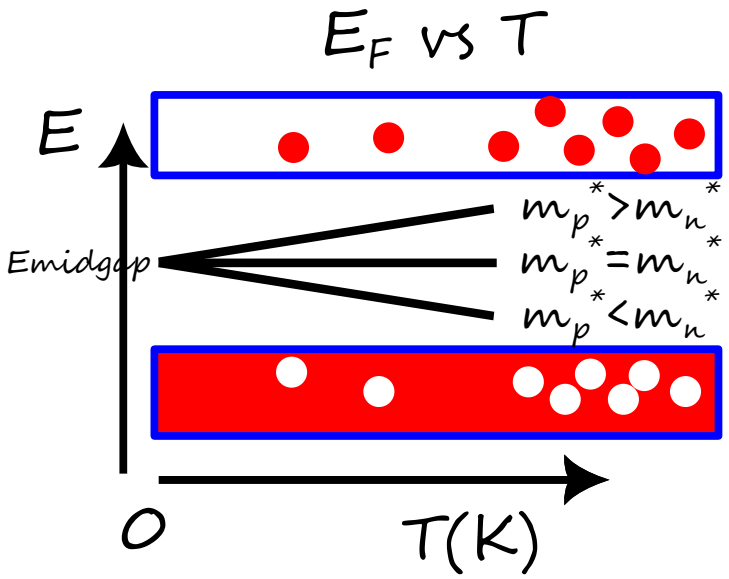
$$\boxed{\therefore E_F = E_{\text{midgap}} + \frac{3k_B T}{4} \ln \frac{m_p^*}{m_n^*}}$$

E_F vs T of intrinsic semiconductor

- Since the Fermi energy level varies with temperature, let us consider two cases – $T = 0\,\mathrm{K}$ and $T = 0\,\mathrm{K}$.
- Also, the Fermi energy level varies with effective masses of electron and hole. So let us consider three cases – $m_p = m_n$, $m_p > m_n$, and $m_p < m_n$.

	$T = 0\,\mathrm{K}$	$T \neq 0\,\mathrm{K}$
$m_p = m_n$	E_{midgap}	E_{midgap}
$m_p > m_n$	E_{midgap}	$E_{\text{midgap}} + \delta$
$m_p < m_n$	E_{midgap}	$E_{\text{midgap}} - \delta$

Table: Here δ is a positive quantity that linearly increases with temperature.



Key Insight

With temperature, E_F deviates from E_{midgap} for semiconductors with differing electron and hole effective masses.

Conductivity of intrinsic semiconductor

- Conduction in a semiconductor is through two channels – electron and hole. Therefore

$$\sigma_i = \sigma_e + \sigma_h$$

- For each channel, the conductivity is given by the product of charge carrier concentration and mobility. Therefore

$$\begin{aligned}\sigma_i &= n_0 e\mu_e + p_0 e\mu_h \\ &= n_i e\left(\mu_e + \mu_h\right)\end{aligned}$$

$$\boxed{\therefore \sigma_i = n_i e\left(\mu_e + \mu_h\right)}$$

- If we express the intrinsic carrier concentration in terms of material properties, then

$$\begin{aligned}\sigma_i &= \sqrt{N_c N_v}\, e\left(\mu_e + \mu_h\right) \exp\left(-\frac{E_g}{2k_B T}\right) \\ &= \sigma_0 \exp\left(-\frac{E_g}{2k_B T}\right)\end{aligned}$$

where σ_0 is a constant in terms of material properties.

Estimation of band gap of intrinsic semiconductor

- Therefore, the variation of conductivity of intrinsic semiconductor with temperature is given by

$$\boxed{\therefore \sigma_i = \sigma_0 \exp\left(-\frac{E_g}{2k_B T}\right)}$$

- If we take the logarithm on both sides of above equation, then

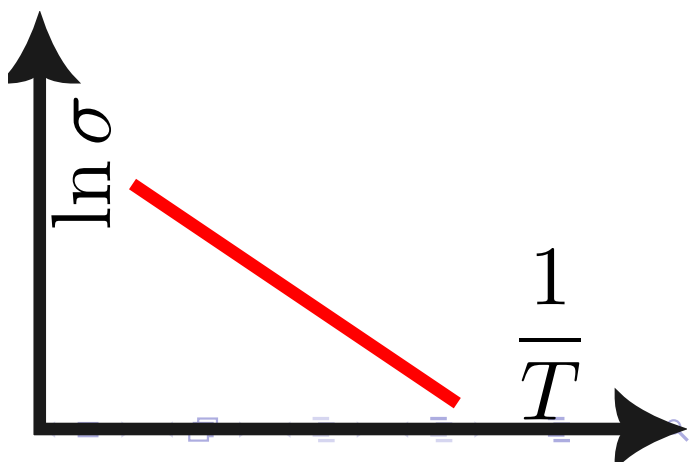
$$\ln \sigma_i = \ln \sigma_0 + \ln\left[\exp\left(-\frac{E_g}{2k_B T}\right)\right]$$

$$= \ln \sigma_0 - \frac{E_g}{2k_B T}$$

- Therefore, a plot of $\ln \sigma$ vs $\frac{1}{T}$ will be straight line with slope m given by

$$m = -\frac{E_g}{2k_B}$$

From the slope of the plot, we can estimate the energy band gap.



Some useful information for calculations

	Si	GaAs	Ge
μ_n ($\mathrm{cm^2\,V^{-1}\,s^{-1}}$)	1350	8500	3900
μ_p ($\mathrm{cm^2\,V^{-1}\,s^{-1}}$)	480	400	1900

Table: Mobility of carriers in Si, GaAs, and Ge at 300 K. Taken from Section 5.1 of Neamen

	Si	GaAs	Ge
n_i ($\mathrm{cm^{-3}}$)	1.5×10^{10}	1.8×10^{6}	2.4×10^{13}

Table: Intrinsic carrier concentration in Si, GaAs, and Ge at 300 K.

Problems on Fermi level of intrinsic semiconductor

Problem

A quantum state in the conduction band is $k_B T$ above conduction band minimum E_c of an intrinsic semiconductor. The Fermi level is $0.25\,\mathrm{eV}$ *below E_c. Find the probability that the quantum state is occupied at* $300\,\mathrm{K}$.

Problem

For the same material in above problem, if the effective density of states in conduction band N_c is $2.8 \times 10^{19}\,\mathrm{cm}^{-3}$ *at* $300\,\mathrm{K}$ *, then find the electron concentration n_0.*

Problem

Calculate the position of the intrinsic Fermi level with respect to the center of the bandgap in Si at $300\,\mathrm{K}$.

Problem

Find the resistivity of intrinsic Ge at $300\,\mathrm{K}$. *[Hint: Check useful info slide]*

Problems on Fermi level of intrinsic semiconductor

Problem

The resistivity of intrinsic Si is $2.3 \times 10^3\,\Omega\,\mathrm{m}$ *at* $300\,\mathrm{K}$. *Calculate its resistivity at* $100\,^\circ\mathrm{C}$. *[Hint:* $E_g^{Si} = 1.12\,\mathrm{eV}$ *]*

Tough problems

Problem

Calculate the thermal equilibrium electron concentration in Si at $400\,\mathrm{K}$. N_c *at* $300\,\mathrm{K}$ *is* $2.8 \times 10^{19}\,\mathrm{cm}^{-3}$. *[Hint: Solve the below problem.]*

Problem

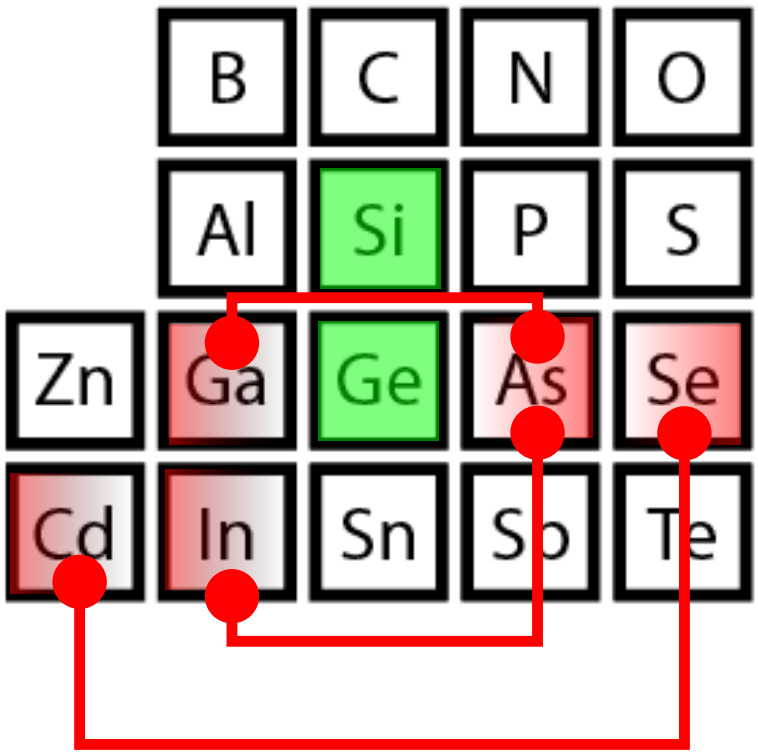
Calculate the ratio of conduction electrons at $400\,\mathrm{K}$ *to conduction electrons at* $300\,\mathrm{K}$. *[Hint: From the explicit expression for* N_c*, observe the form of* N_c *vs* T*.]*

Extrinsic semiconductor

Periodic table

Elemental semiconductor

Compound semiconductor



Elemental	Compound
Si	GaAs
Ge	InAs
	CdSe

Table: Intrinsic semiconductors.

Extrinsic semiconductor – Dopant atoms

Definition

- Extrinsic semiconductor is a semiconductor with impurities added.
- Depending upon the type of impurities added, extrinsic semiconductor is of two types –
  1. n-type extrinsic semiconductor
  2. p-type extrinsic semiconductor

n-type	p-type
P	Al
As	B
Sb	Ga
In	

Table: Dopant elements for elemental semiconductors Si and Ge.

n-type	p-type
Se	Zn
Te	Cd
Si at Ga	Si at As
Ge at Ga	Ge at As

Table: Dopant elements for compound semiconductor GaAs.

Ionization of Hydrogen atom

Definition

- Ionization energy is the energy required to free up a bound electron from an atom'[a].

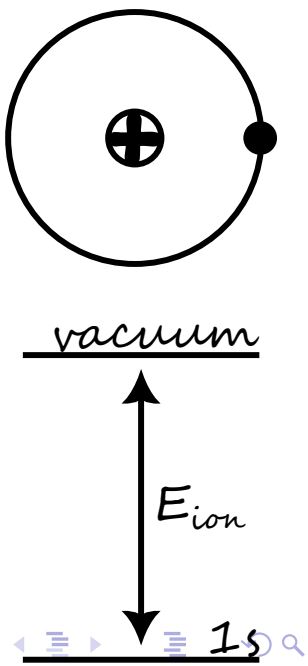
[a] The related concept to ionization energy in the case of solid is work function.

- Consider a hydrogen atom with a proton of charge $+1$ as nucleus and an electron of charge -1 revolving around the nucleus.
- In the ground state, the electron occupies the 1 s energy level. If the ionization energy is ΔE_{ion}, then

$$H + \Delta E_{\text{ion}} \rightarrow \mathrm{H}^{+} + \mathrm{e}^{-}$$

- If the energy of the 1 s level $E_{1\text{s}}$ is calculated, we can estimate ΔE_{ion} as

$$\Delta E_{\text{ion}} = E_{\text{vacuum}} - E_{1\text{s}},$$



Bohr's model of H atom

Postulates

1. Electron revolves around the nucleus due to the Coulomb force of attraction.
2. The angular momentum of electron is quantized and can take only integral multiples of $\hbar$.

- If v is the velocity of the electron and r is the radius of orbit, then the first postulate translates to

$$F_{\text{Coulomb}} = -\frac{mv^2}{r},$$
$$-\frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2} = -\frac{m_0 v^2}{r},$$
$$\Rightarrow v^2 = \frac{1}{4\pi\epsilon_0}\frac{e^2}{m_0 r}$$

- If $L = mvr$ is the angular momentum of electron, then the second postulate translates to

$$L = n\hbar,$$
$$\Rightarrow m_0 vr = \hbar,$$

where $n = 1$ is taken for the ground state.

Ionization energy of H atom

- Bohr radius a_0 of H atom is the radius of electron's orbit in the ground state.
- From the above two equations, the Bohr radius is found to be

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_0 e^2} = 0.529\,\text{Å}. \tag{1}$$

- The total energy E_{1s} of the orbiting 1 s electron is the sum of kinetic energy T and potential energy V so that

$$\begin{aligned} E_{1s} &= T + V, \\ &= \frac{1}{2} m_0 v^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}, \\ &= -\frac{1}{2}\frac{m_0 e^4}{\hbar^2 (4\pi\epsilon_0)^2} = -13.6\,\text{e V} \end{aligned} \tag{2}$$

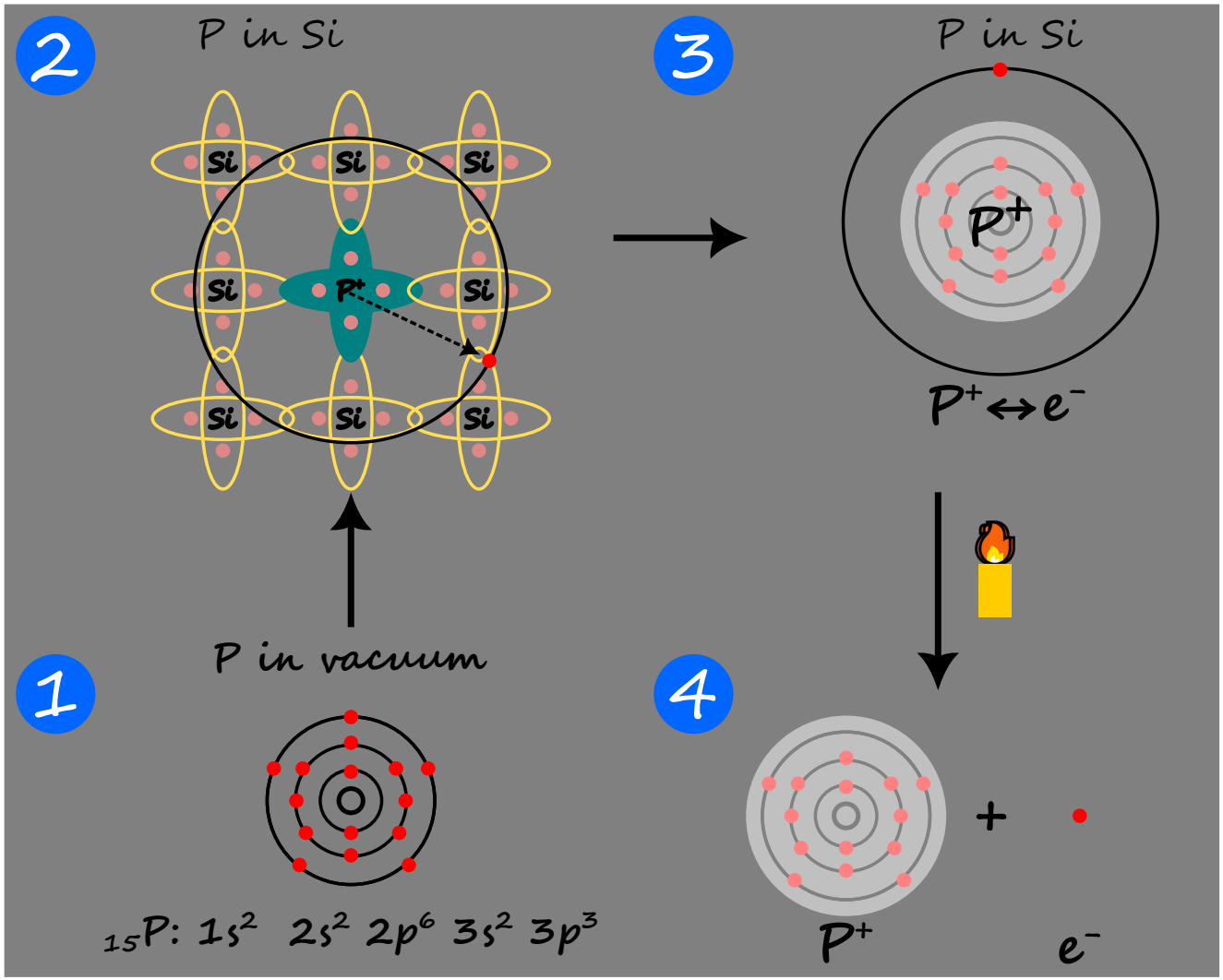
- Therefore, the ionization energy of H atom is given by

$$\Delta E_{\text{ion}} = E_{\text{vacuum}} - E_{1s} = 13.6\,\text{e V}.$$

Key Insight

The Bohr model is applicable to **hydrogenic** or hydrogen-like atoms.

Donor impurity – Hydrogen-like atom



1. P as isolated atom.
2. P as impurity inside Si.
3. P impurity as $\mathrm{P}^{+} \leftrightarrow \mathrm{e}^{-}$ hydrogen like atom.
4. Due to thermal energy, ionization of P impurity gives free electron.

Key Insight

Doping with donor impurity forms an n-type semiconductor.

Donor impurity – Hydrogen-like atom

Definition

- Donor impurity, also called donor dopant, is an atom that donates an electron to the intrinsic semiconductor upon ionization.

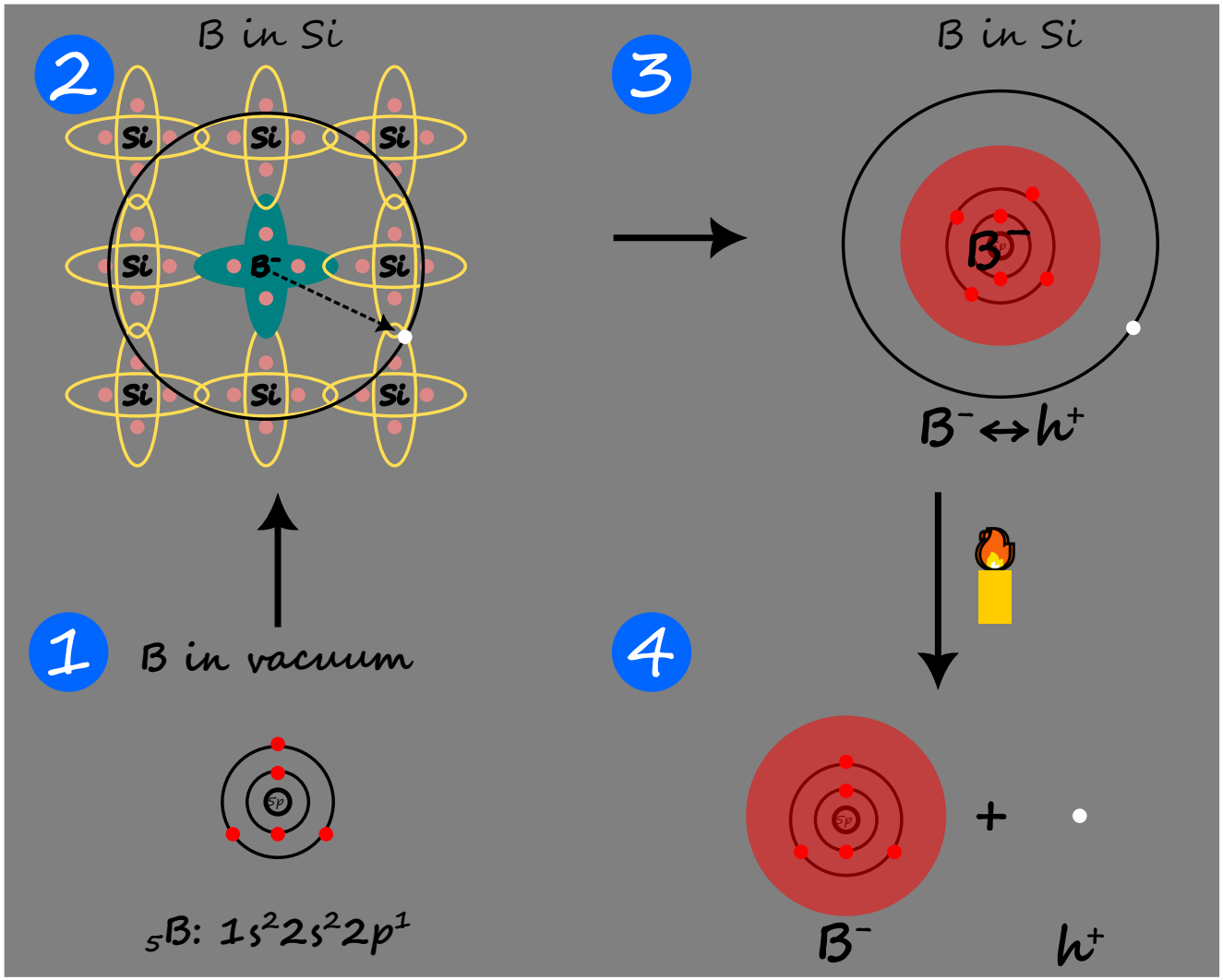
1. Phosphorus in vacuum has 5 electrons in the valence shell.
2. Phosphorus in silicon shares 4 electrons with neighbouring Si atoms for covalent bonding. The **extra** electron is loosely coupled to the phosphorus nucleus.
3. At absolute temperature, phosphorus can be modeled as a hydrogenic atom with nucleus as phosphorus ion of charge $+1$, and a **bound** electron of charge -1 revolving around the nucleus.

$$\mathrm{P\,in\,Si} \equiv \mathrm{P}^{+} \leftrightarrow \mathrm{e}^{-}$$

4. When the thermal energy is sufficient to overcome the attractive force between P^{+} and e^{-}, the electron becomes **free** and is released into the Si lattice.

$$\mathrm{P}^{+} \leftrightarrow \mathrm{e}^{-} + \mathcal{O}(k_B T) \rightarrow \mathrm{P}^{+}_{\square} + \mathrm{e}^{-}$$

Acceptor impurity – Hydrogen-like atom



1. B as isolated atom.
2. B as impurity inside Si.
3. B impurity as $\mathrm{B}^- \leftrightarrow \mathrm{h}^+$ hydrogen like atom.
4. Due to thermal energy, ionization of B impurity gives free hole.

Key Insight

Doping with acceptor impurity forms a p-type semiconductor.

Acceptor impurity – Hydrogen-like atom

Definition

- Acceptor impurity, also called acceptor dopant, is an atom that accepts an electron from the intrinsic semiconductor upon ionization.

1. Boron in vacuum has 3 electrons in the valence shell.
2. Boron in silicon shares 3 electrons with neighbouring Si atoms for covalent bonding. The 4^{th} electron is absent and can be considered as an **extra** hole is loosely coupled to the boron nucleus.
3. At absolute temperature, Boron can be modeled as a hydrogenic atom with nucleus as Boron ion of charge -1, and a **bound** hole of charge $+1$ revolving around the nucleus.

$$\mathrm{B\,in\,Si} \equiv \mathrm{B}^- \leftrightarrow \mathrm{h}^+$$

4. When the thermal energy is sufficient to overcome the attractive force between B^- and h^+, the hole becomes **free** and is released into the Si lattice.

$$\mathrm{B}^- \leftrightarrow \mathrm{h}^+ + \mathcal{O}(k_B T) \rightarrow \mathrm{B}^- + \mathrm{h}^+$$

Ionization energy of dopant atom

- The hydrogenic dopant atom (or acceptor atom) is inside the Si environment. Therefore, the Coulomb force on bound electron due to donor ion (or bound hole on acceptor ion) should be modified to account for permittivity of silicon. Let the permittivity of Si be ϵ_{Si}. [$\epsilon_{\text{Si}} = 11.7\epsilon_0$.]
- Also, the Si lattice alters the effective mass of electron (or hole). Let the effective mass of electron in Si be m_n*. [$m_n* = 0.26m_0$.]

- The Bohr radius of hydrogenic dopant atom a_{dopant} is given by

$$a \propto \frac{\epsilon}{m},$$

$$\Rightarrow \frac{a_{\text{dopant}}}{a_0} = \frac{\epsilon_{\text{Si}}}{\epsilon_0} \cdot \frac{m_0}{m_n*},$$

$$\therefore a_{\text{dopant}} \simeq 25\,\text{Å}.$$

- The ionization energy of dopant $\Delta E_{\text{ion}}^{\text{dopant}}$ is given by

$$\Delta E_{\text{ion}} \propto \frac{m}{\epsilon^2},$$

$$\Rightarrow \frac{\Delta E_{\text{ion}}^{\text{dopant}}}{\Delta E_{\text{ion}}^{\text{H}}} = \frac{m_n*}{m_0} \cdot \left(\frac{\epsilon_0}{\epsilon_{\text{Si}}}\right)^2,$$

$$\therefore \Delta E_{\text{ion}}^{\text{dopant}} \simeq 25\,\text{meV}.$$

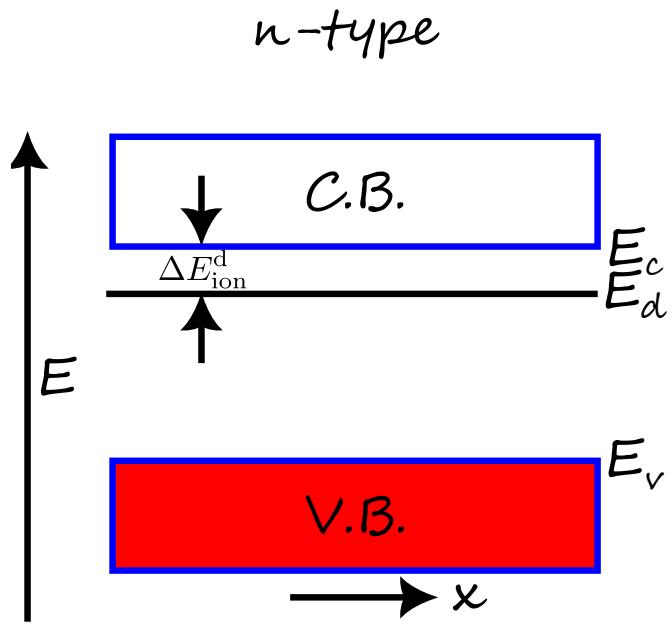
Key Insight

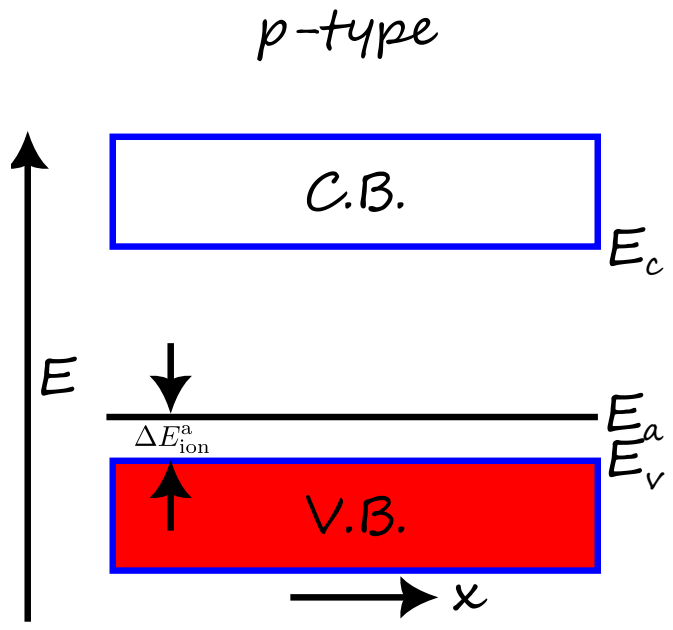
The ionization energy of dopants is of the order of $k_B T_{300\,\text{K}}$.

Dopant energy levels

Definition

- Donor energy level E_d is the ground state of donor dopant atom.
- Acceptor energy level E_a is the ground state of acceptor dopant atom.



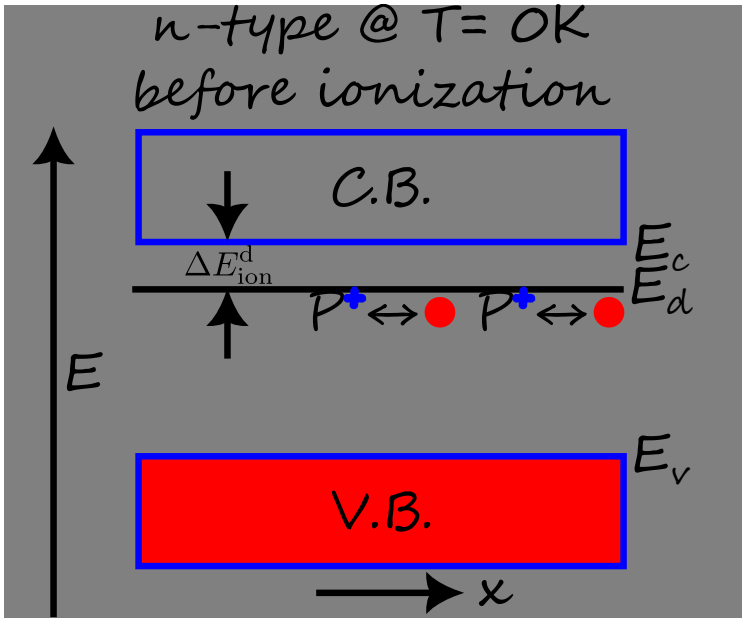


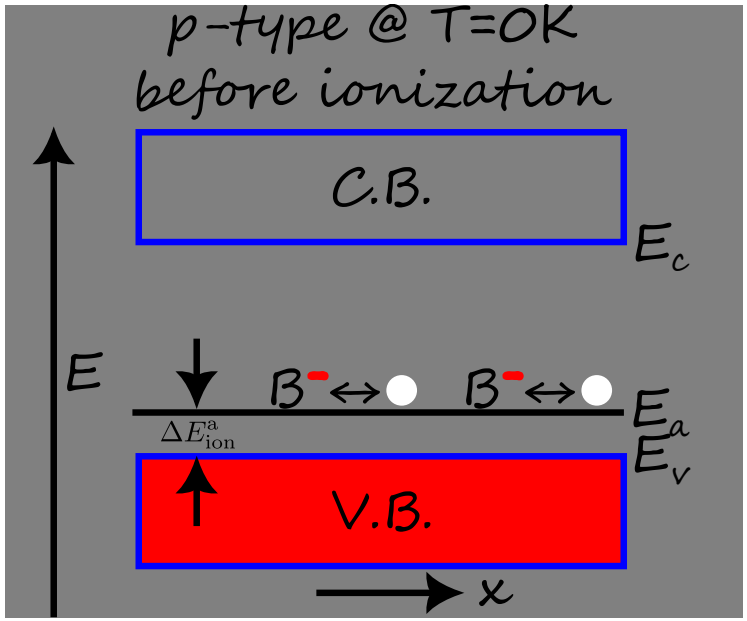
Key Insight

Donor energy level is closer to the conduction band minimum and acceptor energy is closer to the valence band maximum.

Dopant energy levels – before ionization

- At absolute zero temperature, due to lack of thermal energy, the dopant atoms are **not** ionized.

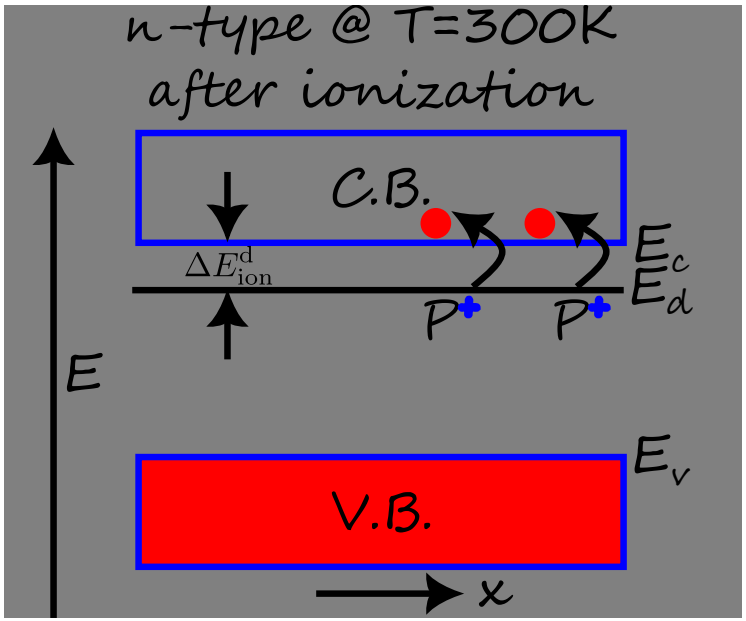


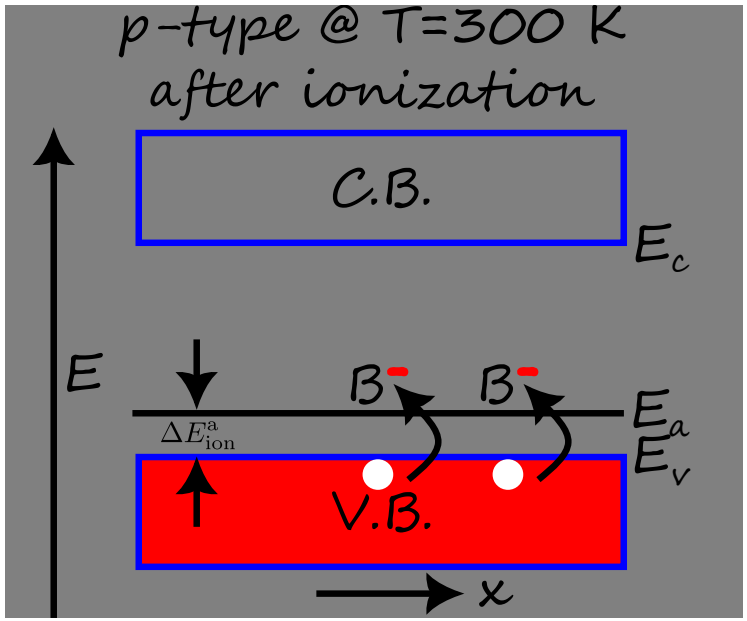


- The electron is **bound** to the donor ion.
- The hole is **bound** to the acceptor ion.

Dopant energy levels – after ionization

- At room temperature, the thermal energy is of the order of ionization energy. This leads to ionization of dopant atoms.

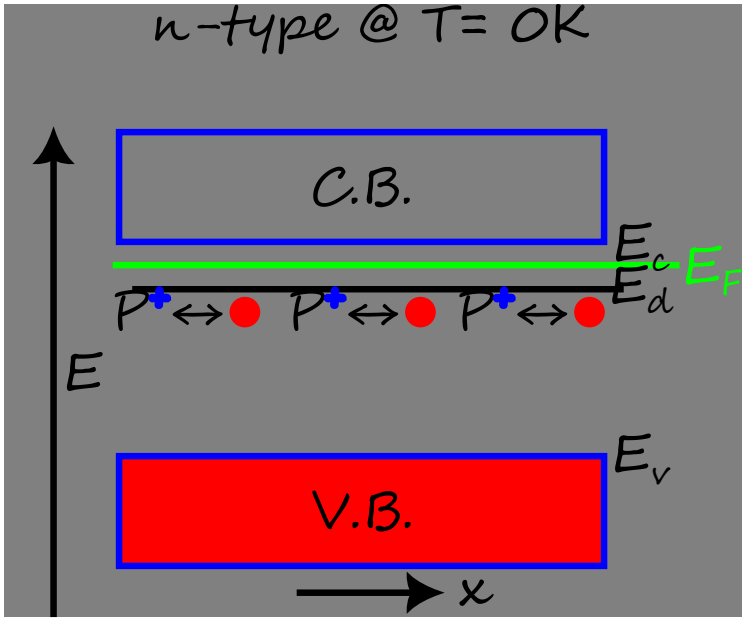


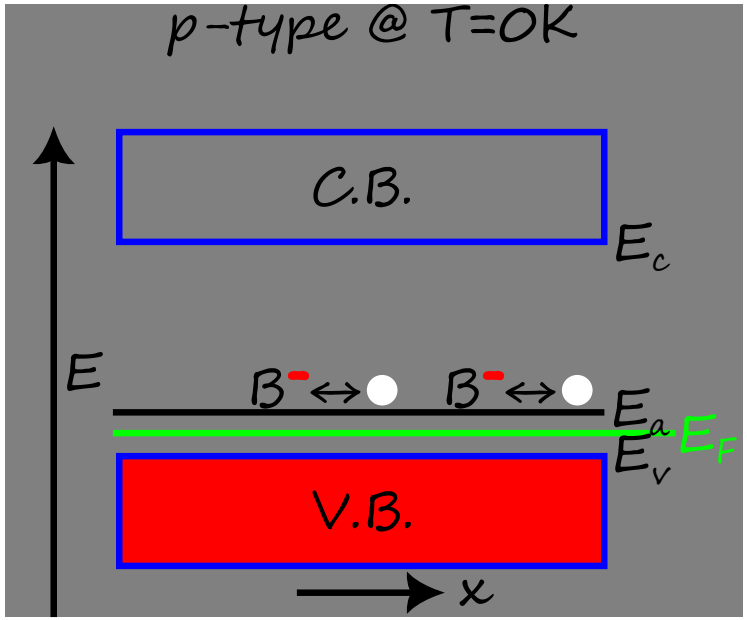


- Upon ionization, the donor dopant releases free electron into the conduction band.
- Upon ionization, the acceptor dopant accepts electron from valence band and creates a hole in the valence band.

Position of Fermi level – @ 0 K

- At absolute zero temperature, all the energy levels below the Fermi levels must be **occupied** by electrons.





The Fermi energy level lies

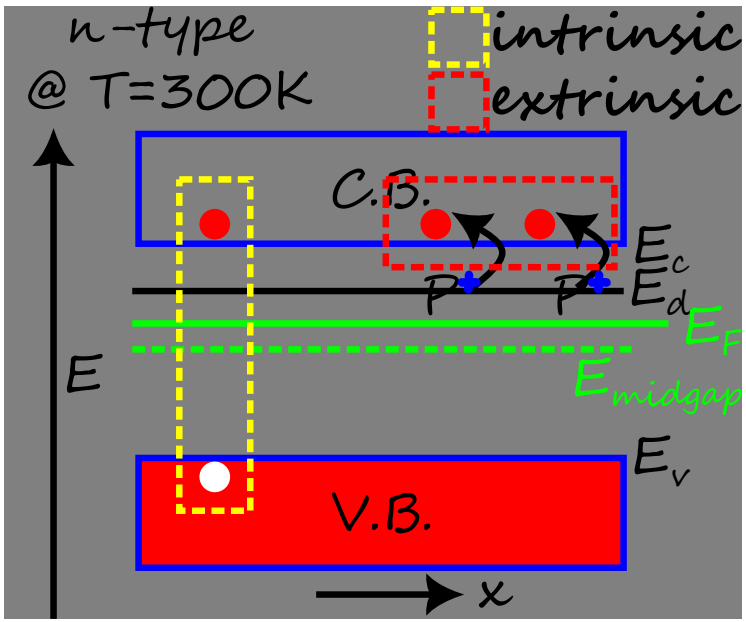
- **above** the donor energy level.
- **below** the conduction band edge.

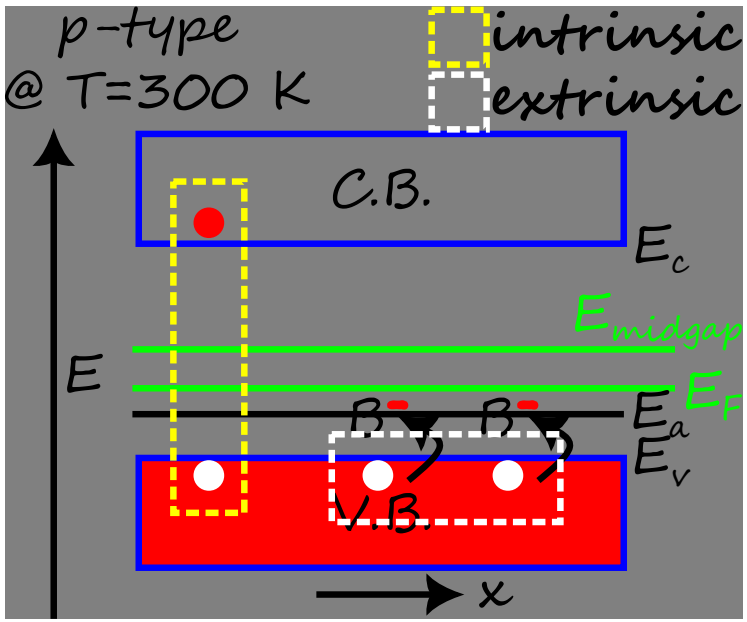
The Fermi energy level lies

- **below** the acceptor energy level.
- **above** the valence band edge.

Position of Fermi level – @ 300 K

- At room temperature, there is contribution to the free carriers from both extr insic and intrinsic





The Fermi energy level lies

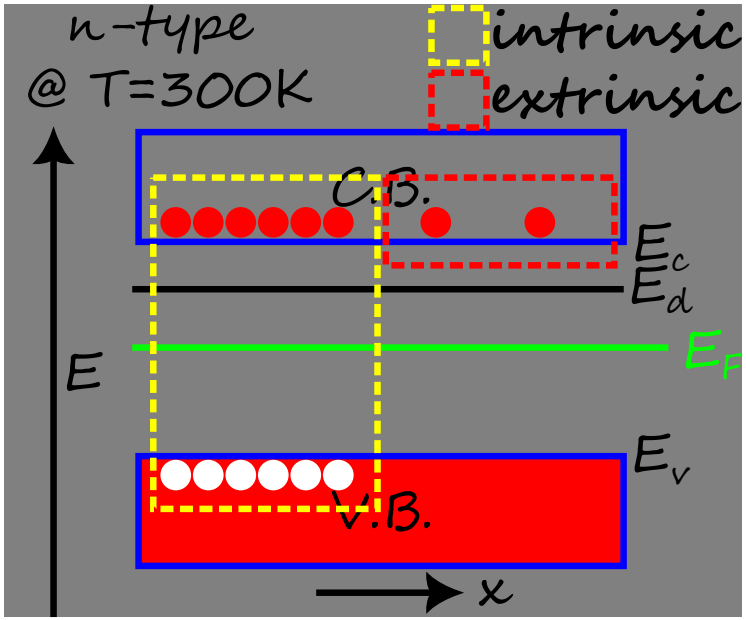
- **below** the donor energy level since donor energy level is **empty**.
- **above** the midgap energy level.

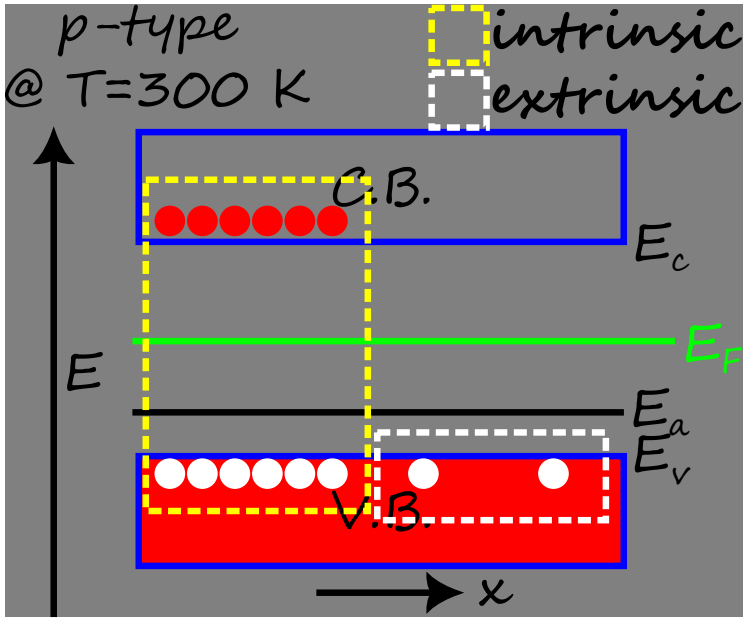
The Fermi energy level lies

- **above** the acceptor energy level since acceptor energy level is **filled**.
- **below** the midgap energy level.

Position of Fermi level – @ $T \gg 300\,\mathrm{K}$

- At very high temperature, the contribution to the free carriers from intrinsic **dominates** the contribution from extr insic





- The Fermi energy level lies near the midgap energy level in both cases.

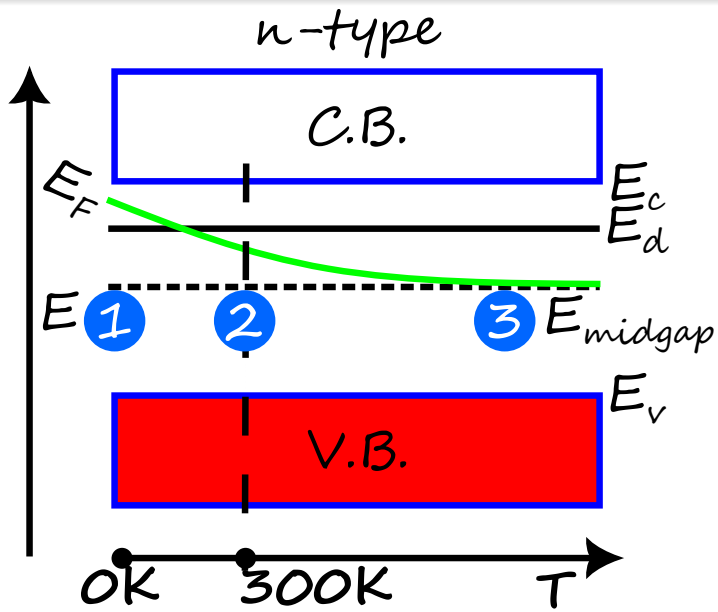
Key Insight

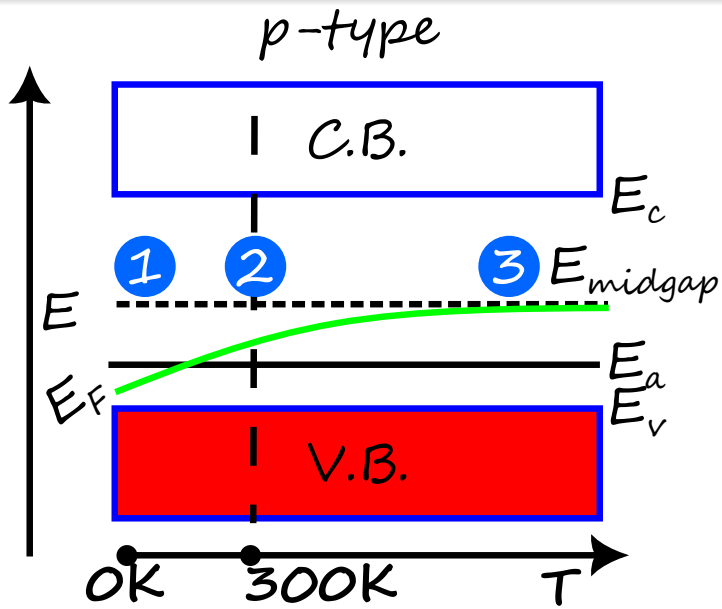
At very high temperature, extrinsic semiconductor behaves nearly as an intrinsic semiconductor.

Variation of Fermi level with temperature

Definition

- **Freeze-out** is the condition when the dopants are not ionized.
- **Complete ionization** is the condition when the dopants are completely ionized.





1. At 0 K, the dopants are under freeze-out condition.
2. At 300 K, the thermal energy is nearly equal to ionization energy of dopants leading to complete ionization condition.
3. At $T \gg 300$ K, the extrinsic s.c. behaves as an intrinsic s.c.

End of M2U1