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

Course Instructor:
Dr. Sreekar Guddeti
Assistant Professor in Physics
Department of Science and Humanities
Vignan's Foundation for Science, Technology and Research

December 7, 2025

M2U1 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

M2U1 Plan

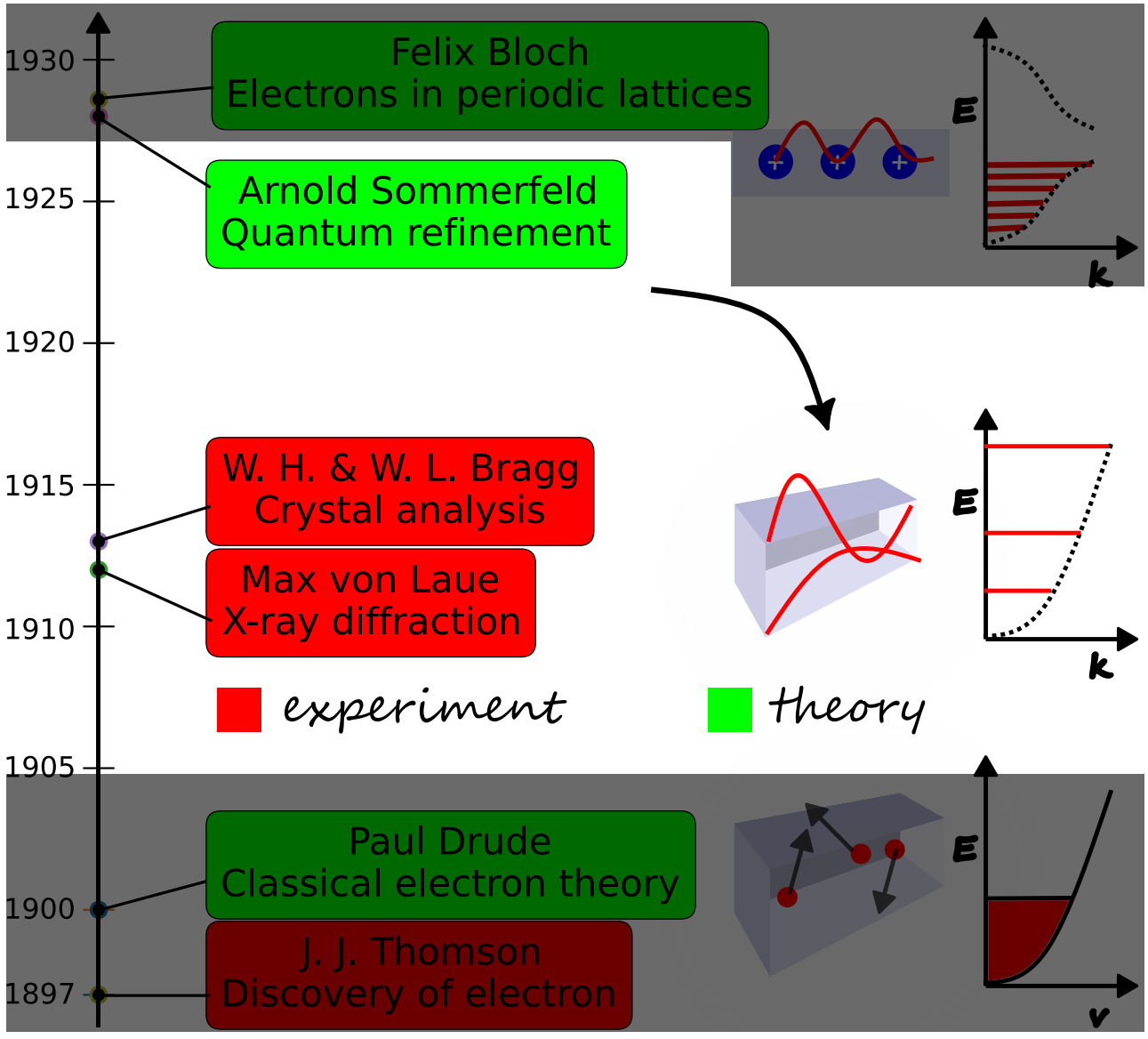
1. Quantum Free Electron Theory
2. Fermi-Dirac distribution
3. Electronic specific heat of solids
4. Density of states (qualitative)
5. Success and Failures of quantum free electron theory of solids
6. E-k diagram
7. Classification of materials based on bands in solids
8. Fermi level in semiconductors-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

Summary of Classical free electron theory (CFET)

- Derived $\sigma = \frac{ne^2\tau}{m}$.
- Connected microscopic electron properties to macroscopic Ohm's law.
- Classical free electron theory has qualitative and quantitative agreement with experiment values of conductivity.
- However, the theory has drawbacks. Some of them are
  - Incorrect prediction for conductivity vs valency.
  - Cannot explain anomalous sign of Hall coefficient in some metals.
  - Underestimation of mean free path.
  - Cannot explain classification of materials into conductors. semi-conductors and insulators.
  - Wrong prediction of conductivity vs temperature.
  - Overestimation of heat capacity.

Electron theories of metals

1. Classical free electron theory
2. Quantum free electron theory
3. Quantum band theory



Quantum free electron theory

A. Sommerfeld, W. Pauli, E. Fermi, and P. Dirac

- Proposed by Arnold Sommerfeld in 1927.
- Considered the **matter wave nature** of electron.
- Mutual repulsion between electrons is neglected i.e. electrons are independent – **independent electron approximation**.
- Assumed "gas" is **free** i.e. not under influence of lattice – **free electron approximation**.
- Electrons obey the **Pauli exclusion principle**.
- Role of lattice is to redistribute the energy distribution that obeys **quantum** Fermi-Dirac statistics – quantum thermodynamics.
- The electron gas is called Fermi gas.

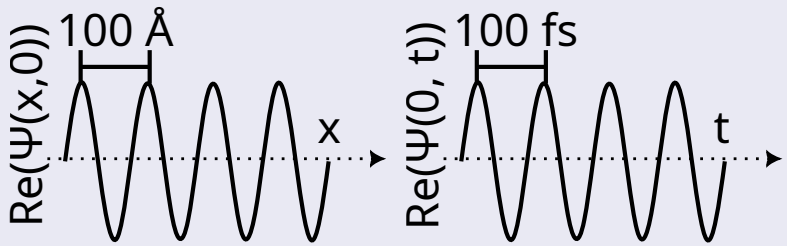
Free electron as a matter wave

Problem

Determine the wave number k, wavelength λ, angular frequency ω and period T of a wave function that describes a thermal electron at room temperature. If it is traveling along $+$ve x direction, write the expression for the wave function.

Problem

The sketches below represent the spatial and temporal parts of wave function of a thermal electron moving along x direction. Determine the temperature.



Key Insight

A matter wave is described by wave vector k and angular frequency ω.

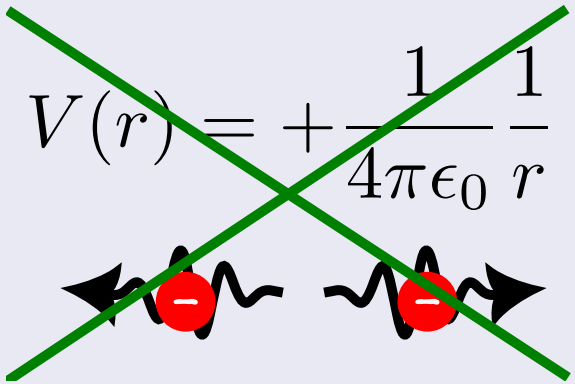
Problem at hand

$$V(r) = +\frac{1}{4\pi\epsilon_0}\frac{1}{r} \qquad V(r) \propto -\frac{1}{r}$$

- The problem at hand is to solve the motion of interacting matter waves– electrons of the order of 10^{23} and ions of the order of 10^{23}.
- This is a tough problem. The idea is to simplify the problem by making **approximations**.

Independent electron approximation

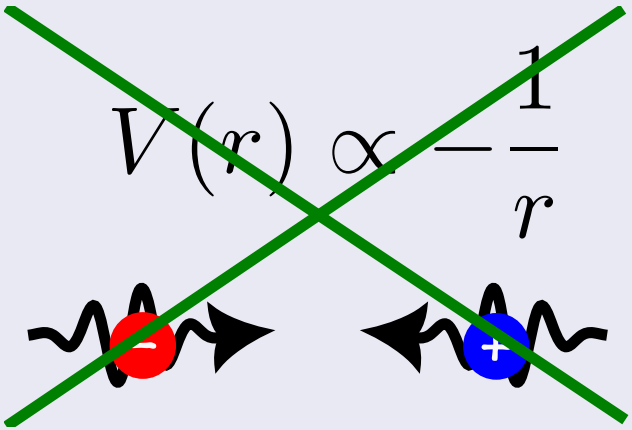
Postulate

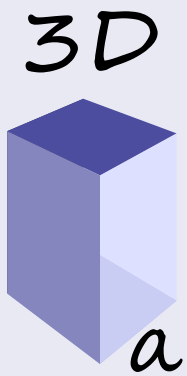


- Mutual repulsion between electrons is neglected i.e. electrons are independent.

Free electron approximation

Postulate





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

- The interaction of electron with ions is neglected i.e. electrons are free.
- The electron is bounded within the metal by 3D infinite potential well.

Pauli's exclusion principle

Postulate

- No two electrons can occupy the same quantum state.
- No two electrons can share the same set of quantum numbers.
- Electron obeys Pauli's exclusion principle since it has spin $\frac{1}{2}$.

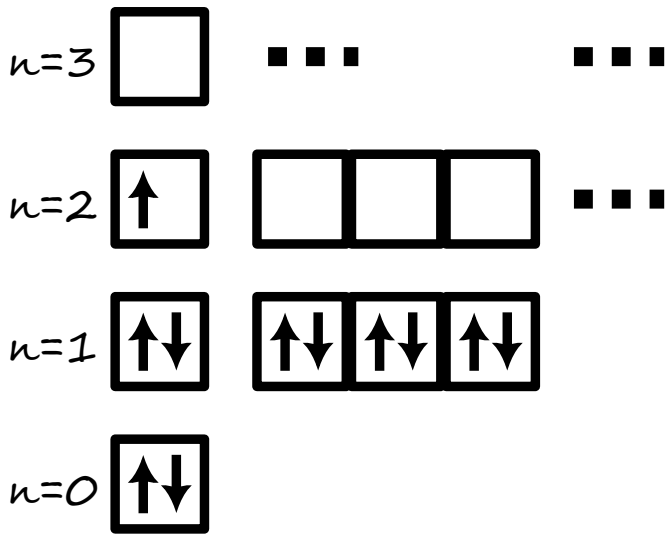
W. Pauli

Definition

A quantum state is defined by a set of quantum numbers.

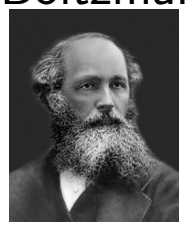
Problem

What quantum state is occupied by valence electron in Na?

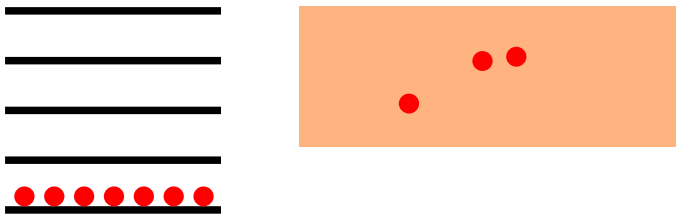


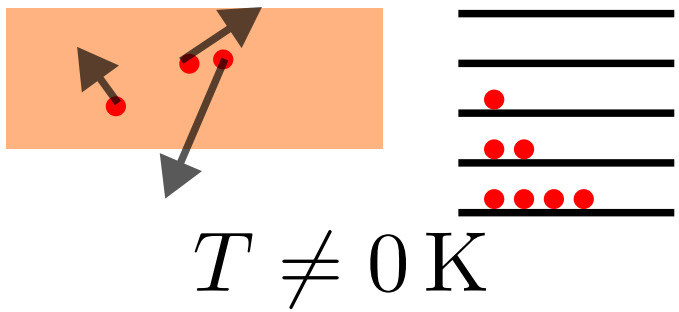
Classical thermodynamics vs Quantum thermodynamics

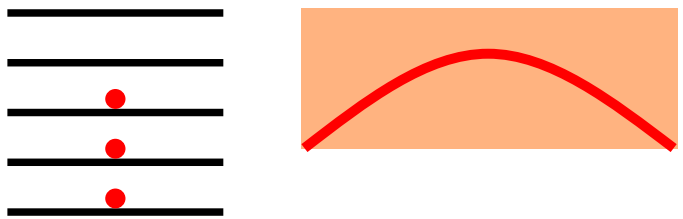
Boltzmann

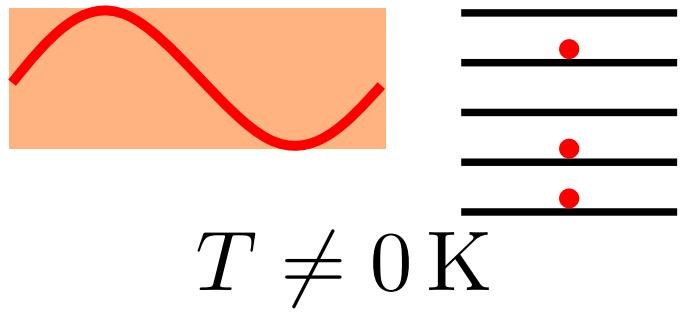


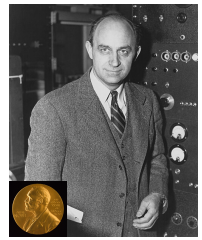
Maxwell



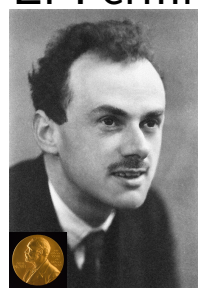








E. Fermi



P. Dirac

- Classical thermodynamics allows electrons to share the same state.
- State is defined by velocity v.
- The occupancy of energy level is governed by Maxwell-Boltzmann statistics.

- Quantum thermodynamics is governed by Pauli exclusion principle and forbids sharing the same state.
- Quantum state is defined by wavevector k.
- The occupancy of energy level is governed by Fermi-Dirac statistics.

Sommerfeld's Quantum Free electron theory – Postulates

Postulates

1. **Waves:** Electrons are quantum waves with wavevector k, angular frequency ω.
2. **Fermion:** Electron is a spin $\frac{1}{2}$ particle and obeys Pauli's exclusion principle.
3. **Independent electron approximation:** Electrons are independent and mutual repulsion between them is ignored.
4. **Free electron approximation:** Electrons are free and move in an infinite potential well.
5. **Quantum Thermodynamics:** The thermalization is governed by Fermi-Dirac statistics.

Quantum states in a cubic box

Consider a particle of mass m confined in a cubic box of side a with infinite walls.

- Wavefunction boundary conditions lead to quantum numbers $n_1, n_2, n_3 \in \{1, 2, 3, \ldots\}$.

$$\psi_{n_1,n_2,n_3}(x, y, z) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_1 \pi x}{a}\right) \sin\left(\frac{n_2 \pi y}{a}\right) \sin\left(\frac{n_3 \pi z}{a}\right),$$

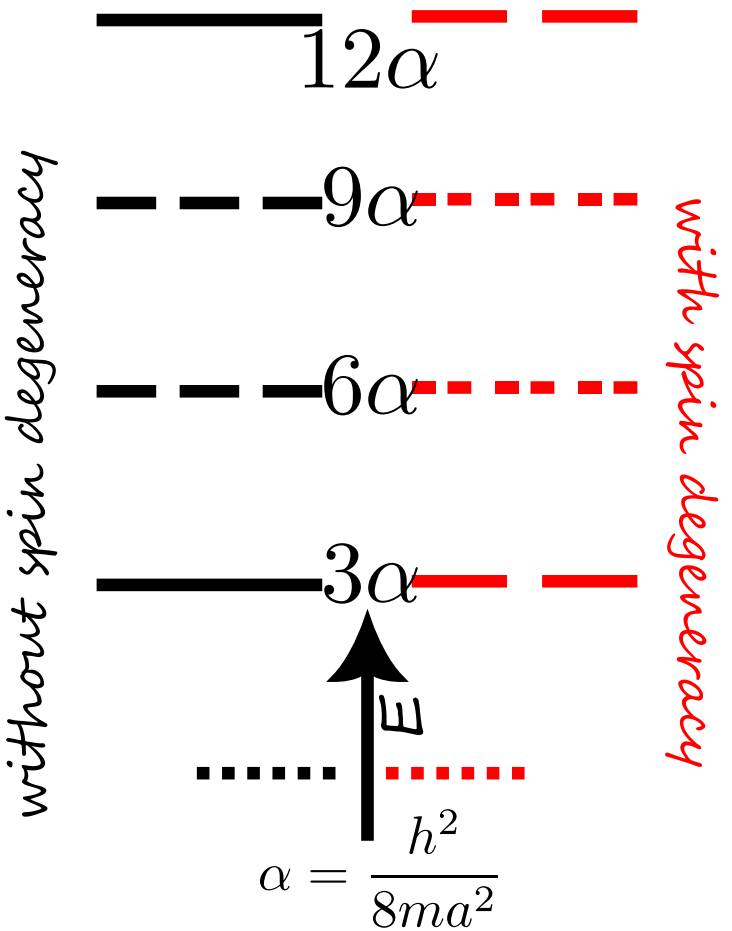
- Energy levels are given by

$$E_{n_1,n_2,n_3} = \frac{h^2}{8ma^2}\left(n_1^2 + n_2^2 + n_3^2\right).$$

Quantum state vs Energy level – Degeneracy

In the 3D box, a quantum state is defined by set of three quantum numbers n_1, n_2, n_3.

n_1	n_2	n_3	E_{n_1,n_2,n_3}	degeneracy without spin	degeneracy with spin
1	1	1	$3 \cdot \frac{h^2}{8ma^2}$	1	2
2	1	1	$6 \cdot \frac{h^2}{8ma^2}$	3	6
1	2	1	$6 \cdot \frac{h^2}{8ma^2}$	3	6
1	1	2	$6 \cdot \frac{h^2}{8ma^2}$	3	6
2	2	1	$9 \cdot \frac{h^2}{8ma^2}$	3	6
1	2	2	$9 \cdot \frac{h^2}{8ma^2}$	3	6
2	1	2	$9 \cdot \frac{h^2}{8ma^2}$	3	6
2	2	2	$12 \cdot \frac{h^2}{8ma^2}$	1	2
⋮	⋮	⋮	⋮	⋮	⋮



Quantum degeneracy

Definition

- Degeneracy is the condition when an energy level has more than one quantum state.
- If n quantum states have same energy level, then degeneracy of the energy level is n.
- Degeneracy is also called multiplicity.

Problem

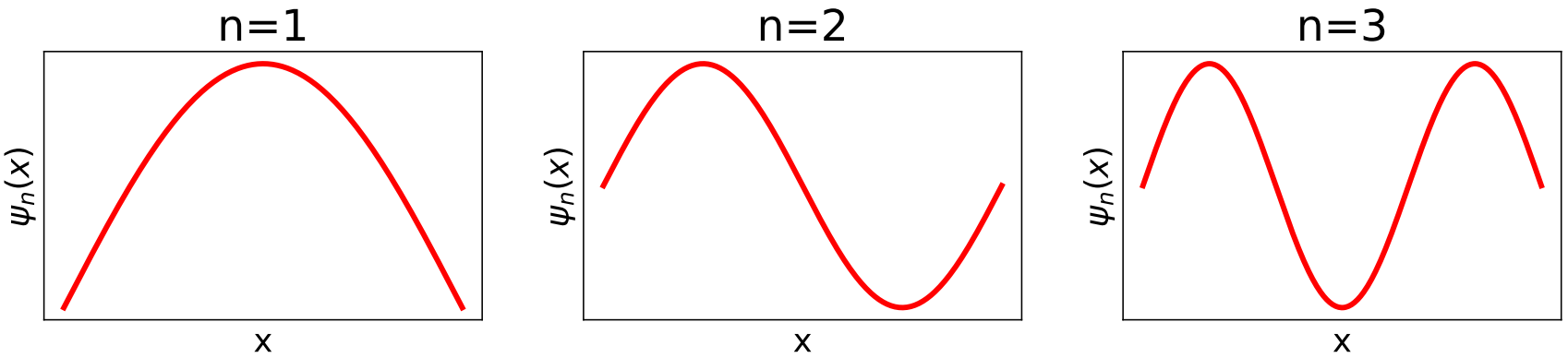
Five free electrons exist in a three dimensional potential well with all three widths equal to $a = 12\,\text{Å}$.

1. *Determine the Fermi energy level at* $T = 0\,\text{K}$.
2. *Repeat part 1 for 13 electrons.*

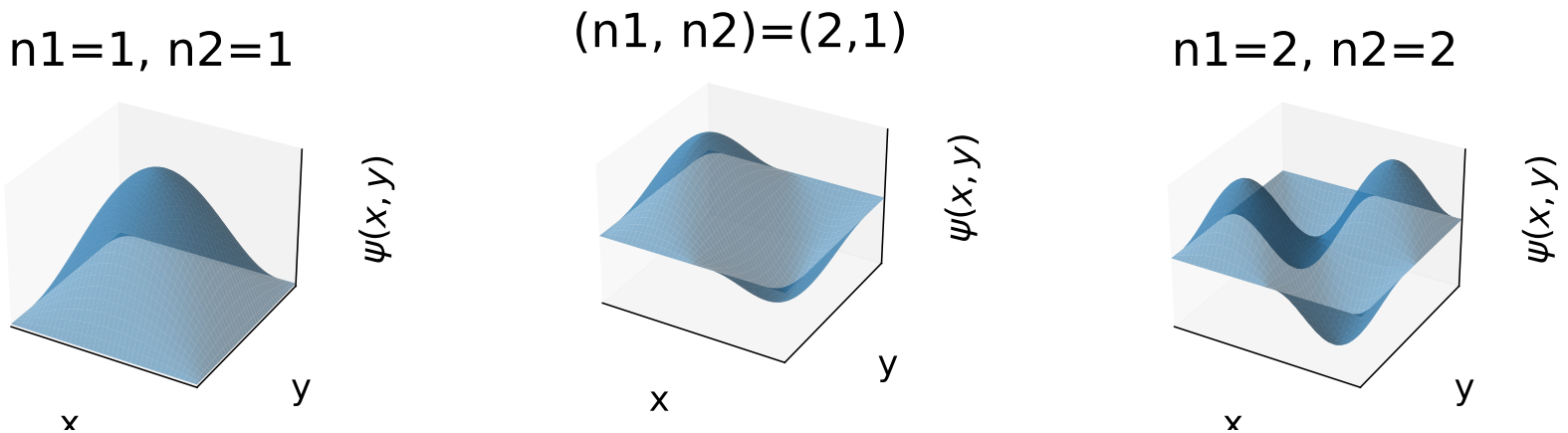
Key Insight

Quantum states can have the same energy level.

Nature of Wavefunctions – 1D, 2D

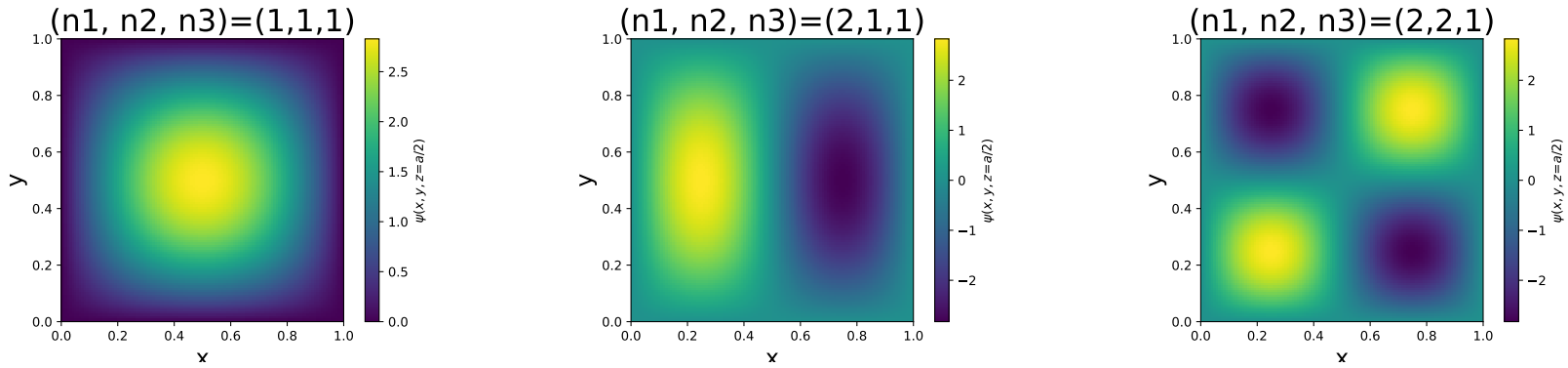


1D wave functions



2D wave functions

Nature of Wavefunctions – 3D Macroscopic atom



3D wave functions

- The above plots are called colormap plots. Each plot is a slice of the wavefunction at $z = \frac{a}{2}$.

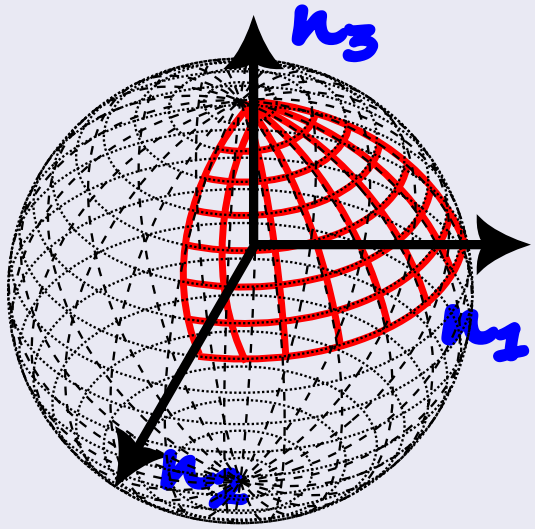
Key Insight

These wavefunctions are similar to s, p, d orbitals of hydrogen atom from chemistry.

Quantum number space

Quantum number space

- A quantum state corresponds to a point with positive integer coordinates (n_1, n_2, n_3) in the **number space**.
- This is an imaginary space.
- Quantum state lies in the positive octant of number space.



- Let us count the number of states up to energy E.
- Define $n \equiv \sqrt{n_1^2 + n_2^2 + n_3^2}$ (radial coordinate in n-space).
- The number of states with n less than some value n_0 equals the number of integer lattice points in the positive octant inside a sphere of radius n_0.
- We count the volume in n-space:

$$N(n \leq n_0) = g \times \frac{1}{8} \times \frac{4}{3}\pi n_0^3 = g\frac{\pi}{6}n_0^3, =$$

Relate n to energy

Using $E = (h^2/8ma^2)n^2$, solve for n:

$$n(E) = \frac{\sqrt{8ma^2E}}{h}.$$

Thus the total number of states with energy less than or equal to E is

$$N(E) \approx g\frac{\pi}{6}n(E)^3 = g\frac{\pi}{6}\left(\frac{\sqrt{8mL^2E}}{h}\right)^3 = g\frac{\pi}{6}\left(\frac{\sqrt{8mE}}{h}\right)^3 L^3.$$

Here, the volume $V = L^3$ and g=2.

Density of states $Z(E) = \frac{d(\frac{N}{V})}{dE}$

Definition

- Density of states $Z(E)$ [a] is defined as the rate of change of the number of states per unit volume upto energy E with respect to energy E.
- Therefore, the the number of states per unit volume from energy E to $E + \mathrm{d}E$ is given by

$$Z(E)\,\mathrm{d}E.$$

[a] In Neamen, density of states is denoted by $g(E)$.

Number of states per unit volume is

$$\rho_N(E) = \frac{N}{V} = \frac{\pi}{3}\left(\frac{\sqrt{8m}}{h}\right)^3 E^{3/2}$$

DOS in textbook form

Differentiate $\rho_N(E)$ with respect to E to get the density of states function:

$$Z(E) = \frac{\mathrm{d}\rho_N(E)}{\mathrm{d}E} = \frac{\pi}{2} \cdot \left(\frac{\sqrt{8m}}{h}\right)^3 E^{1/2}$$

$$Z(E) = \frac{\pi}{2} \cdot 8 \cdot \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}$$

$$\therefore Z(E) = 4\pi \cdot \left(\tfrac{2m}{h^2}\right)^{3/2} E^{1/2}.$$

Key Insight

For 3D infinite potential, $Z(E) \propto \sqrt{E}$.

Problem

Find the form of $Z(E)$ for 2D infinite potential.

Fermi level

Definition

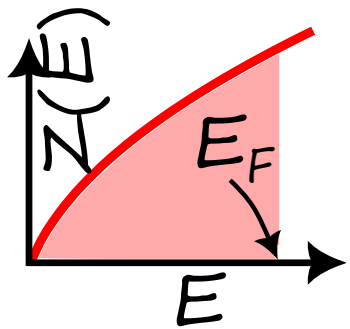
Fermi level of a metal is the maximum energy that an electron can have at $T = 0\,\mathrm{K}$.

At absolute zero all states are filled up to the Fermi energy E_F. The total electron density n_c (electrons per unit volume) is

$$n_c = \frac{N}{V} = \int_0^{E_F} Z(E)\,\mathrm{d}E = 4\pi \cdot \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{E_F} E^{1/2}\,\mathrm{d}E$$

$$= 4\pi \cdot \left(\frac{2m}{h^2}\right)^{3/2} \cdot \frac{2}{3} E_F^{3/2}$$

$$= \frac{8\pi}{3} \left(\frac{2m}{h^2}\right)^{3/2} E_F^{3/2}.$$



Relating Fermi energy to electron density

Invert the relation to get the Fermi energy as a function of density:

$$E_F^{3/2} = \left(\frac{h^2}{2m}\right)^{3/2} \cdot \frac{3n_c}{8\pi}.$$

$$\boxed{\therefore E_F = \frac{h^2}{2m}\left(\frac{3n_c}{8\pi}\right)^{2/3}.}$$

This is the Fermi energy of a free electron gas in three dimensions at $T = 0$.

Problem

Calculate E_F for metal with electron density $n_c = 5.8 \times 10^{28}\,\mathrm{m}^{-3}$.

M2U1 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

Quantum thermodynamics: Fermi–Dirac (FD) Statistics

- Describes occupancy of energy states by electrons that obey **Pauli exclusion principle**.
- The probability of occupation of an energy level E at temperature T and Fermi energy level E_F is given by

$$\boxed{P_{FD}(E) = \frac{1}{\exp\left(\frac{E-E_F}{k_B T}\right)+1}.}$$

  Here k_B is the Boltzmann constant equal to $1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$.
- To understand the FD statistics, let us analyze the probability function in two cases –
  1. $T \to 0$ limit
  2. $T \neq 0$

Key Insight

The Fermi-Dirac function is a result of Pauli exclusion principle.

Fermi–Dirac Statistics at the $T \to 0$ limit

- Take limit $T \to 0$ in definition:

$$P_{FD}(E) = \lim_{T \to 0} \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} = \frac{1}{\exp\left(\frac{E - E_F}{0}\right) + 1}.$$

- This limit needs to analyzed for three cases –
  1. $E < E_F$
  2. $E > E_F$
  3. $E = E_F$

Fermi–Dirac Statistics at the $T \to 0$ limit

1. $E < E_F$

$$
\begin{aligned}
P_{FD}(E) &= \frac{1}{\exp\left(\frac{\text{-ve}}{0}\right)+1} \\
&= \frac{1}{\exp\left(-\infty\right)+1} \\
&= \frac{1}{0+1} \\
&= \frac{1}{1} \\
&= 1
\end{aligned}
$$

2. $E > E_F$

$$
\begin{aligned}
P_{FD}(E) &= \frac{1}{\exp\left(\frac{+\text{ve}}{0}\right)+1} \\
&= \frac{1}{\exp\left(\infty\right)+1} \\
&= \frac{1}{\infty+1} \\
&= \frac{1}{\infty} \\
&= 0
\end{aligned}
$$

3. $E = E_F$

$$P_{FD}(E) = \frac{1}{\exp\left(\frac{0}{0}\right)+1}$$

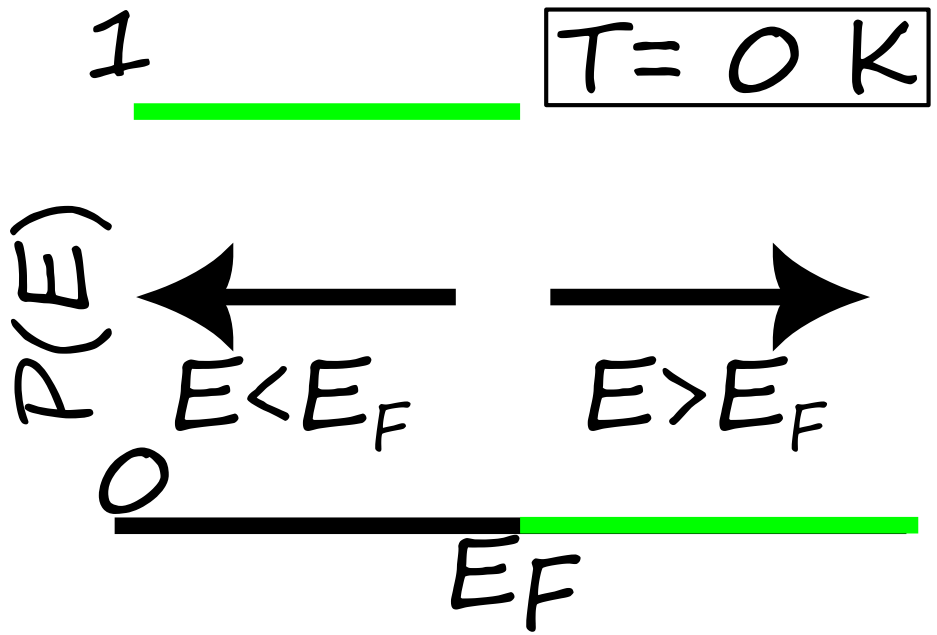
- Since $\frac{0}{0}$ is indeterminate form, $P_{FD}(E)$ is not defined at $T = 0\,\text{K}, E = E_F$.

Fermi–Dirac Statistics at the $T \to 0$ limit

- Hence, at $T = 0\,\mathrm{K}$ the distribution becomes a step function

$$P_{FD}(E) = \begin{cases} 1, & E < E_F \\ 0, & E > E_F \end{cases}$$

where E_F is the Fermi energy.



Key Insight

At $T = 0\,\mathrm{K}$, the Fermi-Dirac distribution is a step function.

Fermi–Dirac Statistics at $T \neq 0$

- At $T \neq 0$, consider $k_B T$ is a small positive quantity +ve.

$$P_{FD}(E) = \frac{1}{\exp\left(\frac{E - E_F}{+\text{ve}}\right) + 1}.$$

- This limit needs to analyzed for three cases –[1]
  1. $E \ll E_F$ so that $E - E_F$ is a big negative number i.e. --ve
  2. $E \gg E_F$ so that $E - E_F$ is a big positive number i.e. ++ve
  3. $E = E_F$

[1] $\gg$ is symbol for very greater than and $\ll$ is symbol for very lesser than

Fermi–Dirac Statistics at $T \neq 0$

1. $E \ll E_F$ [a]

$$P_{FD}(E) = \frac{1}{\exp\left(\frac{\text{--ve}}{+ve}\right) + 1}$$
$$\simeq \frac{1}{\exp(-\infty) + 1}$$
$$= \frac{1}{0 + 1}$$
$$= \frac{1}{1}$$
$$= 1$$

$\therefore P_{FD}(E) \simeq 1$

2. $E \gg E_F$

$$P_{FD}(E) = \frac{1}{\exp\left(\frac{\text{++ve}}{+ve}\right) + 1}$$
$$\simeq \frac{1}{\exp(\infty) + 1}$$
$$= \frac{1}{\infty + 1}$$
$$= \frac{1}{\infty}$$
$$= 0$$

$\therefore P_{FD}(E) \simeq 0$

3. $E = E_F$

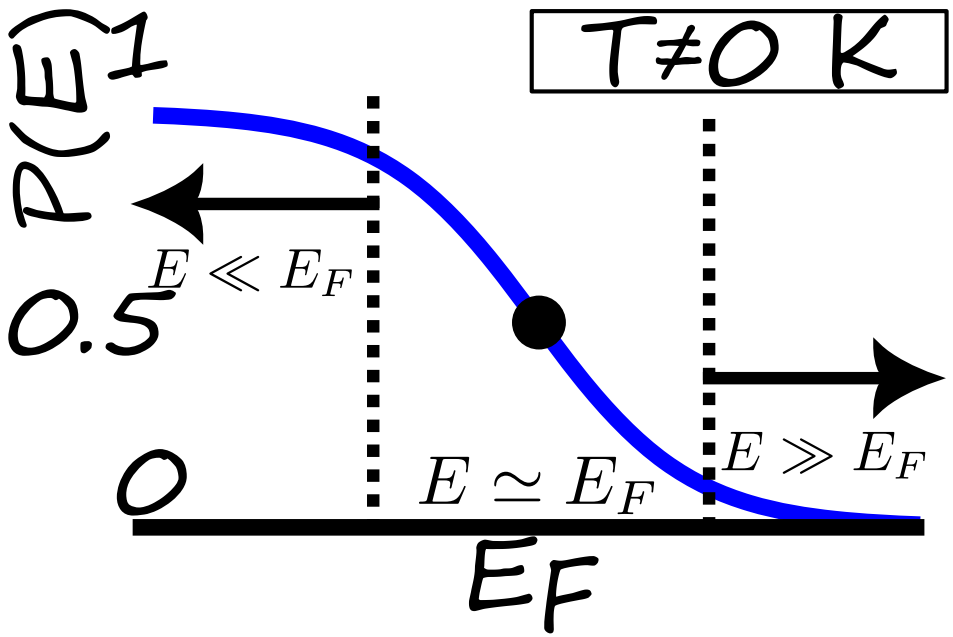
$$P_{FD}(E) = \frac{1}{\exp\left(\frac{0}{+ve}\right) + 1}$$
$$= \frac{1}{1 + 1}$$
$$= \frac{1}{2}$$

[a] $\simeq$ is symbol for nearly equal

Fermi–Dirac Statistics at $T \neq 0$

- Hence, at $T \neq 0\,\mathrm{K}$ the distribution becomes a "smeared" [2] step function

$$P_{FD}(E) = \begin{cases} \simeq 1 & E \ll E_F \\ \simeq 0 & E \gg E_F \end{cases}$$



Key Insight

At $T = 0\,\mathrm{K}$, the Fermi-Dirac distribution is a "smeared" step function.

[2] smear means smoothened.

Problems on Fermi Dirac statistics

Problem

Calculate the probability that an energy level $3k_BT$ above the Fermi energy is occupied by an electron

Problem

Calculate the probability that an energy level $3k_BT$ below the Fermi level is empty

Problem

Fermi energy of a metal is $6.25\,\mathrm{eV}$. *Calculate the temperature at which there is a* $1\,\%$ *probability that a state* $0.30\,\mathrm{eV}$ *below the Fermi energy level will not contain an electron.*

Problem

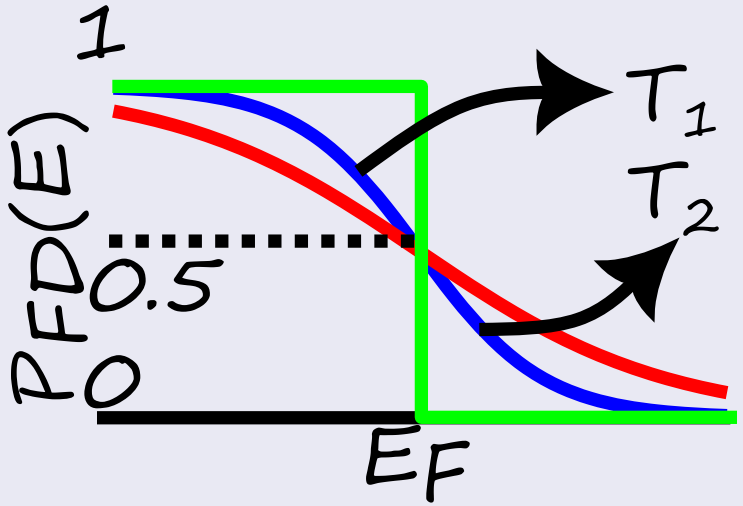
Calculate the temperature at which the probability that an energy level $0.3\,\mathrm{eV}$ *below the Fermi level is occupied is 0.7.*

Problems on Fermi Dirac statistics

Problem

Calculate the temperature at which the probability that an energy level $3k_BT$ above the Fermi level is occupied is 0.7. [Hint: This is a wrong question]

Problem



Statement: $T_1 > T_2$.

Is the statement true or false?

Boltzmann approximation to Fermi Dirac distribution

- In the limit of $E - E_F \gg k_B T$,

$$P_{FD}(E) \simeq \exp\left[-\frac{E - E_F}{k_B T}\right]$$

- This is called the Boltzmann approximation

Problem

Calculate the energy at which the difference between Boltzmann approximation and the Fermi-Dirac function is 5 % of the Fermi function.

M2U1 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

Specific heat capacity

Definition

- Specific heat capacity [a] C is defined as the rate of change of energy E with temperature T per unit mole of material.

$$C = \frac{\mathrm{d}E}{\mathrm{d}T} \qquad \text{SI unit} \quad [C] = \left[\frac{E}{T} \cdot \frac{1}{\text{mole}}\right] = \mathrm{J\,K^{-1}\,mol^{-1}}.$$

[a] It is also called simply as specific heat.

- Metals heat "quickly". When we heat a metal, the heat energy is transferred to electrons. The quickness is measured in terms of heat capacity.

Problem

Specific heat of mercury is $0.14\,\mathrm{J\,g^{-1}\,K^{-1}}$, *water is* $1\,\mathrm{cal\,g^{-1}\,^{\circ}C^{-1}}$, *ethanol is* $2.44\,\mathrm{J\,g^{-1}\,^{\circ}C^{-1}}$. *Which has more specific heat? Which better material for thermometer?* [${}^{200}_{80}Hg$, 1 cal=4.2 J, *ethanol* = CH_3CH_2OH]

Specific heat capacity – CFET

- Energy of electron at temperature T is $E_{\mathrm{el}} = \frac{3}{2} k_B T$.
- Energy of a mole of electrons is

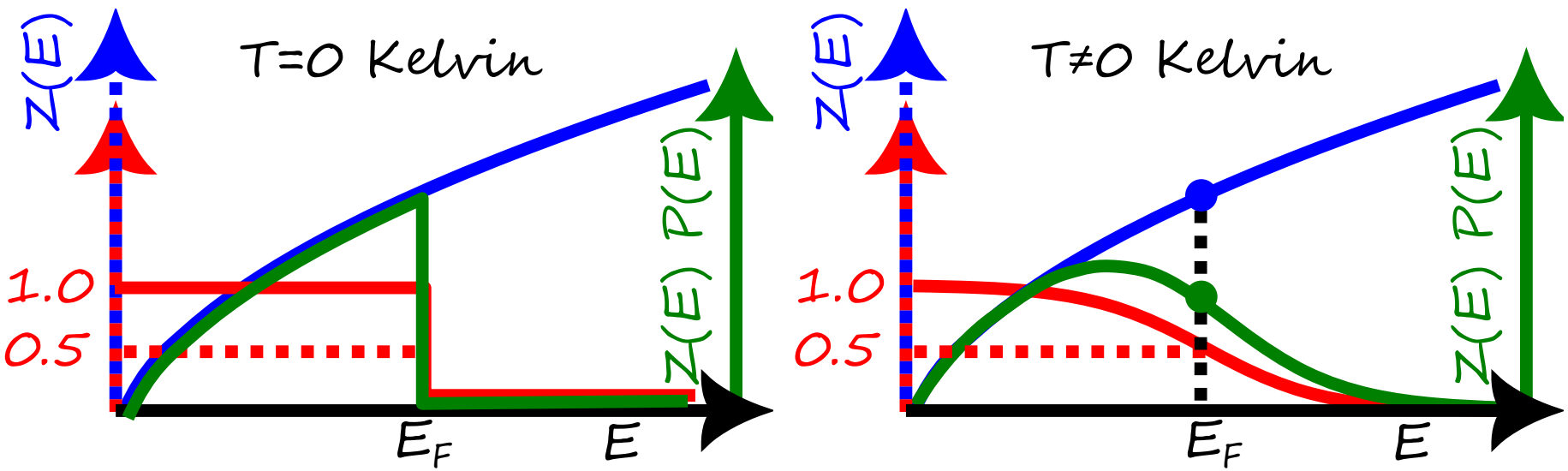
$$E = E_{\mathrm{el}} N_A = \frac{3}{2} k_B N_A T = \frac{3}{2} RT. \qquad \left[R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}\right]$$

- Therefore, specific heat capacity is

$$C_{\mathrm{theory}}^{\mathrm{classical}} = \frac{\mathrm{d}E}{\mathrm{d}T} = \frac{3}{2} R \sim 12\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

- But experimental values of specific heat capacity $C_{\mathrm{experiment}}$ are **smaller by two orders** of magnitude.

Specific heat capacity – QFET



- For the derivation of specific heat capacity, only the **form** of density of states functions is necessary and not the exact expression. For 3D metal, $Z(E) \propto \sqrt{E}$ so that

$$Z(E) = \alpha\sqrt{E}, \qquad \text{where } \alpha \text{ is a constant}$$

Specific heat capacity – Form of $Z(E)$

- At $T = 0\,\mathrm{K}$, electron has energy less than or equal to Fermi energy level.
- The number of electrons per unit volume n_c at $T = 0\,\mathrm{K}$ is given by

$$
\begin{aligned}
n_c &= \int_0^{E_F} Z(E)P(E)\,\mathrm{d}E \\
&= \int_0^{E_F} Z(E)\,\mathrm{d}E \\
&= \int_0^{E_F} \alpha\sqrt{E}\,\mathrm{d}E \\
&= \frac{2}{3}\alpha E_F^{3/2}
\end{aligned}
$$

$$
\boxed{\therefore n_c = \tfrac{2}{3}\alpha E_F^{3/2}.}
$$

Specific heat capacity – Conduction electron density n_c

- At $T \neq 0\,\mathrm{K}$, due to thermalization, some of the electrons vacate the lower energy levels and occupy the higher energy levels.
- The number of electrons per unit volume n_c at $T \neq 0\,\mathrm{K}$ is given by

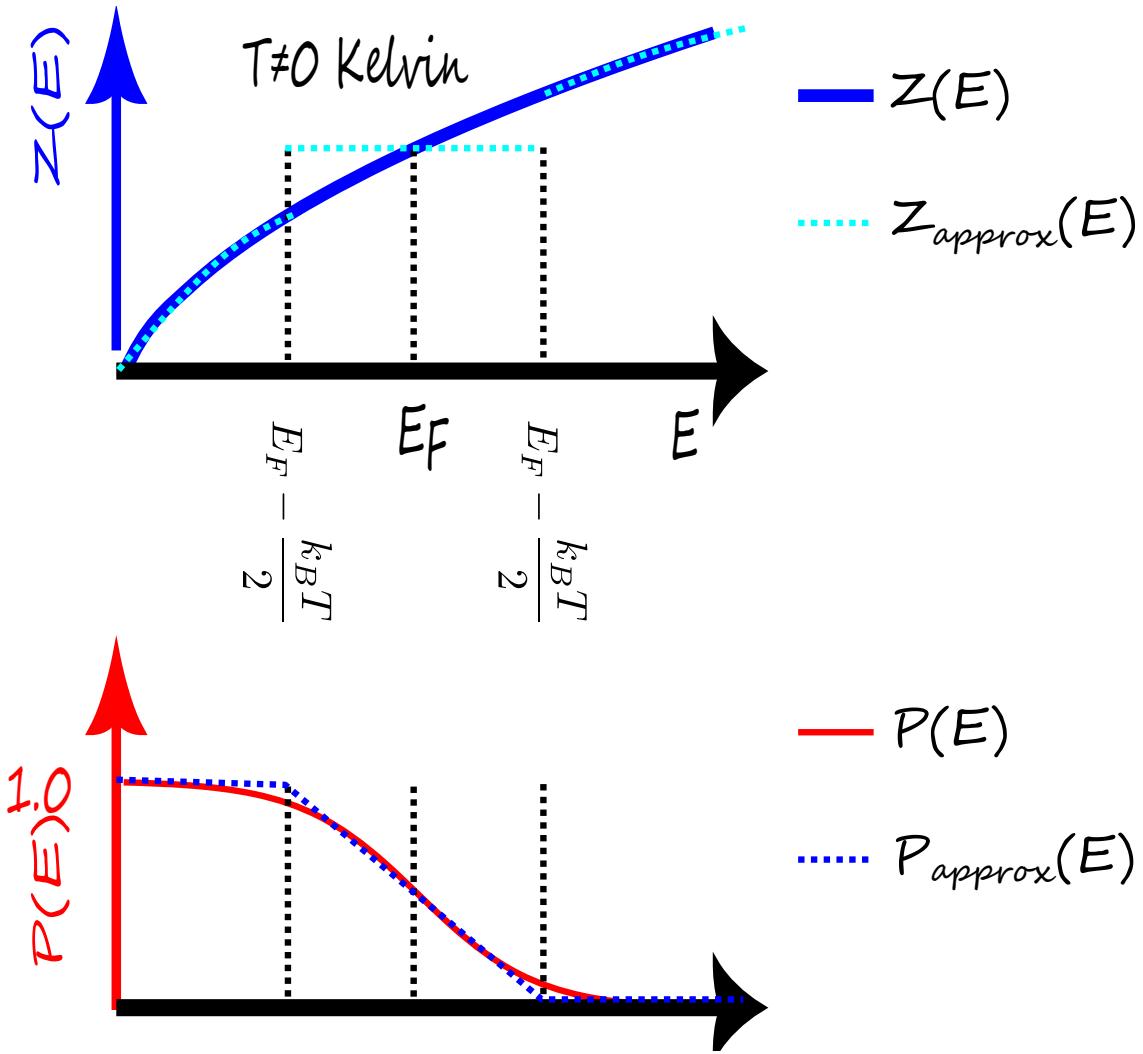
$$n_c = \int_0^\infty Z(E)P(E)\,\mathrm{d}E$$
$$= \int_0^\infty \frac{\alpha\sqrt{E}}{\exp\left(\frac{E-E_F}{k_B T}\right)+1}\,\mathrm{d}E$$

  Note that integration limits are 0 to ∞!
- We observe that because of the strong variation of Fermi Dirac distribution only near the Fermi level, the electron with energy belonging to range $E_F - \frac{k_B T}{2}$ to E_F jumps to energy in the range E_F to $E_F + \frac{k_B T}{2}$. Let us use this to **approximate** the integral.

Key Insight

Electrons with energy very much less than Fermi energy level do not participate in the thermalization process.

Specific heat capacity – Approximations to $Z(E), P(E)$

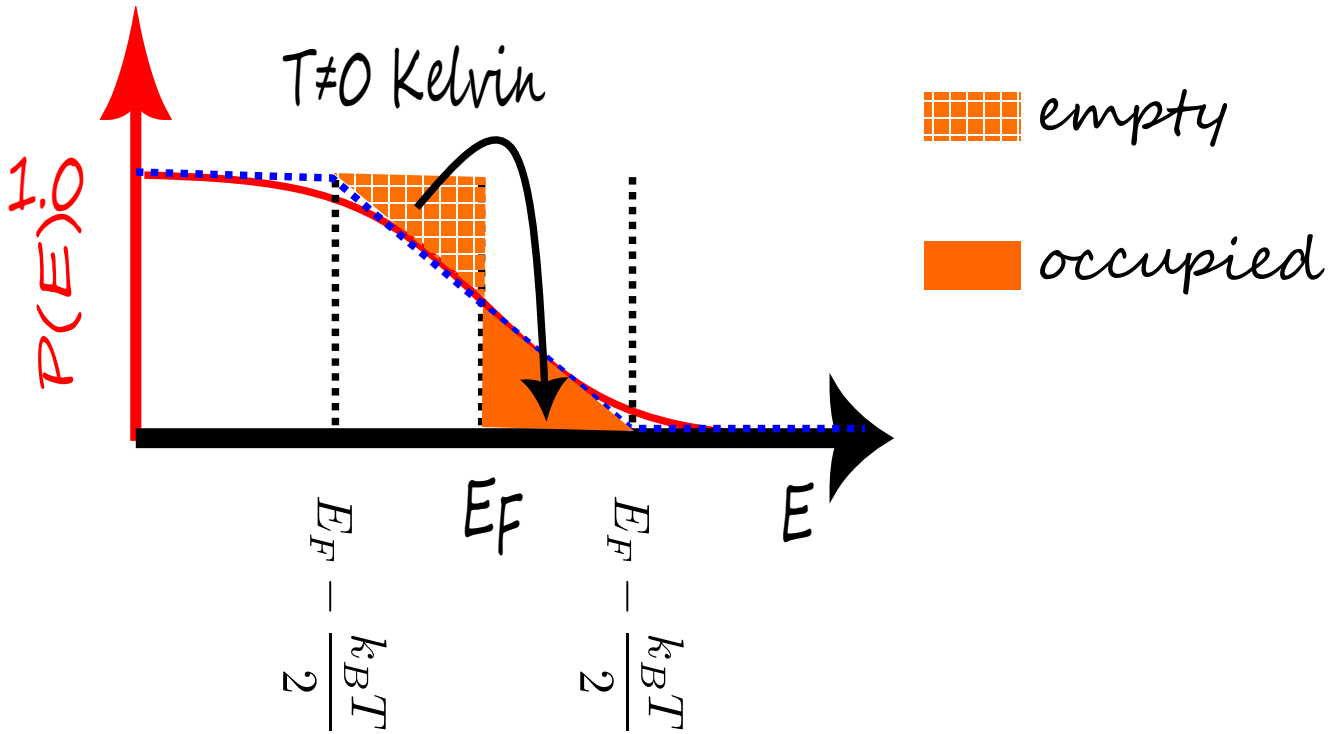


- Let us approximate the density of states in the neighbourhood of E_F as

$$Z(E) \simeq Z(E_F)$$

- Let us approximate probability distribution as piece-wise straight line function.

Specific heat capacity – Fraction of thermalized electrons



- The number of thermalized electrons is equal to area of the filled triangle multiplied by the density of states in the neighbourhood.
- Area of the filled triangle is

$$A = \frac{1}{2}\frac{k_B T}{2}\frac{1}{2} = \frac{1}{8}k_B T$$

$$\therefore n_{\text{thermal}} = \frac{1}{8}k_B T \cdot Z(E_F) = \frac{1}{8}\alpha k_B T\sqrt{E}$$

Specific heat capacity – Fraction of thermalized electrons

- The fraction of thermalized electrons is given by ratio of thermalized electrons to total electrons

$$\begin{aligned} f_{\text{thermalized}} &= \frac{n_{\text{thermal}}}{n_c} \\ &= \frac{1}{8} k_B T \frac{\alpha\sqrt{E}}{\frac{2}{3}\alpha E_F^{3/2}} \\ &= \frac{3}{16} \frac{k_B T}{E_F} \end{aligned}$$

Problem

The Fermi level of silver is 5.5 eV*. Calculate the fraction of free electrons at room temperature.*

Key Insight

The fraction of thermalized electrons is of the order of $\frac{k_B T}{E_F}$.

Specific heat capacity – Energy of thermalized electron

- The net increase in energy of thermalized electron is

$$\Delta E_{\text{thermalized}} = E_F + \frac{k_B T}{2} - \left(E_F - \frac{k_B T}{2} \right) = k_B T$$

- Since only a fraction of the electrons are thermalized, the net increase in energy of 1 electron is

$$\begin{aligned} \Delta E_{1\text{ el}} &= \Delta E_{\text{thermalized}} \cdot f_{\text{thermalized}} \\ &= \frac{3}{16} k_B T \cdot \frac{k_B T}{E_F} \end{aligned}$$

- Therefore, the net increase in energy of 1 mole of electrons is

$$\begin{aligned} \Delta E_{1\text{ mole}} &= \Delta E_{1\text{ el}} \cdot N_A \\ &= \frac{3}{16} (k_B N_A) T \cdot \frac{k_B T}{E_F} \\ &= \frac{3}{16} R \frac{k_B T^2}{E_F} \end{aligned}$$

Specific heat capacity – Electronic contribution

- The specific heat capacity is given by

$$\begin{aligned} C_{\text{theory}}^{\text{quantum}} &= \frac{\mathrm{d}E_{1\ \text{el}}}{\mathrm{d}T} \\ &= \frac{3}{8}R\frac{k_B T}{E_F} \\ &= \frac{3}{2}R \cdot \left(\frac{1}{4}\frac{k_B T}{E_F}\right) \\ &= C_{\text{theory}}^{\text{classical}} \cdot \left(\frac{1}{4}\frac{k_B T}{E_F}\right) \end{aligned}$$

$$\therefore C_{\text{theory}}^{\text{quantum}} \simeq \left(\frac{k_B T}{E_F}\right) \cdot C_{\text{theory}}^{\text{classical}}.$$

- Therefore, quantum theory corrects the classical expression by the fraction $\frac{k_B T}{E_F}$. At room temperature, specific heat capacity is given by

$$C_{\text{theory}}^{\text{quantum}} = C_{\text{theory}}^{\text{classical}} \cdot \frac{k_B T_{300\,\text{K}}}{E_F} \simeq 0.01\, C_{\text{theory}}^{\text{classical}} \simeq C_{\text{experiment}}$$

This validates Quantum Free Electron Theory.

Specific heat capacity – Phonon contribution

- Electronic contribution to specific heat at low T is **linear**.
- In addition to electrons, phonons i.e. quanta of lattice vibrations also contribute to specific heat capacity C_{phonon}.
- The contribution from phonons has cubic form.

$$\begin{aligned} \therefore C_{\text{theory}}^{\text{quantum}} &= C_{\text{electron}} + C_{\text{phonon}} \\ &= AT + BT^3 \end{aligned}$$

Key Insight

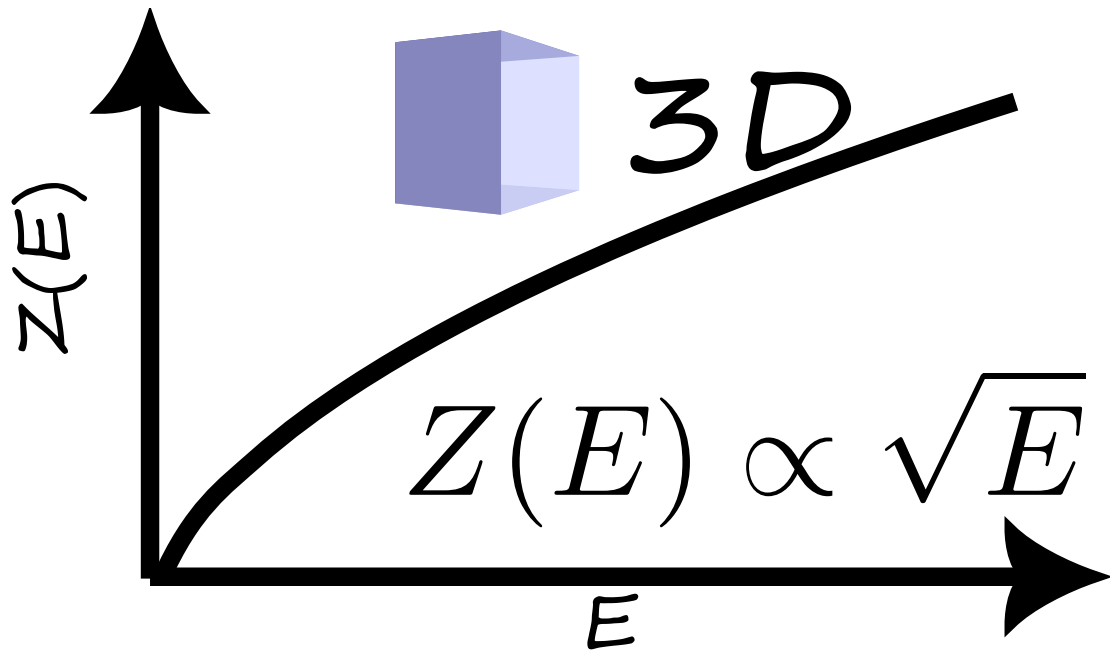
Phonon contribution is significant compared to electronic contribution to the specific heat capacity of metals.

M2U1 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

Density of states (3D)

- The form of the DOS in 3D is $Z(E) \propto \sqrt{E}$

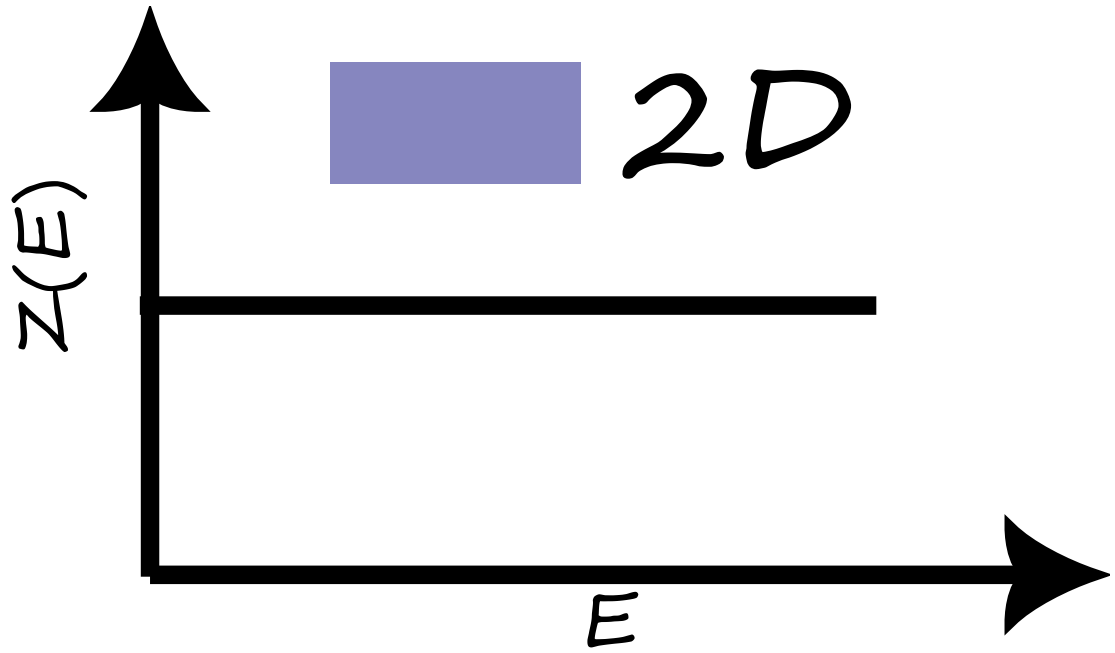


Problem

If $Z_{3D}(E) = k\sqrt{E}$, where k is a constant, find the expression for conduction electron number density n_c in terms of Fermi level E_F at $T = 0\,\mathrm{K}$ in a 3D material.

Density of states (2D)

- The form of the DOS in 2D is $Z(E) = \text{const}$



Problem

If $Z_{2D}(E) = k$, where k is a constant, find the expression for conduction electron number density n_c in terms of Fermi level E_F at $T = 0\,\mathrm{K}$ in a 2D material.

M2U1 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

Merits and demerits of QFET

Merits

- Electrical conductivity
- Thermal conductivity
- Heat capacity

Demerits

- Cannot explain classification of condensed matter into metals, semiconductors and insulators
- Occurence of positive Hall coefficient in some metals like Zn.

M2U1 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

$E - k$ diagram – 1D case

- In a 1D metal, the electron is free as well as independent.
- For a free electron, the energy is related to the momentum p by

$$E = \frac{p^2}{2m}.$$

- However, since the electron behaves also as a wave, its wavelength λ is related to the momentum by the de Broglie relation

$$\lambda = \frac{h}{p} \quad \Rightarrow \quad p = \frac{h}{\lambda}.$$

- By definition, the wavevector k of the electron is inversely related to the wavelength as

$$k = \frac{2\pi}{\lambda}$$

- Therefore, the energy is related to the wavevector by

$$E = \frac{1}{2m}\left(\frac{h}{\lambda}\right)^2 = \frac{1}{2m}\left(\frac{hk}{2\pi}\right)^2 = \frac{\hbar^2 k^2}{2m}.$$

$E - k$ diagram – 3D case

- The analysis for 1D case can be extended to the 3D case by considering the components of momentum p_x, p_y, p_z

$$\vec{p} = p_x \hat{i} + p_y \hat{j} + p_z \hat{k}$$

so that

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m}.$$

- The wavevector has three components k_x, k_y, k_z so that

$$\vec{k} = k_x \hat{i} + k_y \hat{j} + k_z \hat{k}.$$

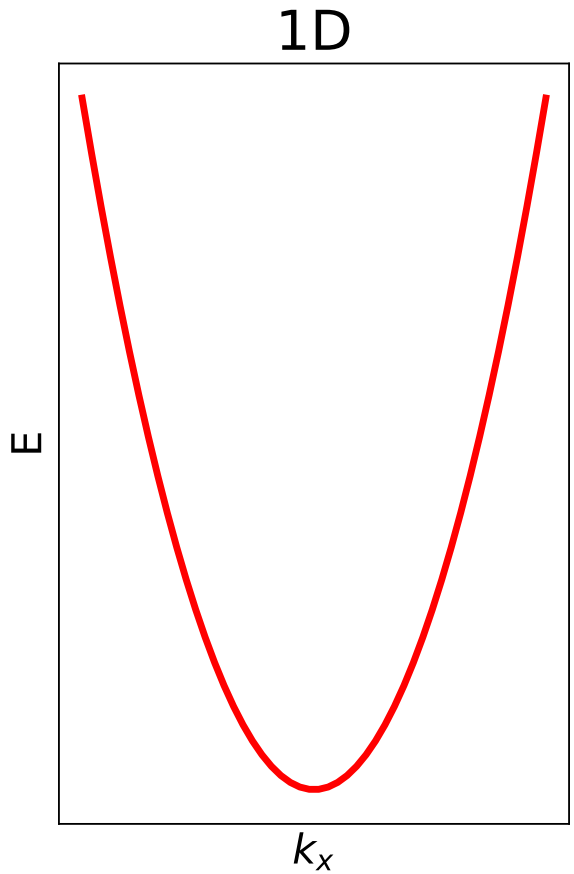
- The energy of the free electron is given by

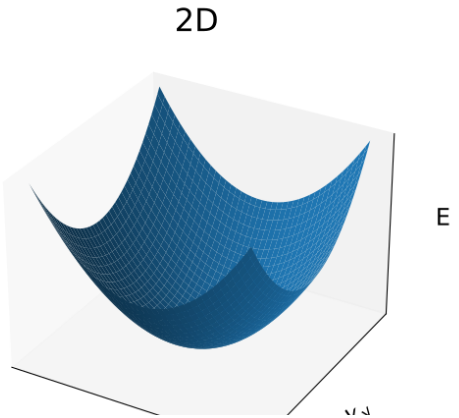
$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$

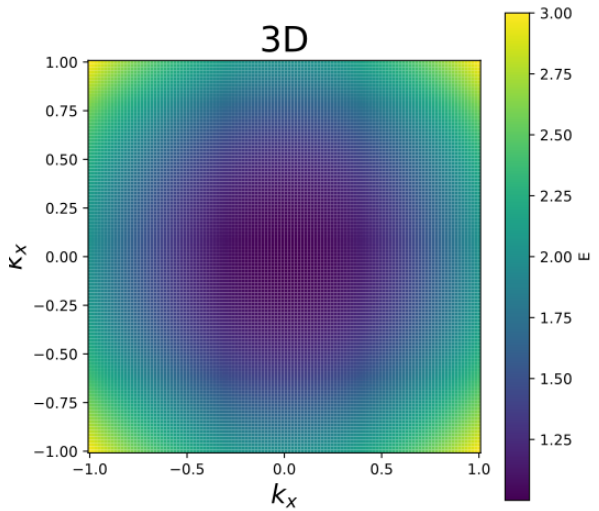
Problem

Fermi wavector k_F If the Fermi energy is $E_F = 5\,\mathrm{eV}$, find the Fermi wavevector.

Form of $E - k$ diagram – 1D, 2D, 3D







Key Insight

Form of $E - k$ is parabolic.

Summary of Quantum free electron theory (QFET)

- Derived density of states function $Z(E)$.
- Quantum free electron theory addressed the electronic contribution to specific heat of metals
- However, the theory has drawbacks. Some of them are
  - Cannot explain anomalous sign of Hall coefficient in some metals.
  - Cannot explain classification of materials into conductors. semi-conductors and insulators.

Reason for drawbacks

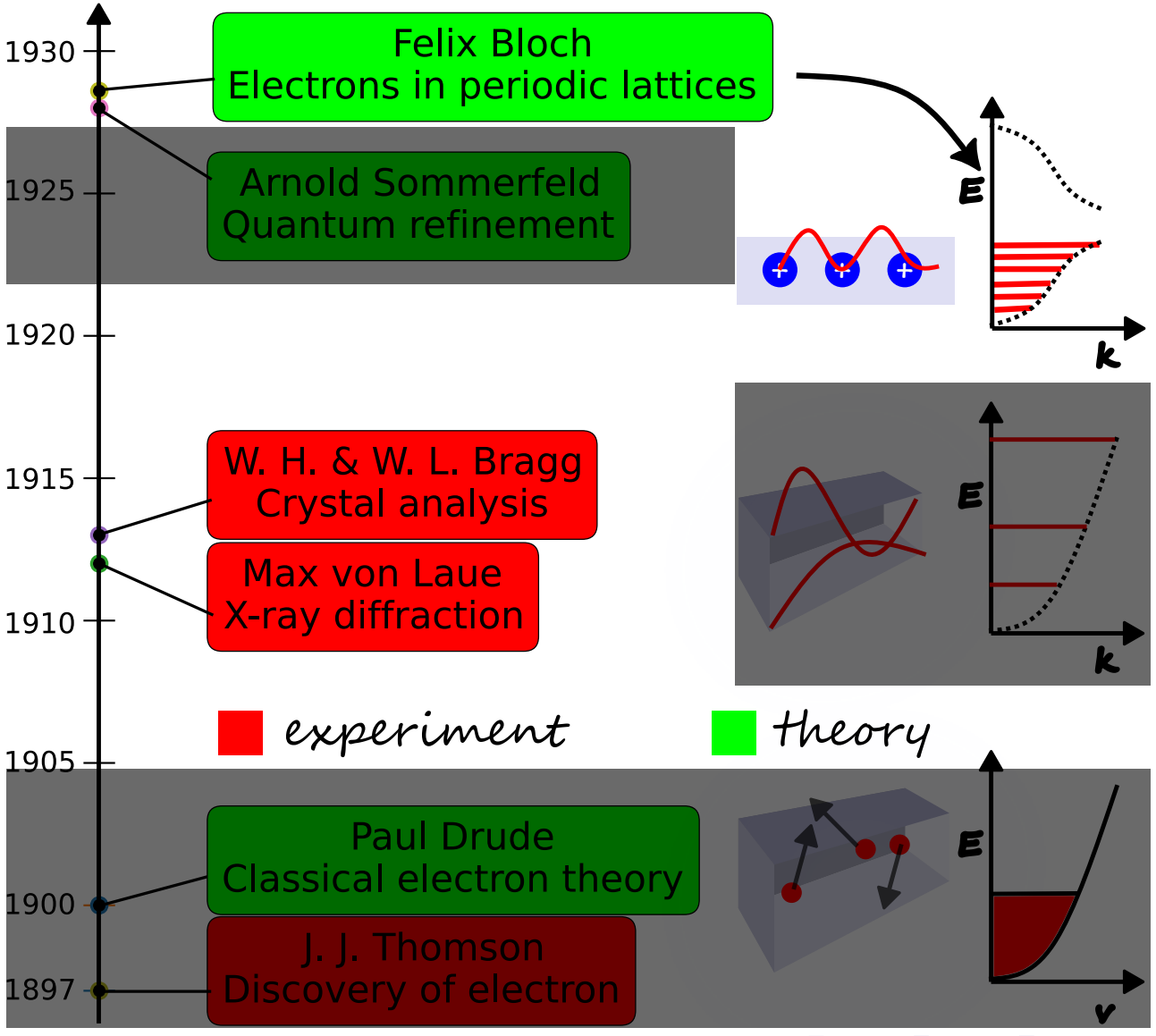
- Invalidity of free electron approximation.
- Drawbacks addressed by Bloch's quantum band theory.

M2U1 Plan

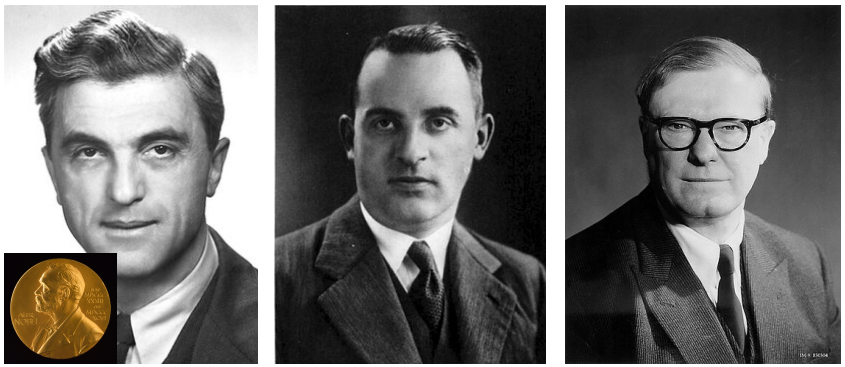
1. Quantum Free Electron Theory
2. Fermi-Dirac distribution
3. Electronic specific heat of solids
4. Density of states (qualitative)
5. Success and Failures of quantum free electron theory of solids
6. E-k diagram
7. Classification of materials based on bands in solids
8. Fermi level in semiconductors-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

Electron theories of metals

1. Classical free electron theory
2. Quantum free electron theory
3. Quantum band theory (QBT)



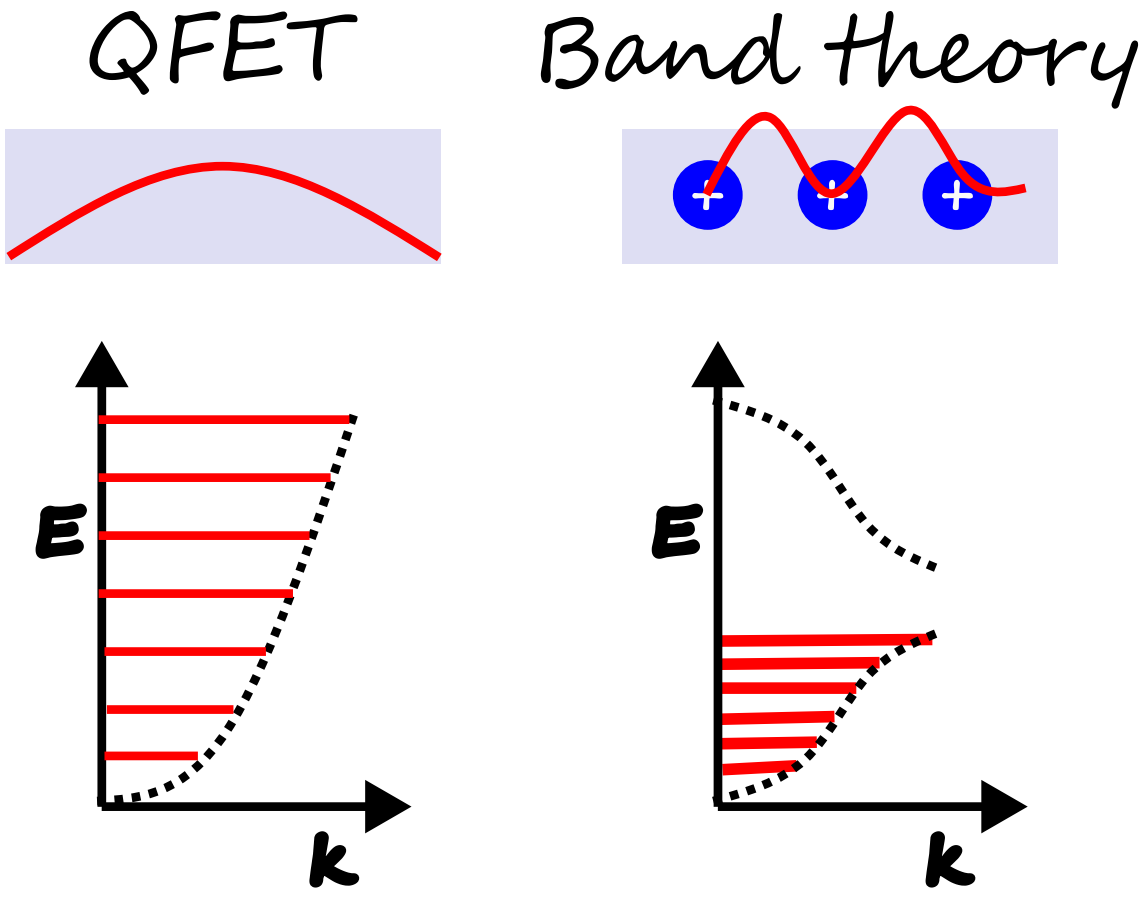
Quantum band theory (QBT)



F. Bloch, R. Kronig, W. Penney

- Proposed by Felix Bloch, Ralph Kronig, William Penney and co-workers in 1928 by extending QFET.
- Assumed "electron gas" is **not free** and is under the influence of lattice – **periodic potential approximation**.

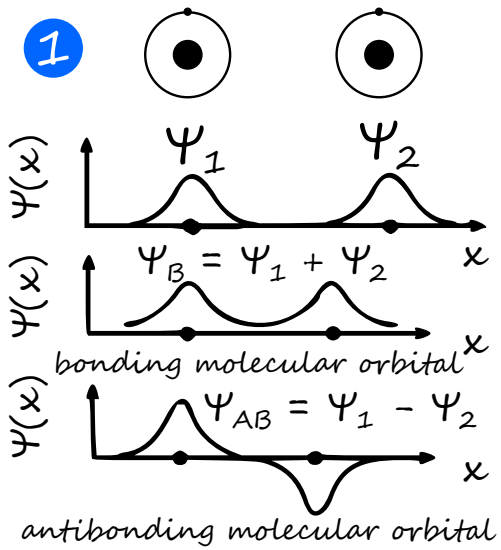
$V(x)$: QFET vs QBT

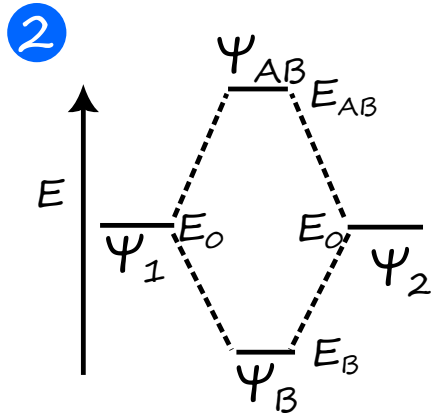


Key Insight

In Quantum band theory, the electron is **not** free!

Splitting of energy levels – Formation of H_2 molecule



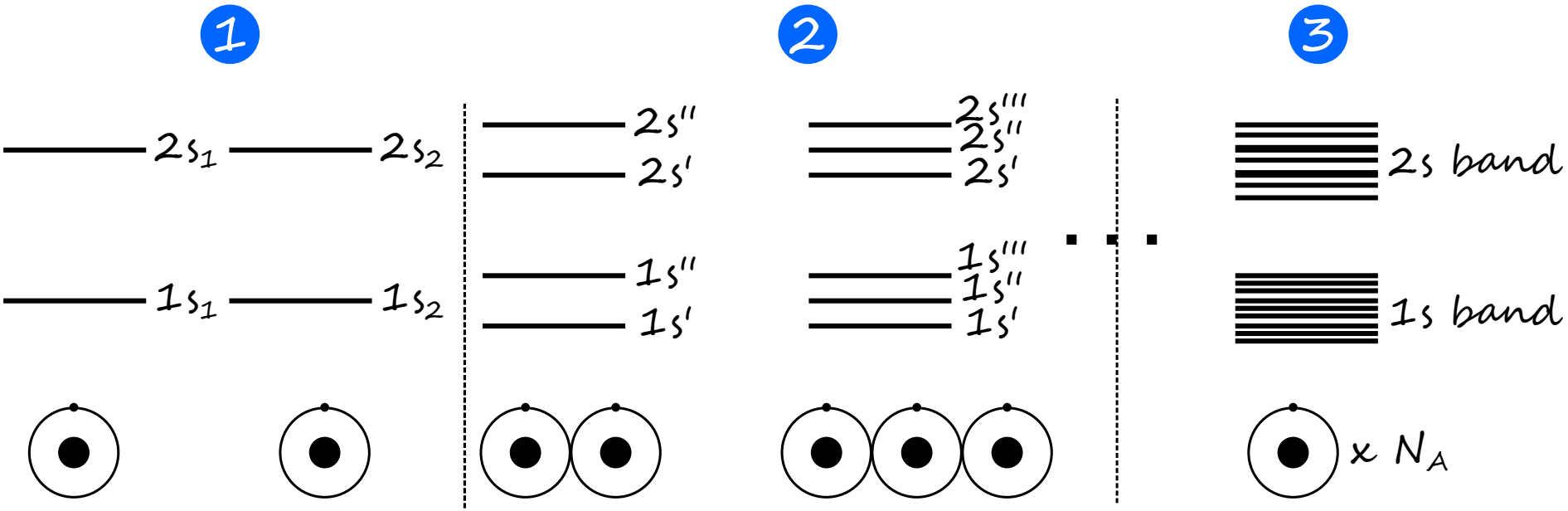


1. At large inter atomic distance, the wavefunction of electron in each H atom is 1 s. As the separation decreases, due to Pauli exclusion principle, the wavefunctions **hybridize** to form **bonding** and **anti-bonding** molecular orbitals.
2. The energy levels of individual H atoms **split** into bonding molecular orbital with lower energy and anti-bonding molecular orbital with higher energy.

Key Insight

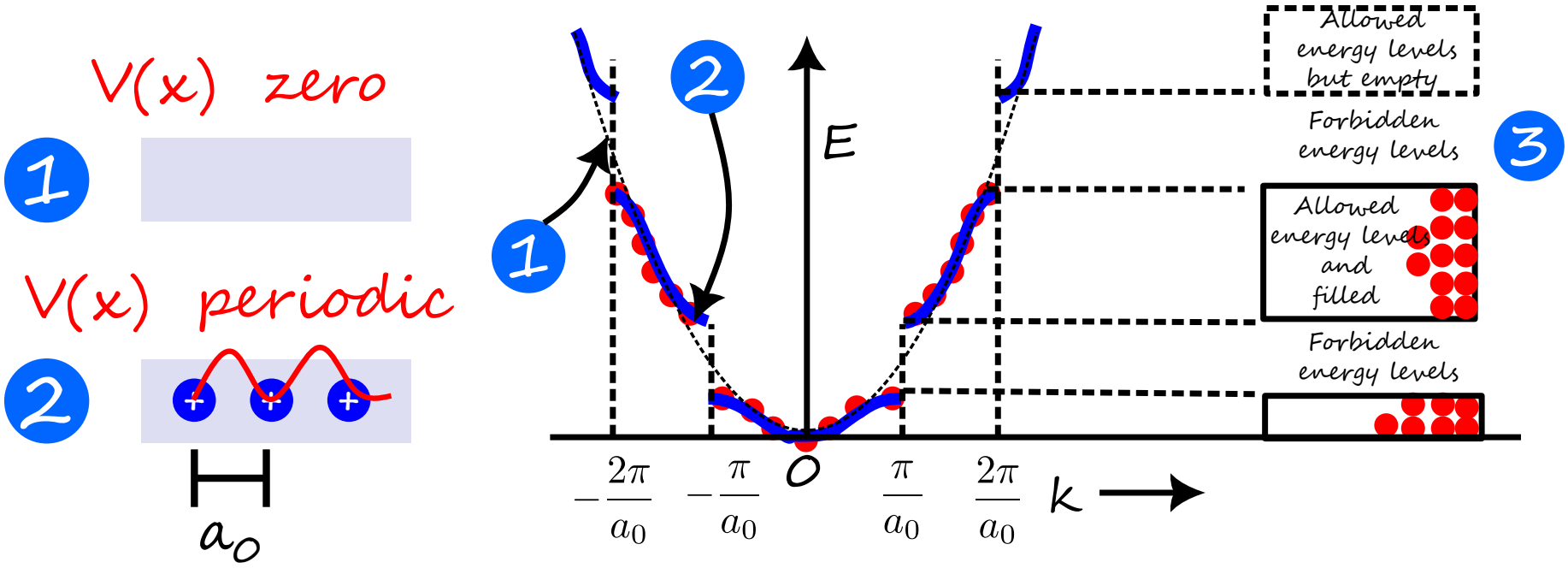
Splitting of energy levels is due to Pauli exclusion principle.

Band formation – discrete to continuous



1. At large interatomic separation, the energy levels of two H atom system match the energy levels of isolated H atom.
2. At the equilibrium separation, as the number of H atoms increase, there is splitting of energy levels.
3. For an Avagadro number of H atoms, the **discrete** energy levels group into a "band" of continuous energy levels.
   - The width of the band is called **energy bandwidth**.
   - The bandwidth is of the order of 1 e V.

Mapping of dispersion relation to band structure



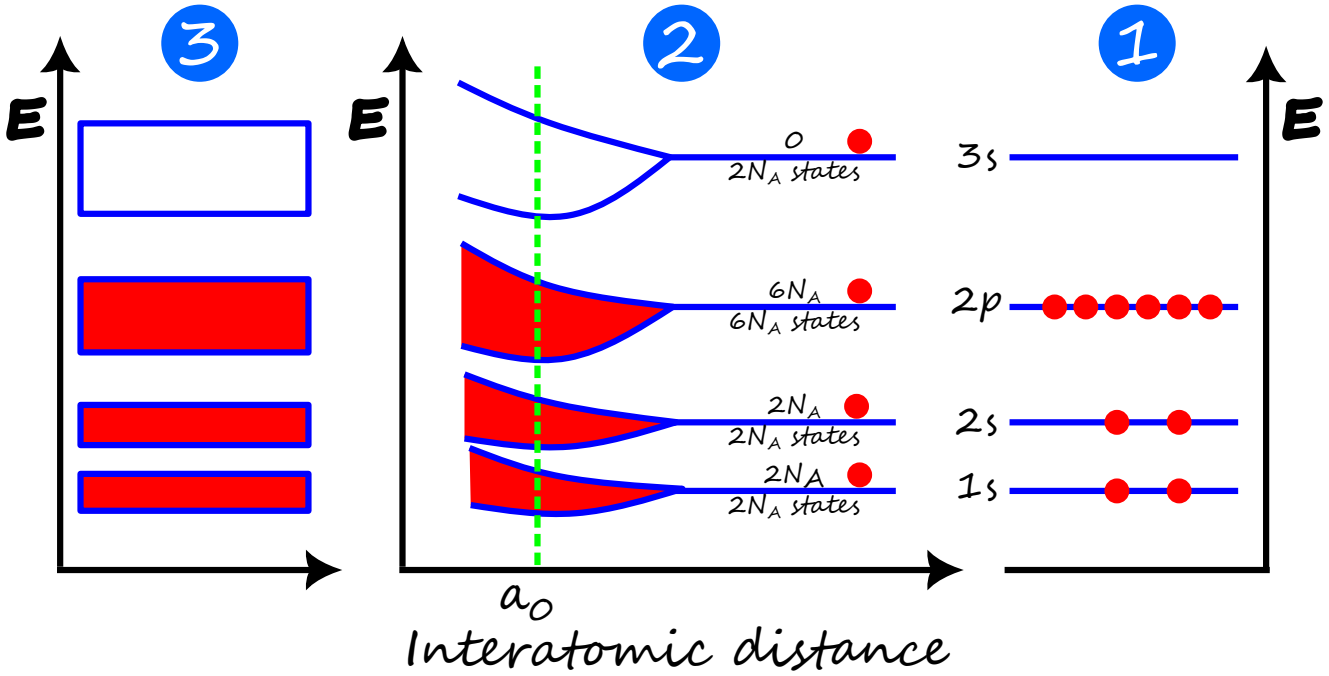
1. For a free electron, potential is zero and the dispersion relation E vs k has parabolic form.
2. For an electron in crystalline solid with lattice constant a_0, the potential is periodic and the E vs k **opens up** at specific values of $k = \pm\frac{\pi}{a_0}, \pm\frac{2\pi}{a_0}, \ldots$.
3. The mapping of energy levels leads to collection of **allowed** and **forbidden** bands.

Quantum Band theory – Postulates

Postulates

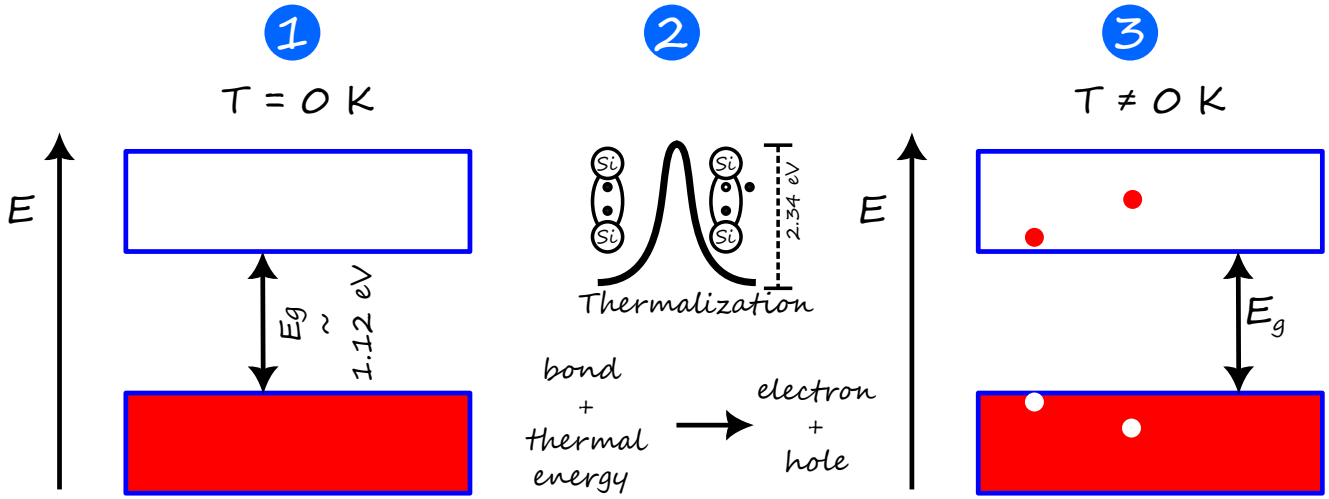
1. **Waves:** Electrons are quantum waves with wavevector k, angular frequency ω.
2. **Fermion:** Electron is a spin $\frac{1}{2}$ particle and obeys Pauli's exclusion principle.
3. **Independent electron approximation:** Electrons are independent and mutual repulsion between them is ignored.
4. **Periodic potential approximation:** Electrons move in a periodic potential.
5. **Quantum Thermodynamics:** The thermalization is governed by Fermi-Dirac statistics.

Energy band structure of Ne – gas to solid



1. Consider Avagadro number of Ne atoms at infinity – Ne gas. The energy levels are given by atomic energy levels
2. As the interatomic separation **decreases**, due to Pauli exclusion principle, band formation happens and bandwidths **increase**.
3. At equilibrium lattice constant a_0 – Ne solid, there are allowed and forbidden bands.

Energy band diagram



1. At $T = 0\,\mathrm{K}$,
   - The topmost occupied band is called **valence band**.
   - The lower most unoccupied is called **conduction band**.
   - These two bands are separated by a forbidden gap called the **energy band gap**.
2. When temperature is increased, the covalent bond is broken due to thermalization. This results in the formation of **electron-hole pair** [3].
3. At $T \neq 0\,\mathrm{K}$, the electron occupies energy level in the conduction band whereas the hole occupies energy level in the valence band.

[3] Hole is the absence of electron in the valence band.

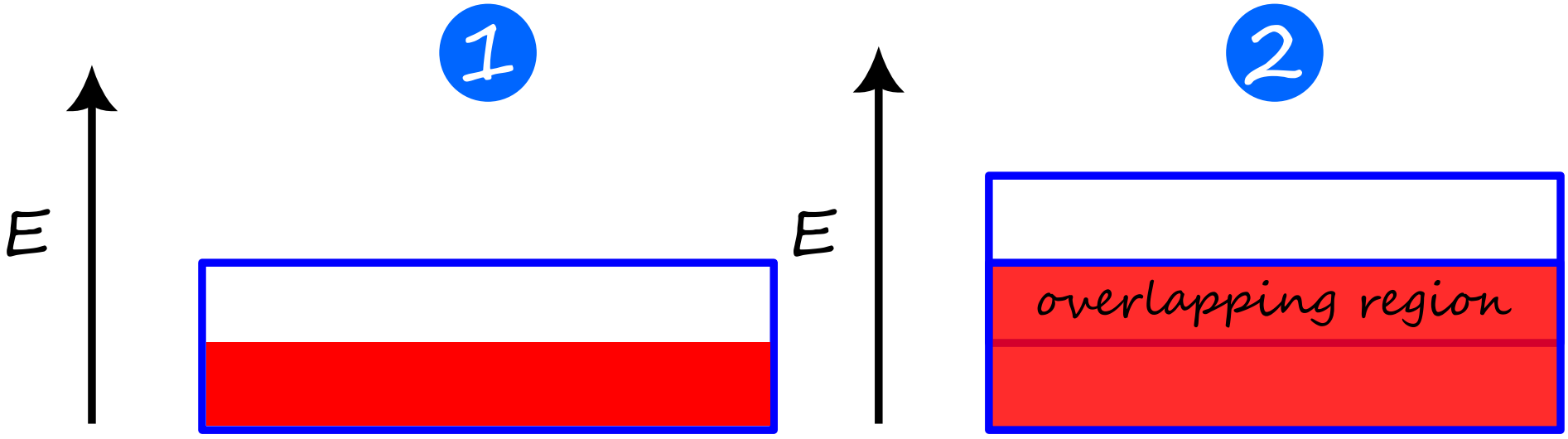
Classification of solids

- According to band theory, conductivity of solid is determined by the band gap separating the conduction band and valence band.
- Based on the band gap, the solids are classified into
  1. metals or conductors
  2. semiconductors
  3. insulators

Key Insight

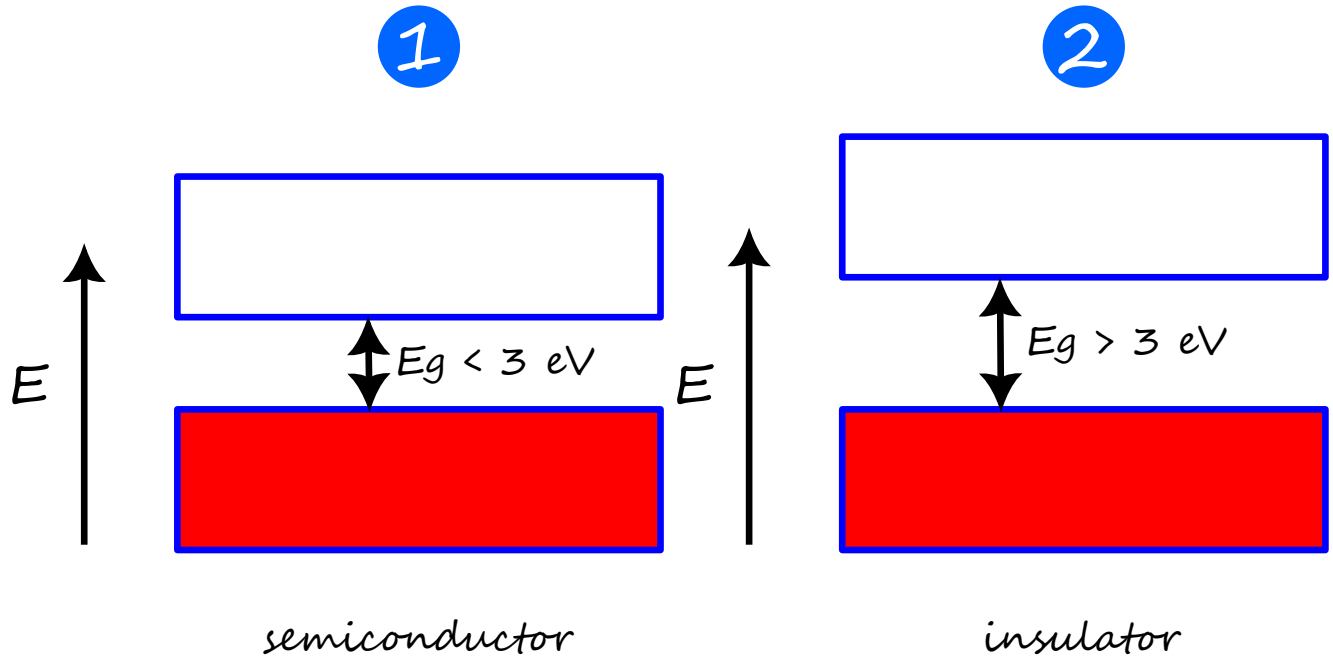
The classification of solids is based on energy band gap.

Energy band diagram – Conductor



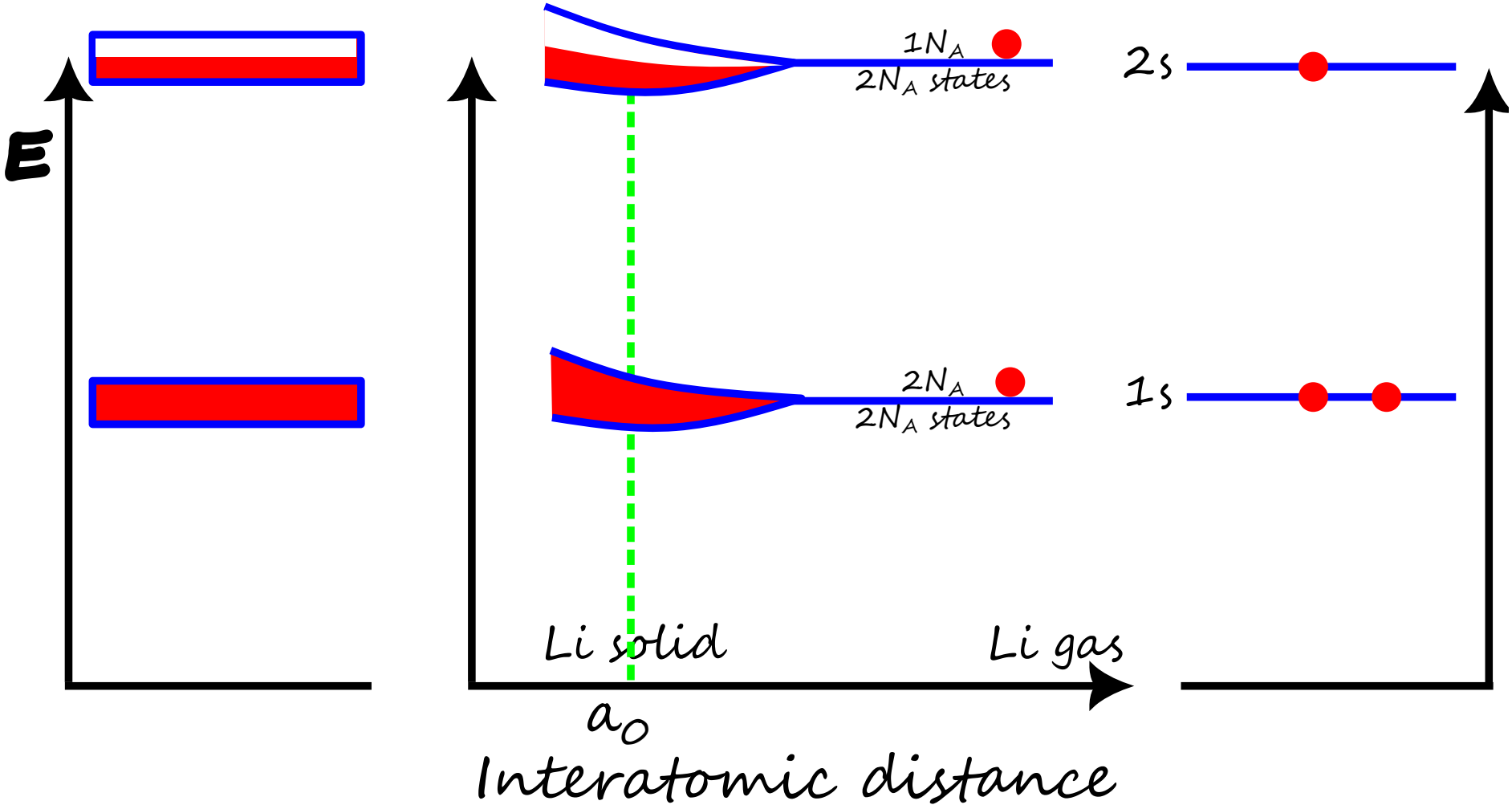
- In conductors, there are two cases
  1. the conduction band is half filled.
  2. the conduction band overlaps with empty upper band.
- In both cases, there is no band gap so that empty states are available for conduction.
- Since there is no band gap, there is no absence of electron at $T \neq 0$. Therefore, there are no holes in conductors.

Energy band diagram – Semiconductor



- In either semiconductor or insulator, there is a band gap so that empty states are not available for conduction.
  1. The energy band gap is less than 3 e V for semiconductor.
  2. The energy band gap is greater than 3 e V for insulator

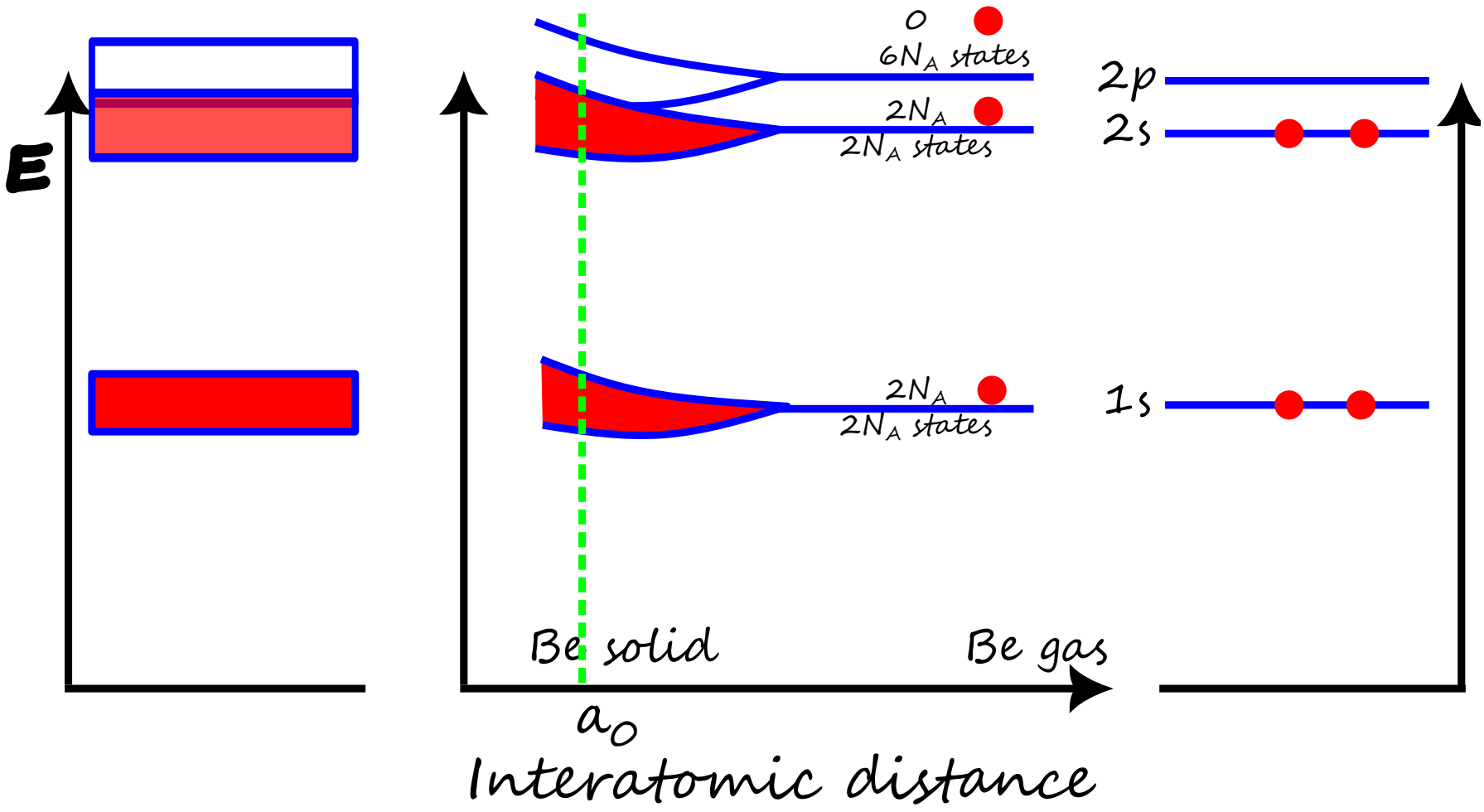
Energy band diagram of Li – half filled conduction band



Key Insight

The conduction band is only half filled for lithium.

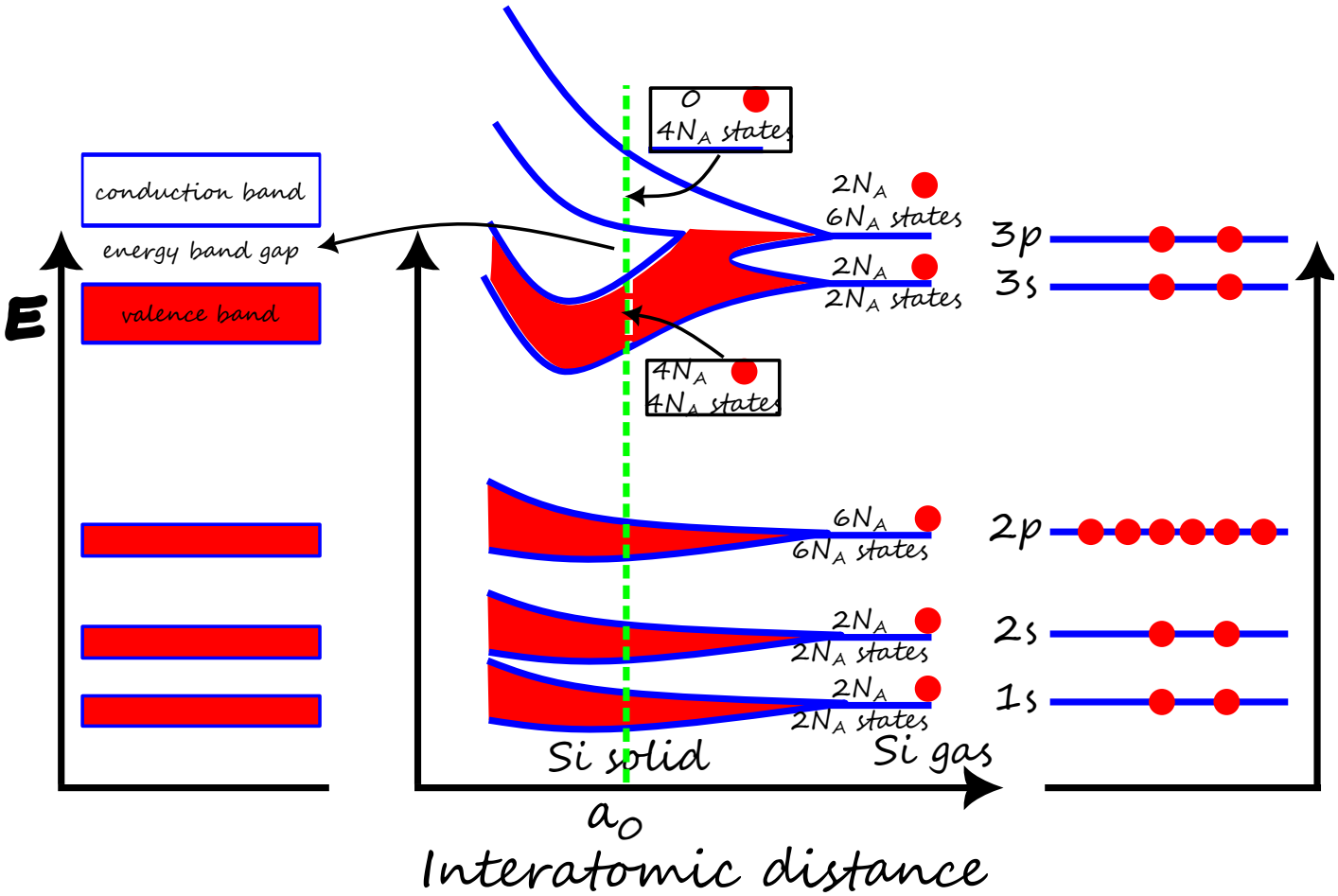
Energy band diagram of Be – overlapping conduction bands



Key Insight

The conduction band overlaps with next empty band for beryllium.

Energy band diagram – Si



Key Insight

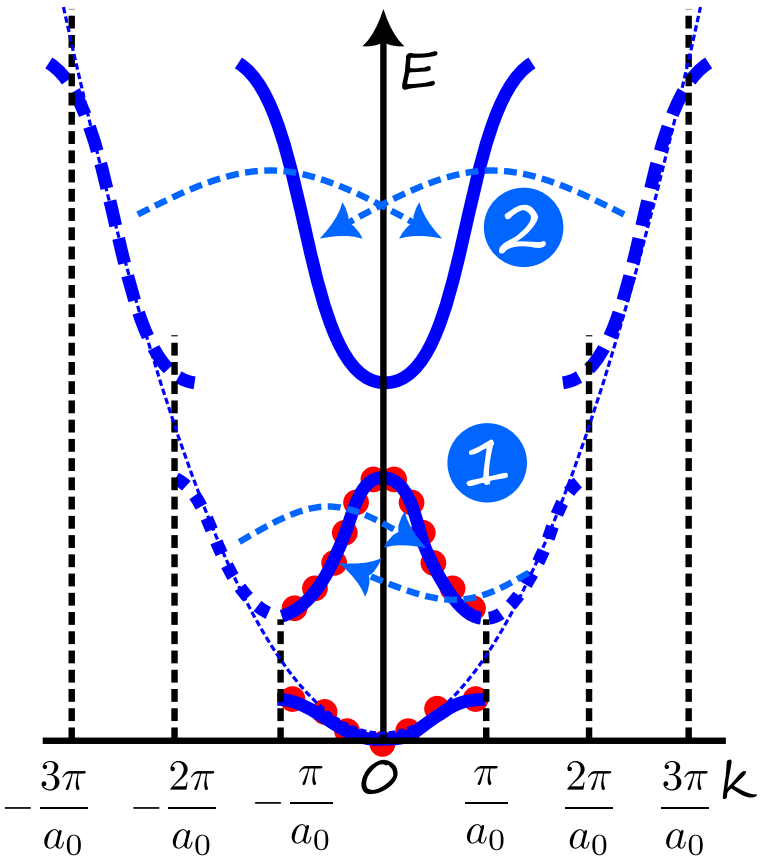
The valence band is completely filled and the conduction band is completely empty at $T = 0\,\mathrm{K}$.

M2U1 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

Intrinsic semiconductor

Reduced band dispersion – Band structure

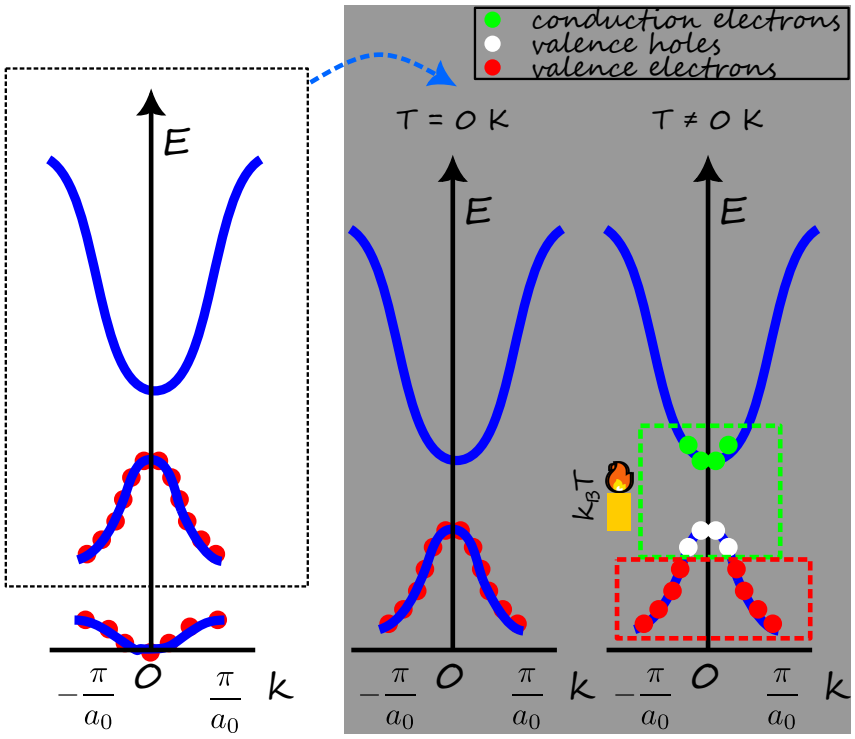


- Due to the periodicity of lattice, the band dispersion can be analyzed within the **zone** from $k = -\frac{\pi}{a_0}$ to $k = +\frac{\pi}{a_0}$.
- The original band dispersion can be reduced to the zone by folding the "arms" of the parabola resulting in the reduced band dispersion. This process is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

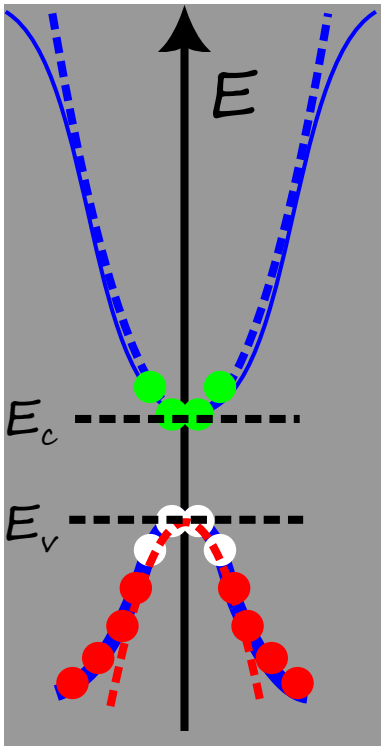


- For a semiconductor, due to the presence of energy band gap, there are no free electrons at $T = 0\,\mathrm{K}$.
- At $T \neq 0\,\mathrm{K}$, the electrons near the valence band maximum thermalize and jump to the levels near the conduction band minimum. This results in quantum vacancy in the valence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

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

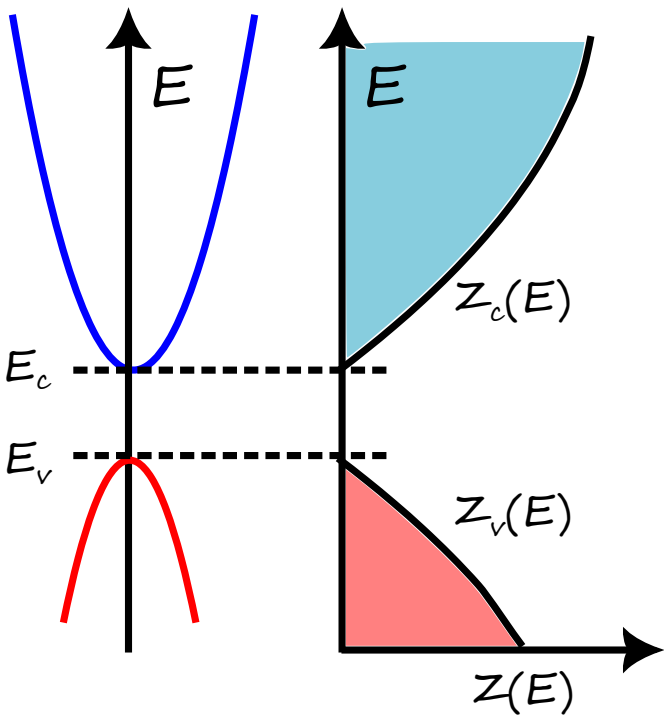
where m_n^* is the **effective electron mass** and E_c is the minimum of conduction band.

- 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

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

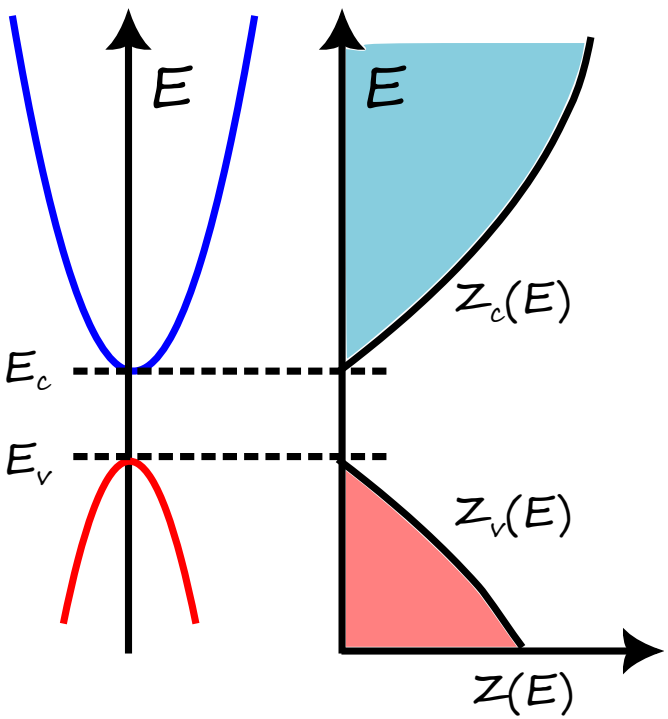
so that the form is similar to the free electron dispersion relation. Thus, the density of states in the conduction band $Z_c(E)$ is given by

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

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

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

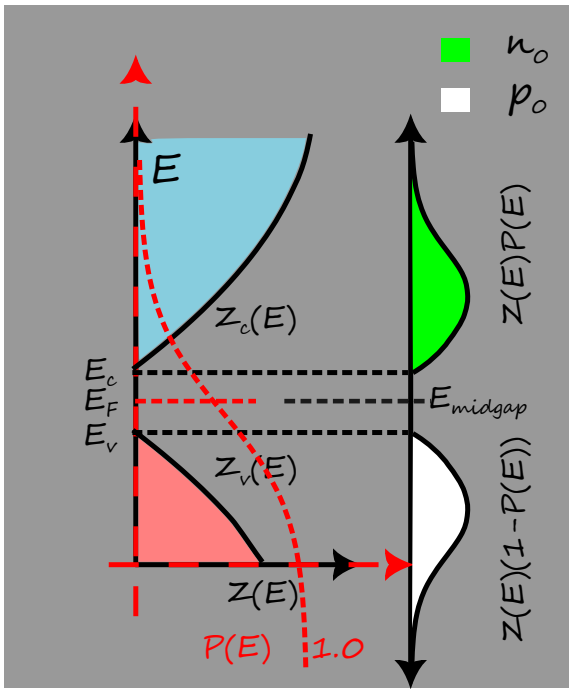
so that the density of states in the valence band $Z_v(E)$ is given by

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

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

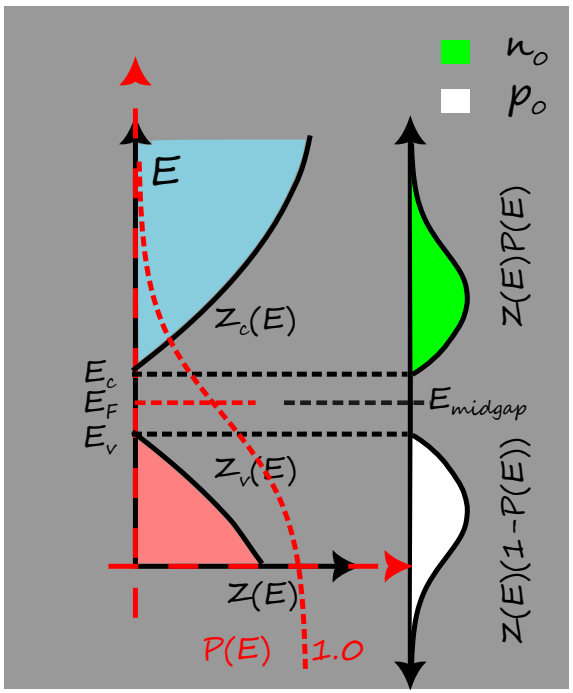
$$n_0 = \int_{E_c}^{\infty} Z_c(E)P(E)\,\mathrm{d}E$$
$$= \int_{E_c}^{\infty} \frac{\alpha^* \sqrt{E - E_c}}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}\,\mathrm{d}E$$

- 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

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

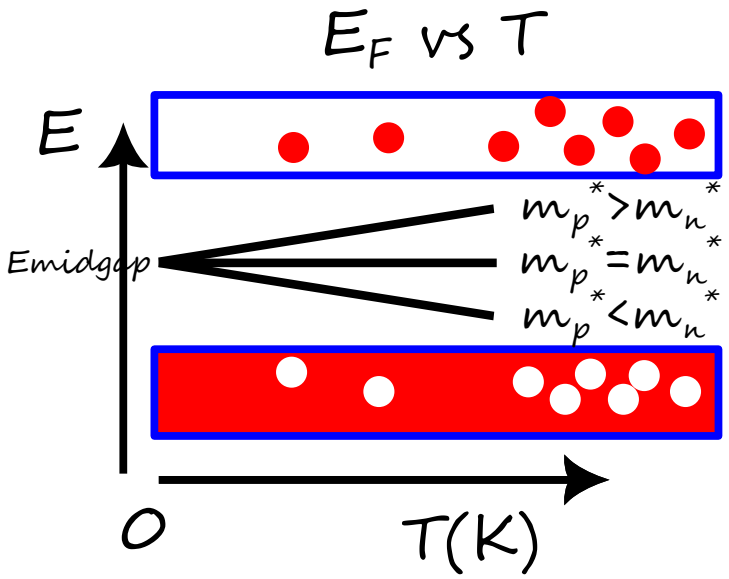
$$\boxed{\therefore E_F = E_{\text{midgap}} + \frac{3k_B T}{4} \ln \frac{m_p^*}{m_n^*}}$$

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

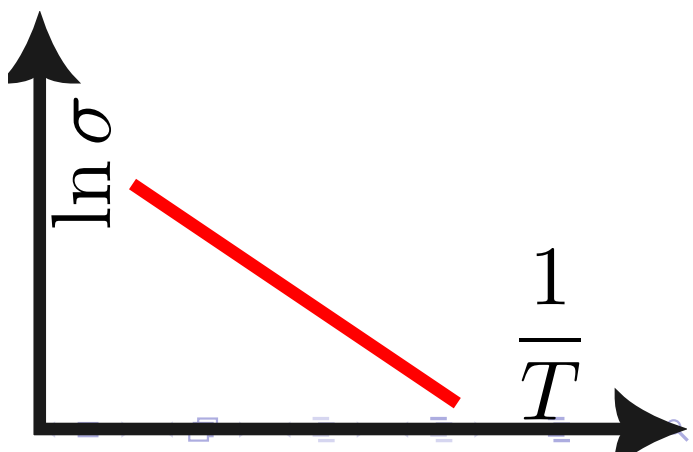
$$\ln \sigma_i = \ln \sigma_0 + \ln\left[\exp\left(-\frac{E_g}{2k_B T}\right)\right]$$

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

- 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

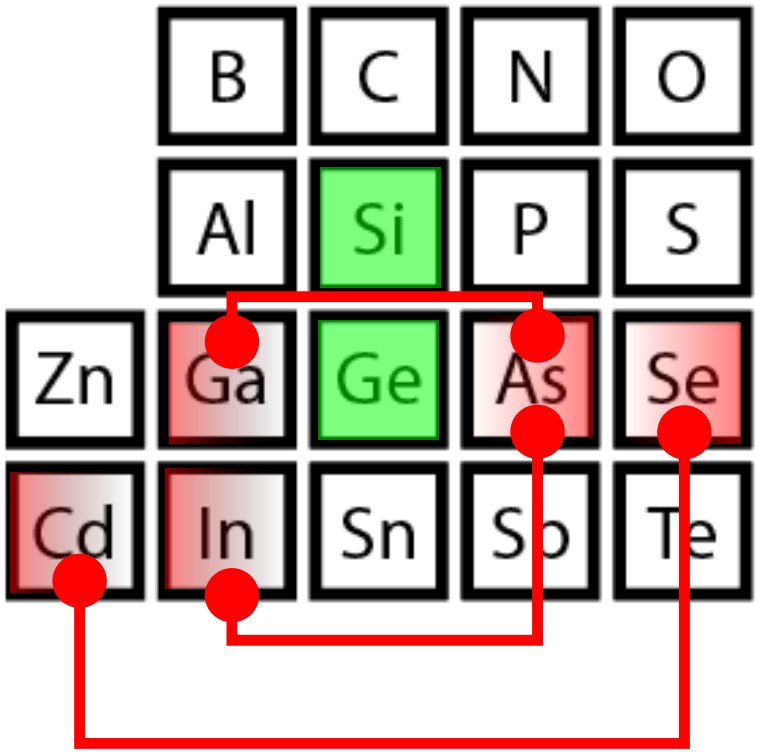
Calculate the ratio of conduction electrons at $400\,\mathrm{K}$ *to conduction electrons at* $300\,\mathrm{K}$. *[Hint: From the explicit expression for* N_c*, observe the form of* N_c *vs* T. *]*

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].

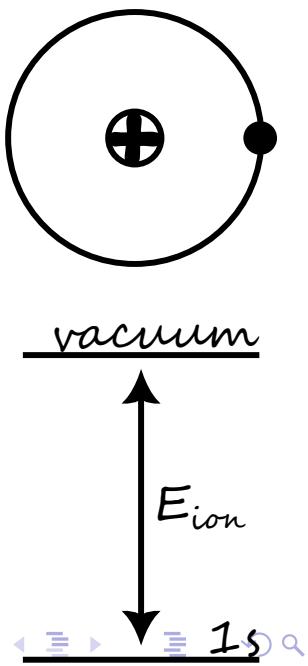
[a] The related concept to ionization energy in the case of solid is work function.

- 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

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

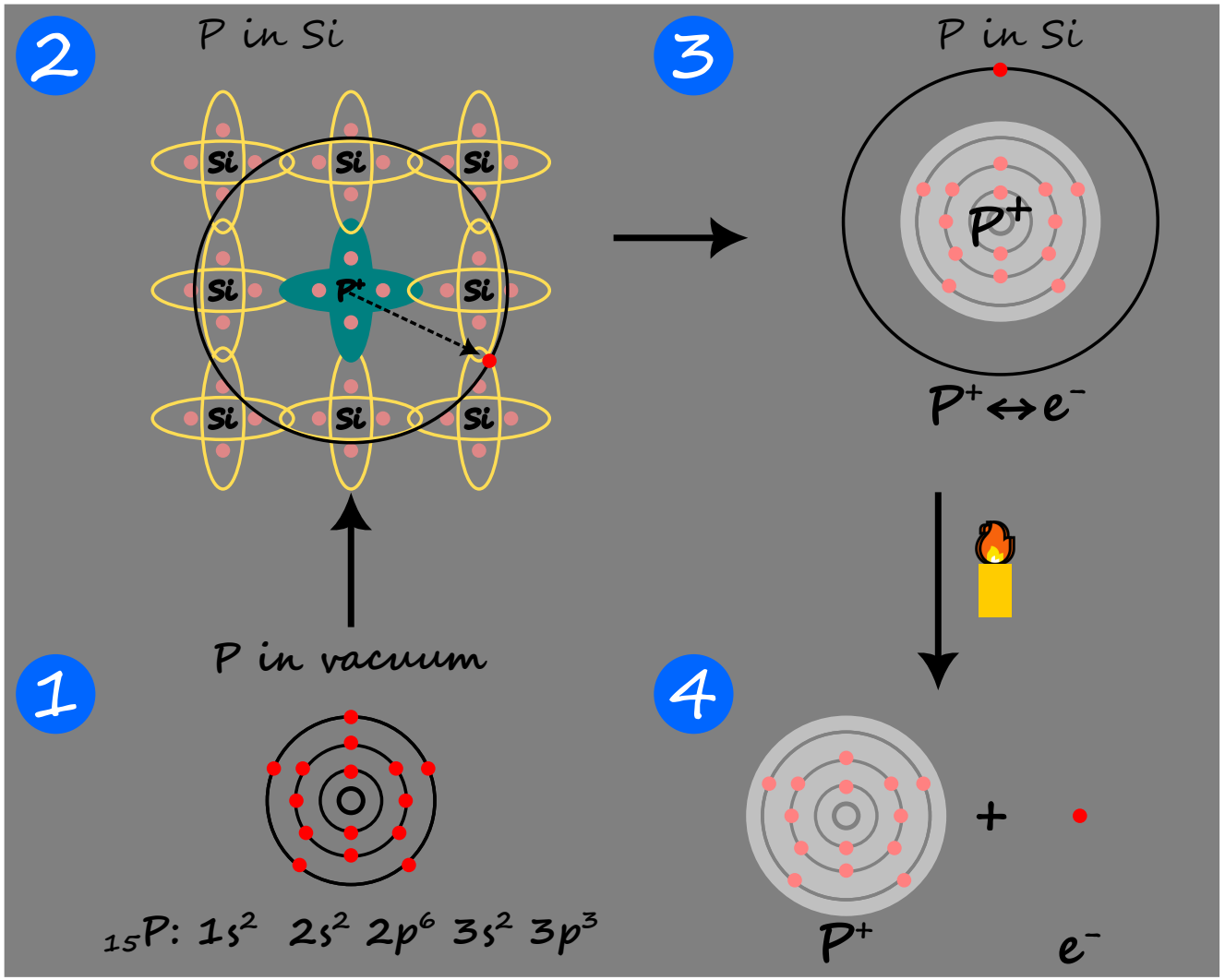
- Therefore, the ionization energy of H atom is given by

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

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.

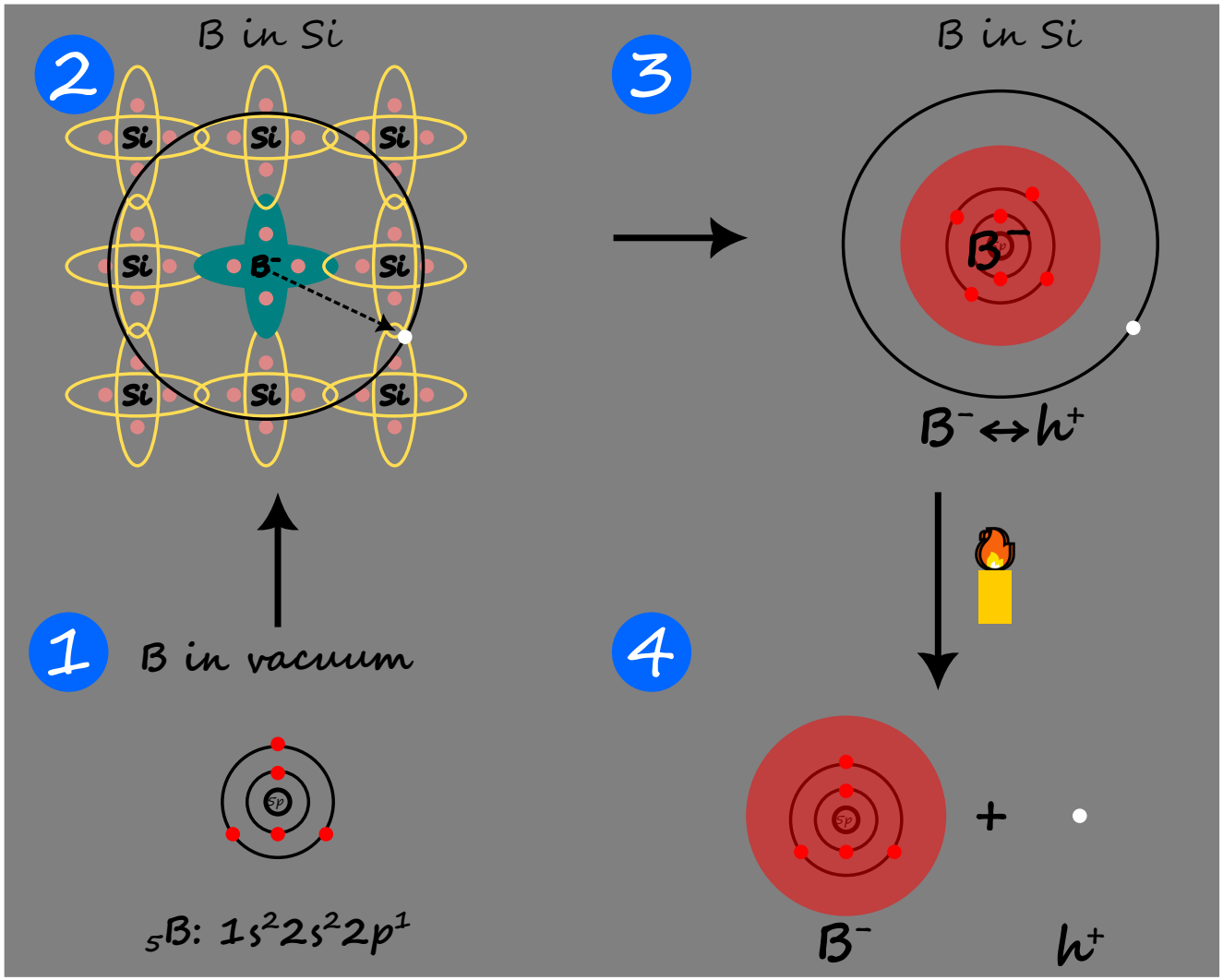
1. Phosphorus in vacuum has 5 electrons in the valence shell.
2. Phosphorus in silicon shares 4 electrons with neighbouring Si atoms for covalent bonding. The **extra** electron is loosely coupled to the phosphorus nucleus.
3. At absolute zero temperature, phosphorus can be modeled as a hydrogenic atom 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 that is loosely coupled to the boron nucleus.
3. At absolute zero 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*. [$m_n* = 0.26 m_0$.]

- 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

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

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

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

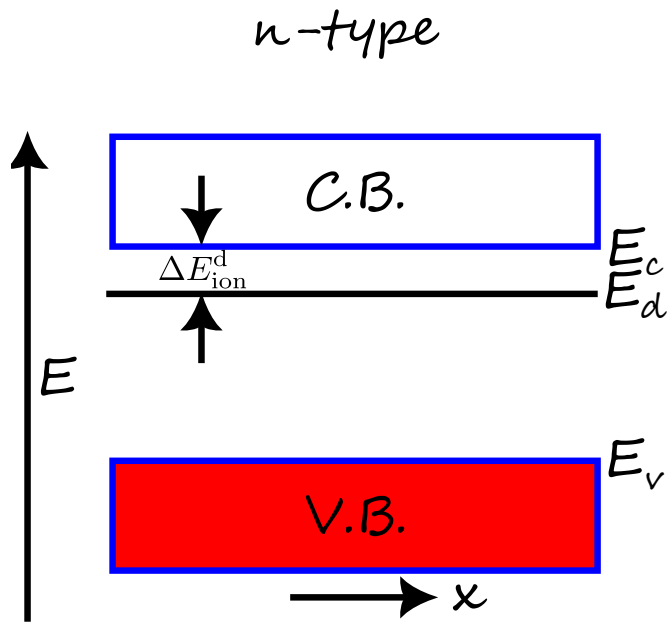
Key Insight

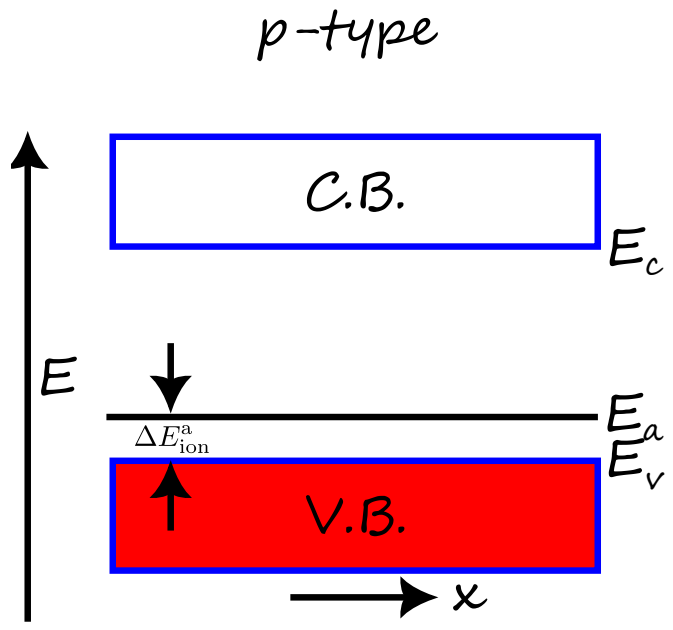
The ionization energy of dopants is of the order of $k_B T_{300\,\text{K}}$.

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.



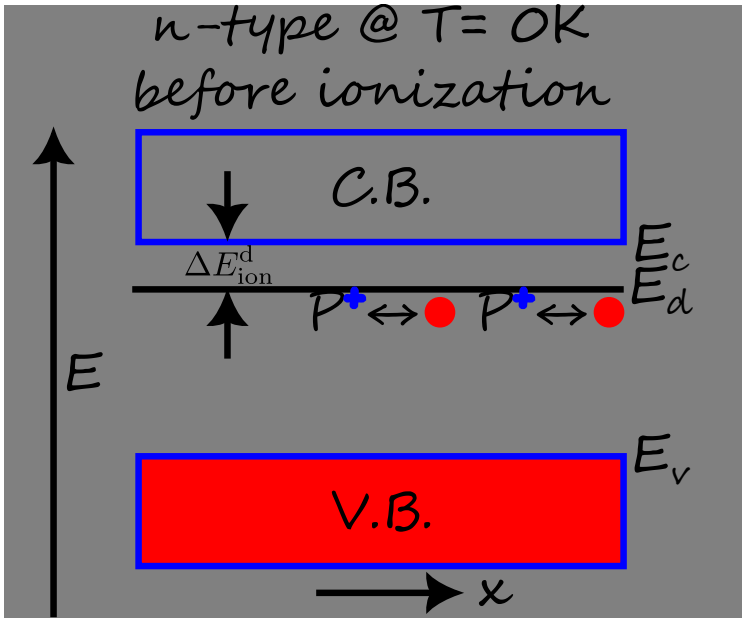


Key Insight

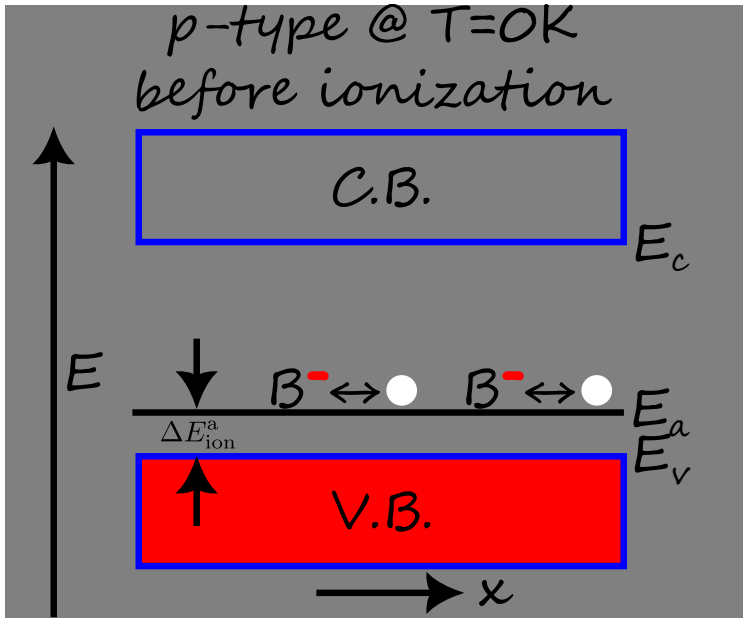
Donor energy level is closer to the conduction band minimum and acceptor energy is closer to the valence band maximum.

Dopant energy levels – before ionization

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



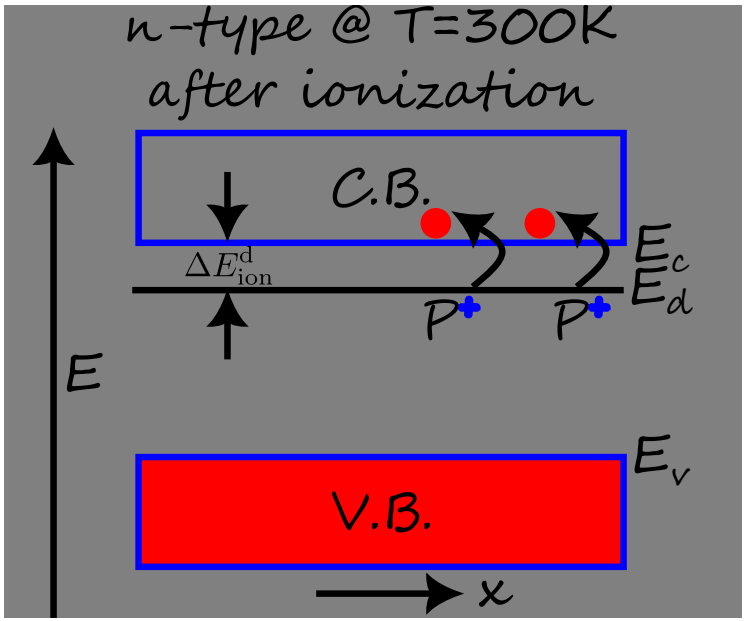
- The electron is **bound** to the donor ion.

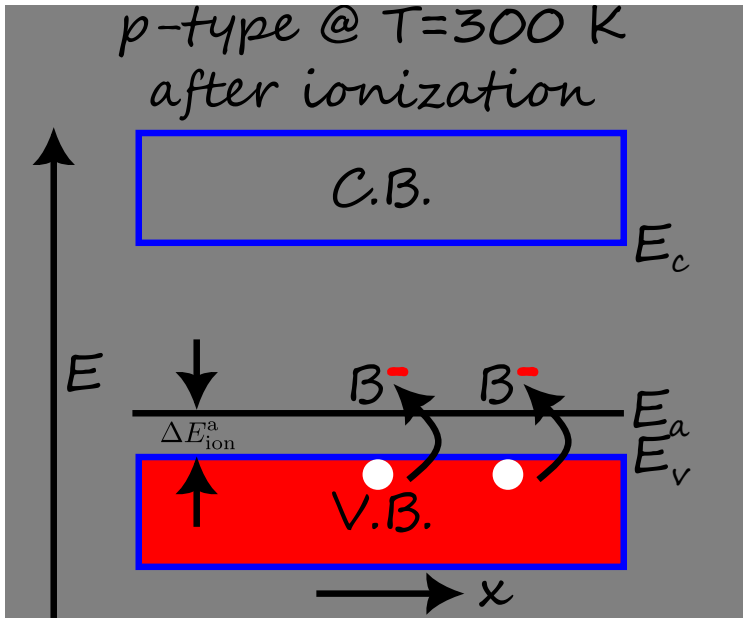


- The hole is **bound** to the acceptor ion.

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.

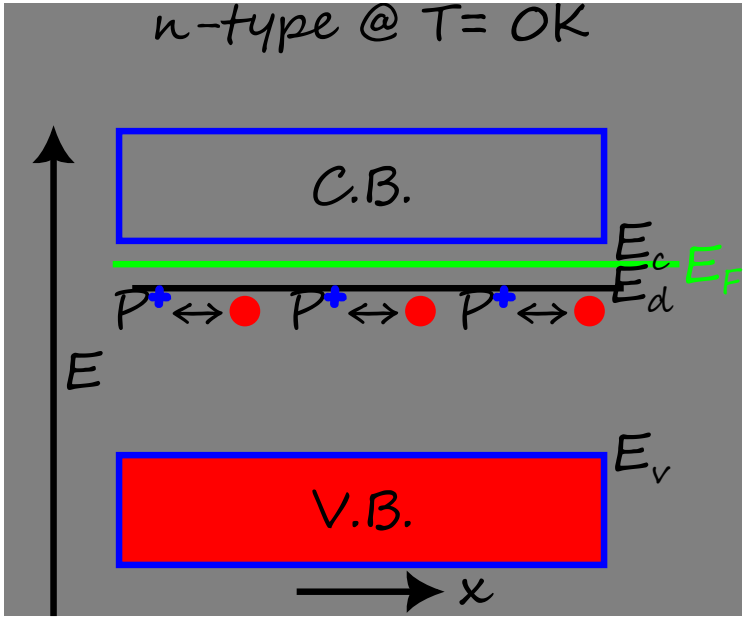


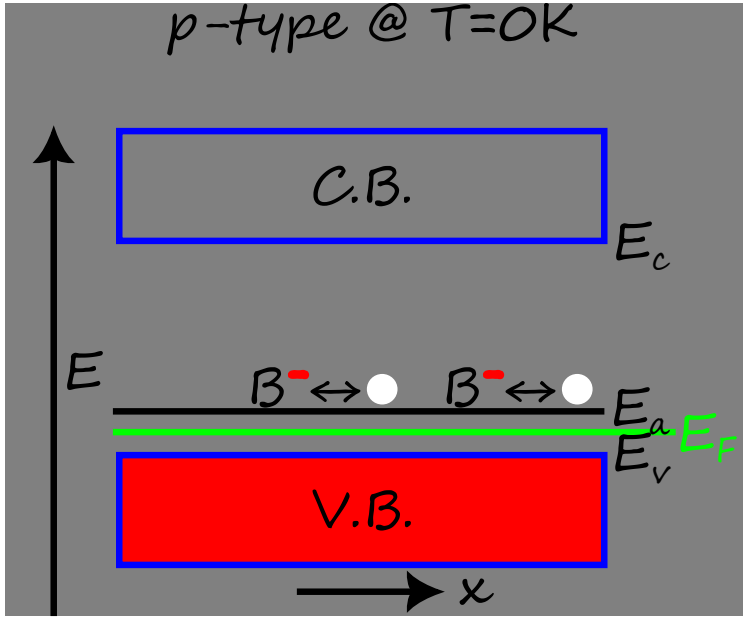


- Upon ionization, the donor dopant releases free electron into the conduction band.
- Upon ionization, the acceptor dopant accepts electron from valence band and creates a hole in the valence band.

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

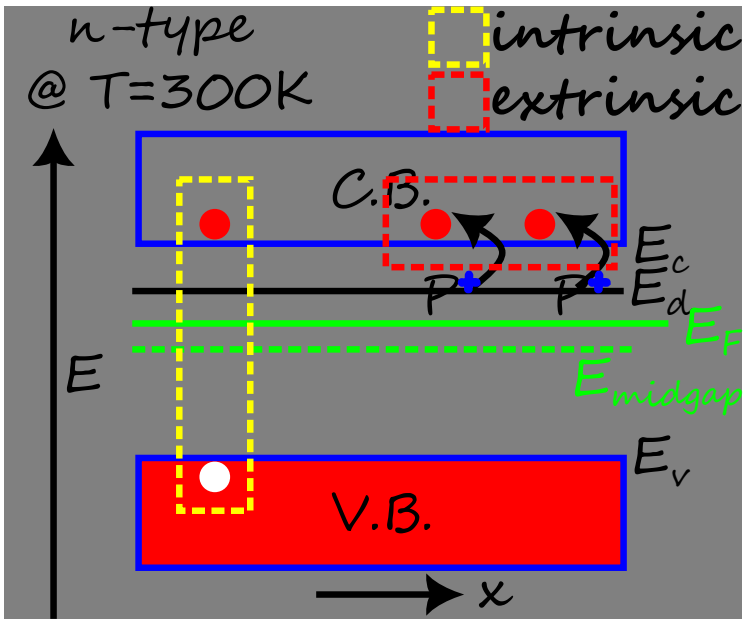
- **above** the donor energy level.
- **below** the conduction band edge.

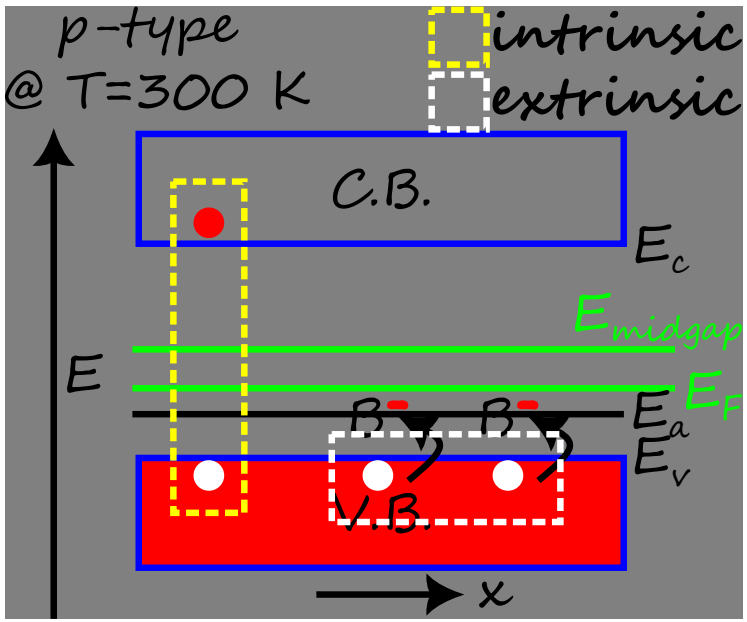
The Fermi energy level lies

- **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

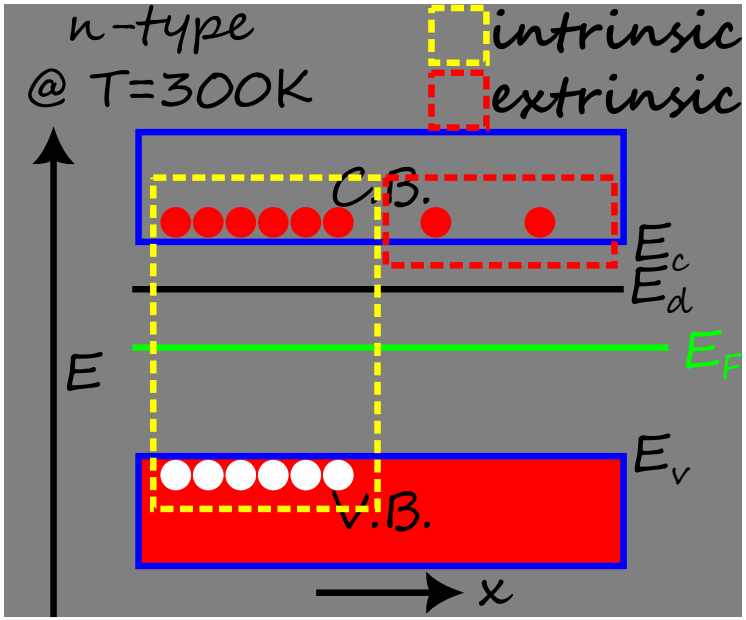
- **below** the donor energy level since donor energy level is **empty**.
- **above** the midgap energy level.

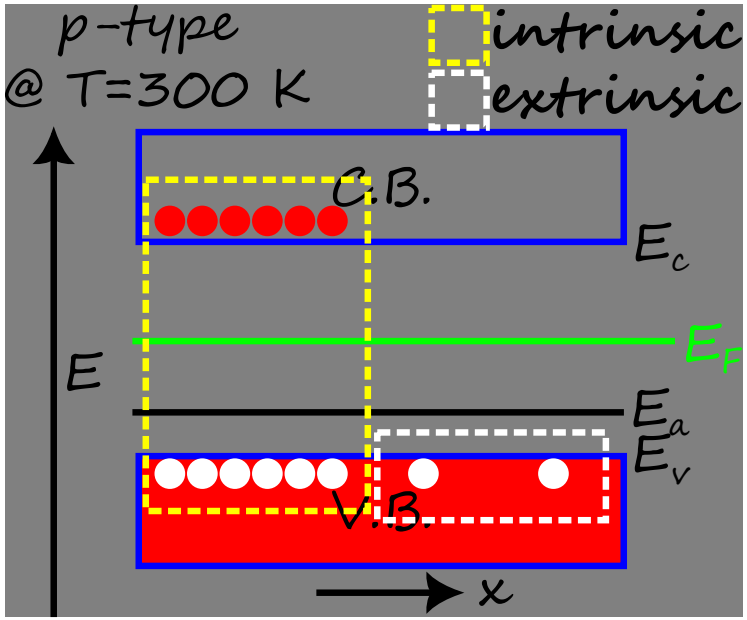
The Fermi energy level lies

- **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.

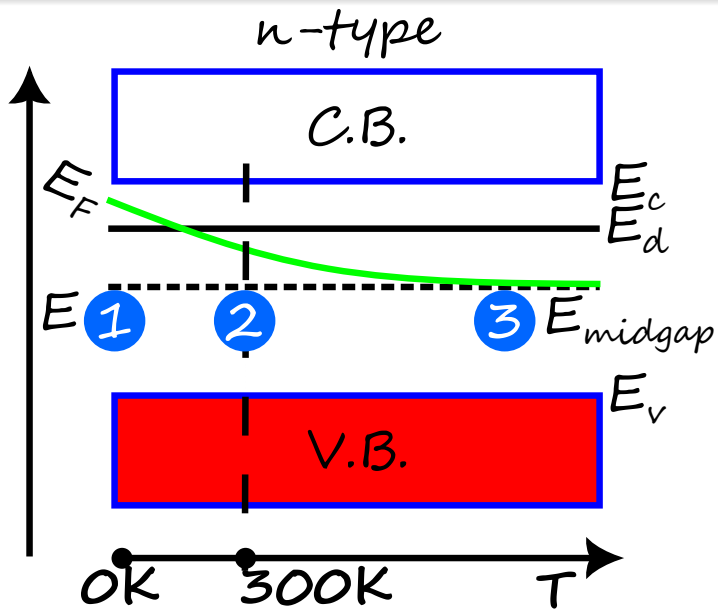
Key Insight

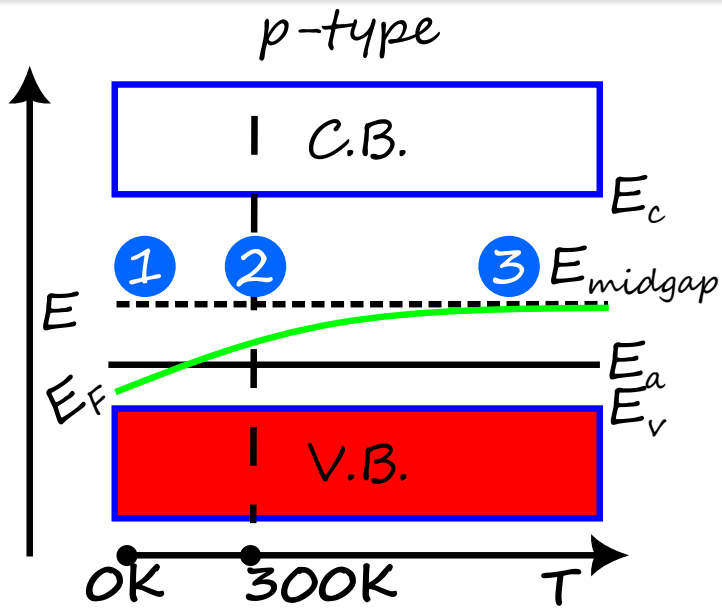
At very high temperature, extrinsic semiconductor behaves nearly as an intrinsic semiconductor.

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