QUANTUM MATERIALS
UES022

Band theory of solids

Concepts of Modern Physics by Arthur Beiser (Chapter 10)

Quantum Electron Gas

- Transition from classical to quantum nature of the electron gas results in shift to the Fermi-Dirac statistics.
- The use of F-D statistics affects only those predictions of classical model which need the electron velocity distribution.
- Now, all properties are determined by behaviour of electrons near the fermi level.

Correct temperature dependence of σ for metals.

$\sigma \alpha T$

Correct thermoelectric coefficient values.

Classical values were 100 times larger

Correct heat capacity and thermal conductivity (κ) for metals.

Wiedemann-Franz Law

$\frac{\kappa}{\sigma} = LT$

L: Lorenz Number = $2.44 \times 10^{-8}\ V^2\ K^{-2}$

Magnetic susceptibility for metals

Quantum Electron Gas

Electron gas in the solid was considered to be a quantum gas.

- Fermi-Dirac statistics and E_f
- Quantization of k-space
- Only electrons near the fermi level (E_f) contribute to conduction/transport phenomenon.
- Velocity of conduction electrons = v_f = fermi velocity
- Energy of conduction electrons in solids is independent of temperature,

$$\frac{E}{N} = \frac{3}{5} E_f$$

Independent electron approximation:

- Interaction between the electrons is neglected.

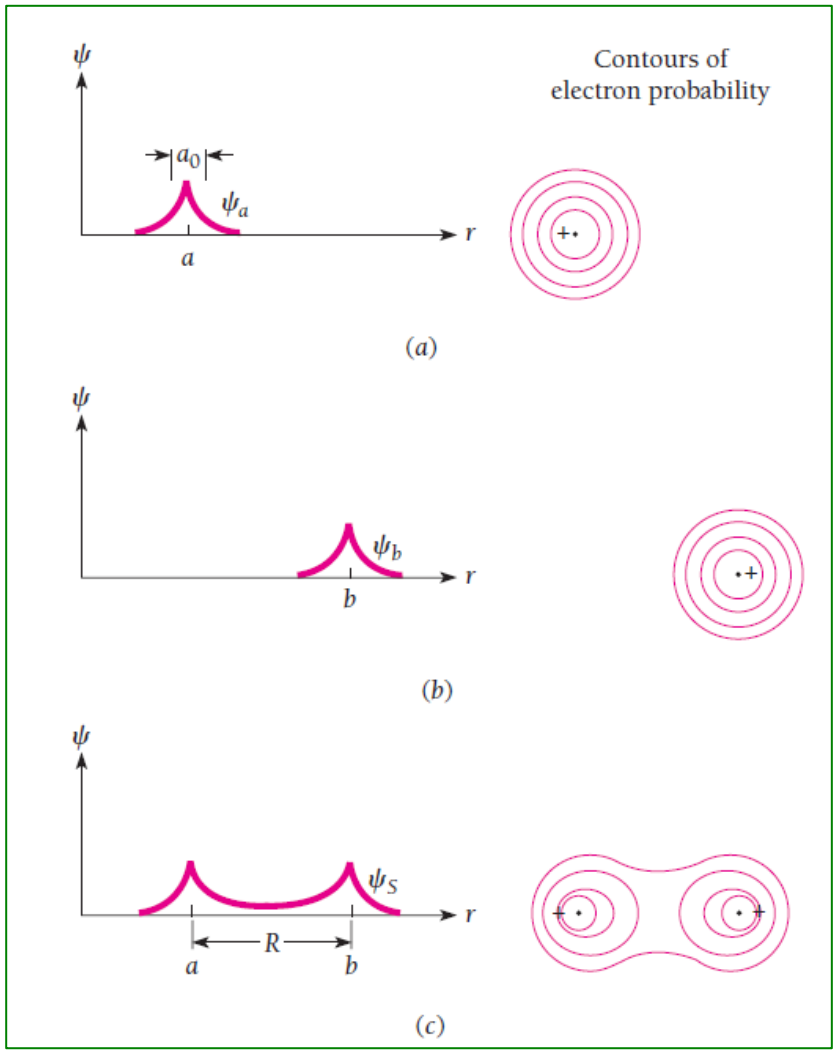
Free electron approximation:

- Interaction between the electrons and cores is neglected.

There are many experimental observations, which could NOT be explained.

(Conductivity in semiconductors, Magneto-resistance, Low temp. specific heat, Superconductivity, etc.)

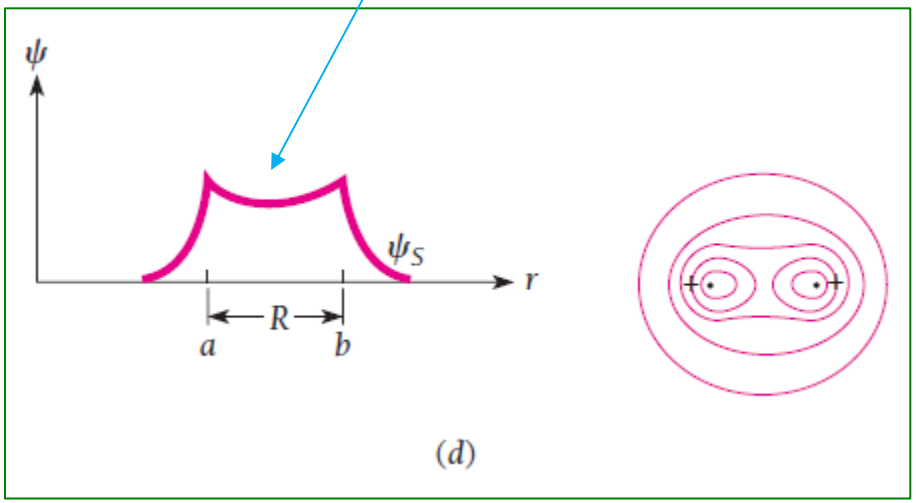
Band theory of solids



- a and b denote position of protons.

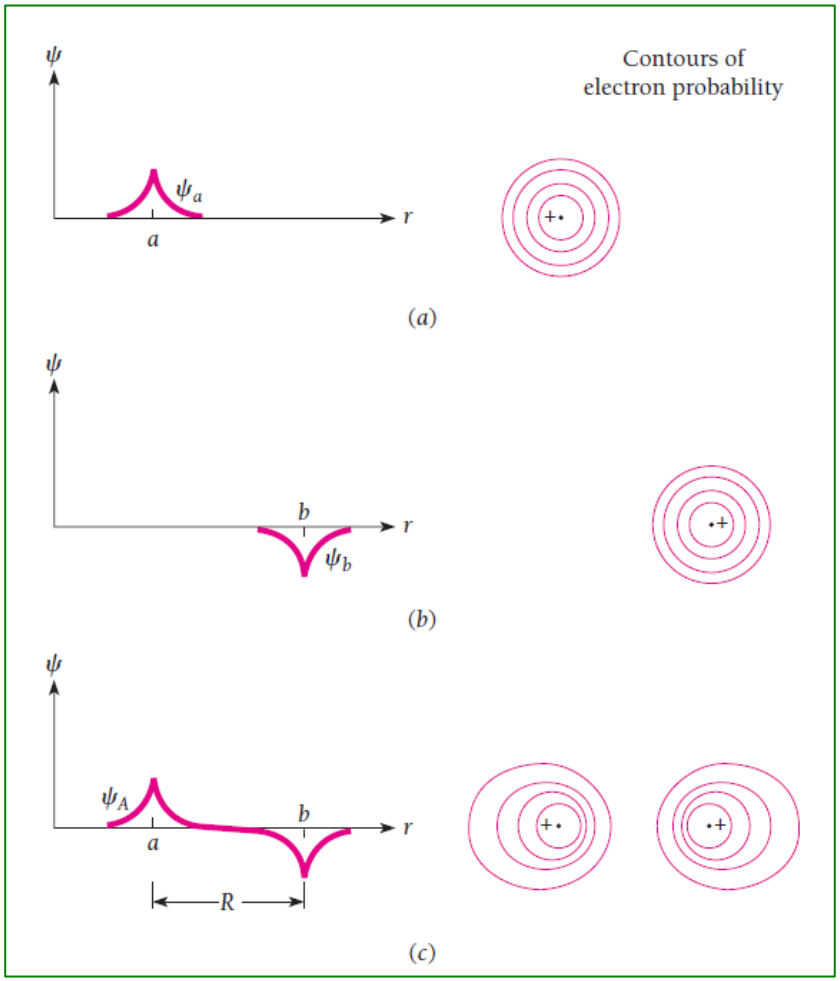
electron has a greater probability of being between the protons than outside them.

- Bonding

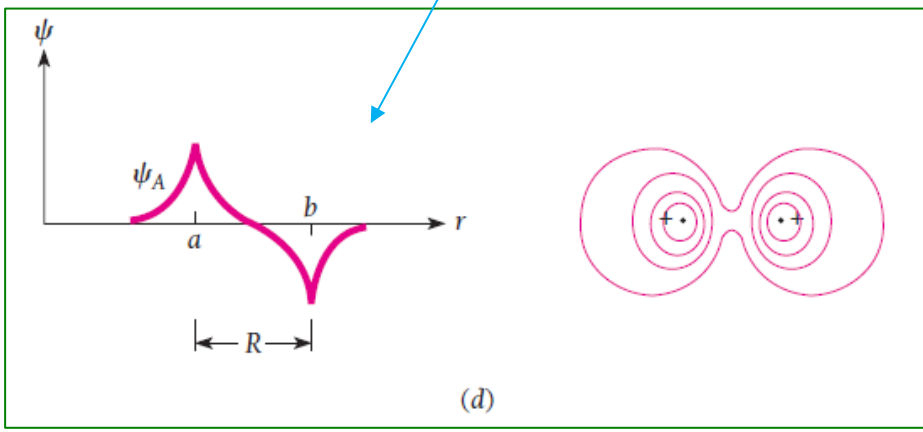


The combination of ψ_a and ψ_b is symmetric, since exchanging *a* and *b* does not affect ψ.

Band theory of solids



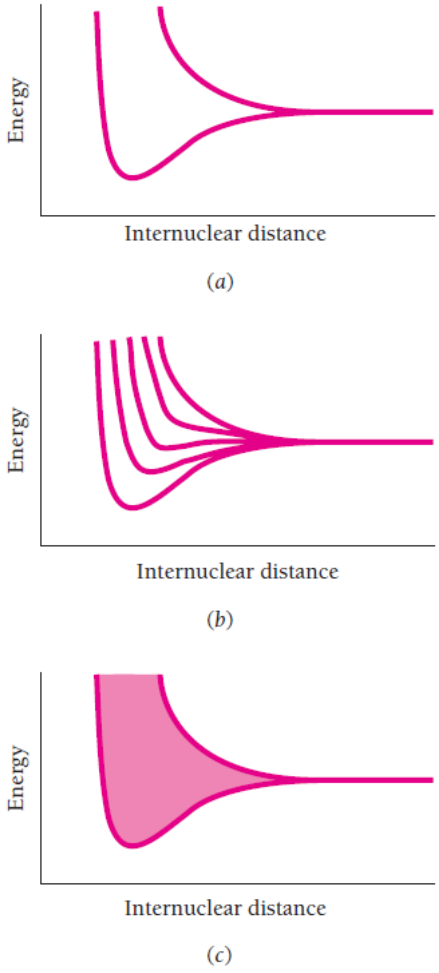
- electron has a lower probability of being between the protons than outside them.
- deficiency of negative charge between the protons
- a repulsive force between them
- bonding cannot occur - Antibonding

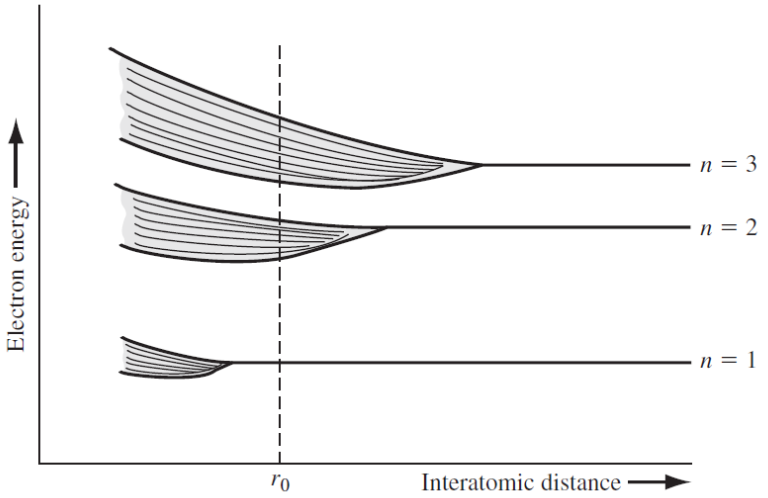


The combination of ψ_a and ψ_b is Antisymmetric.

- a and b denote position of protons.

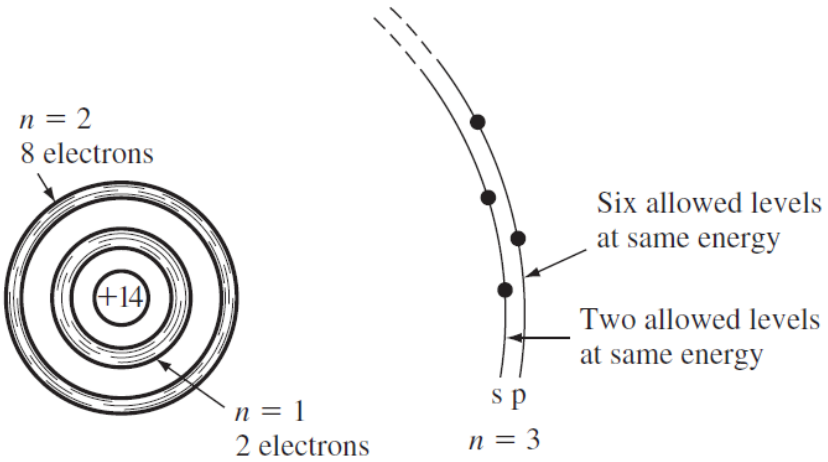
Band theory of solids



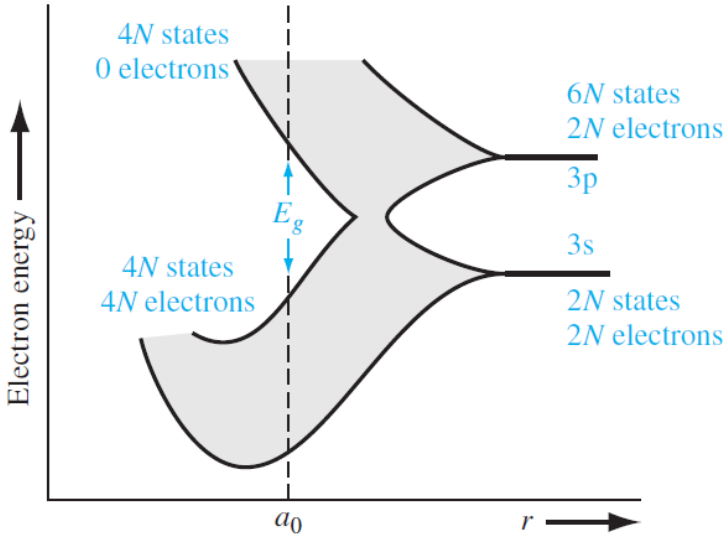


Band theory of solids

Case study for Si

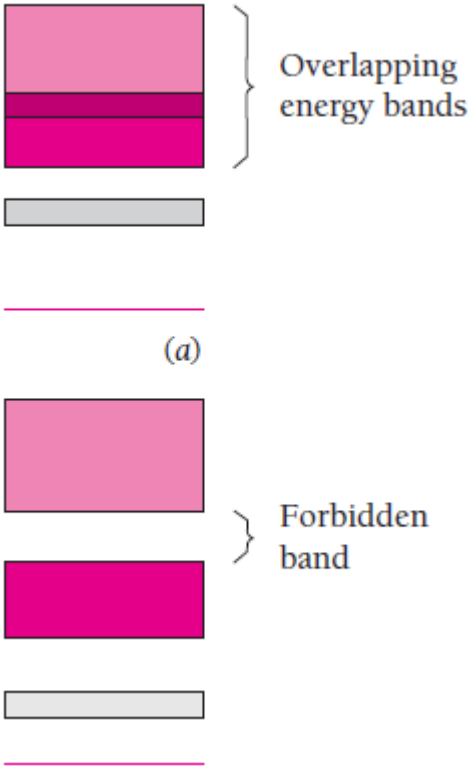


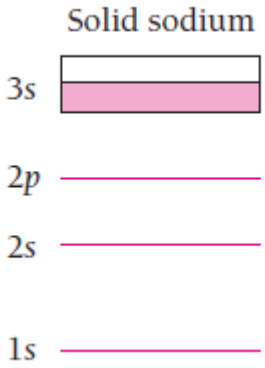
(a)



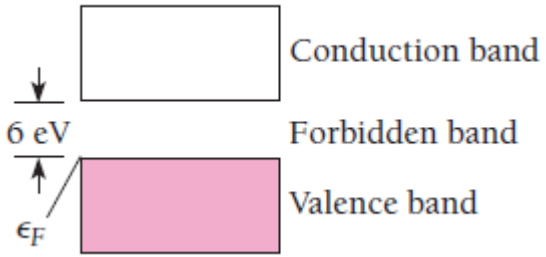
(b)

Band theory of solids





Diamond

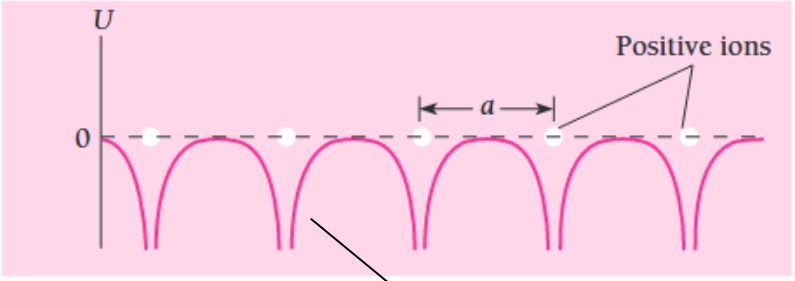


ENERGY BANDS: ALTERNATIVE ANALYSIS

How the periodicity of a crystal lattice leads to allowed and forbidden bands

Band theory of solids

Consider an electron in a crystal moves in a region of periodically varying potential.



Why is this shape?

The de Broglie wavelength of a free electron of momentum p is

$$\lambda = h/p$$

Unbound low-energy electrons can travel freely through a crystal since their wavelengths are long relative to the lattice spacing a.

More energetic electrons have wavelengths comparable with a, and such electrons are diffracted.

An electron of wavelength λ undergoes Bragg reflection from one of the atomic planes in a crystal when it approaches the plane at an angle θ,

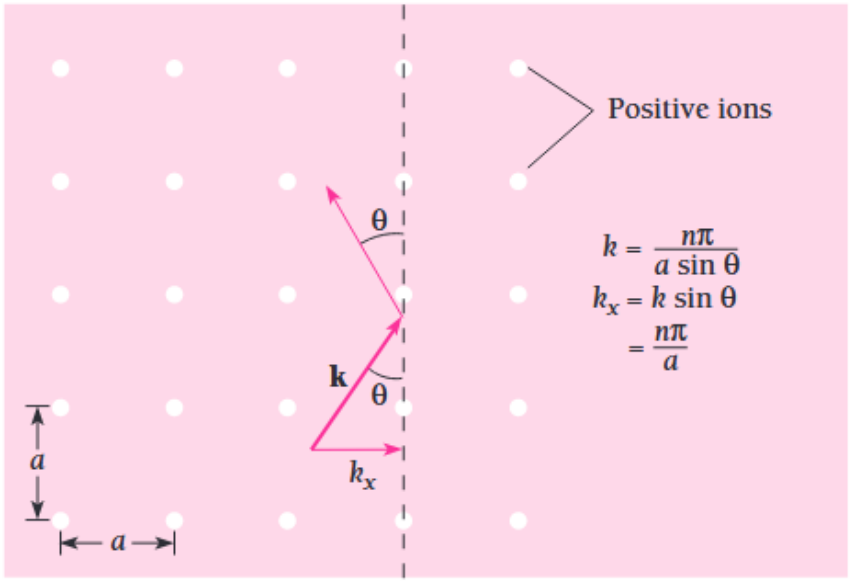
$$n\lambda = 2a \sin\theta, \quad n = 1, 2, 3, \ldots$$

Band theory of solids

Bragg's law of reflection:

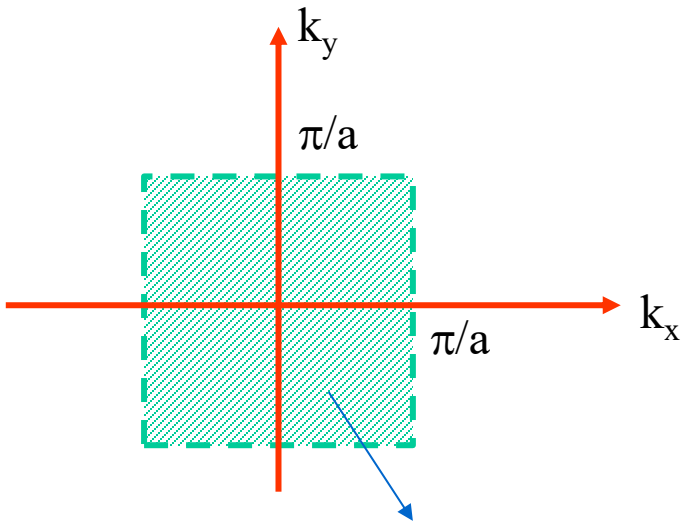
$n\lambda = 2a \sin\theta$, n = 1, 2, 3, . . .

$k = \frac{n\pi}{a \sin\theta}$ when $k = 2\pi/\lambda$,



Reflection from the vertical rows of ions occurs when $k_x = n\pi/a$.

Similarly, reflection from the horizontal rows occurs when $k_y = n\pi/a$.



First Brillouin zone

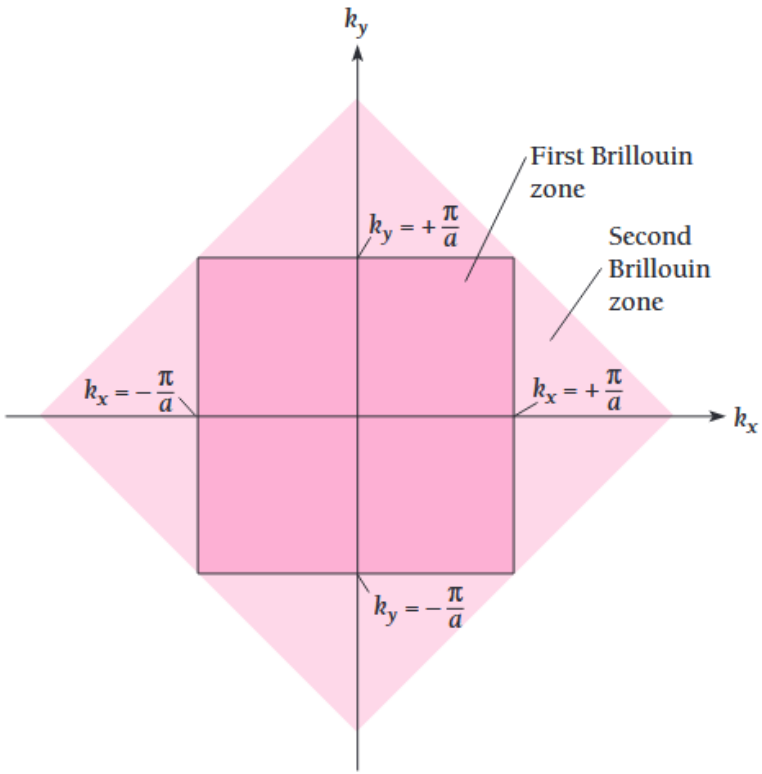
If $k < \pi/a$, the electron can move freely through the lattice in any direction.

When $k = \pi/a$, they are prevented from moving in the x or y directions by reflection.

Band theory of solids

Reflection from the vertical rows of ions occurs when $k_x = n\pi/a$.

Similarly, reflection from the horizontal rows occurs when $k_y = n\pi/a$.

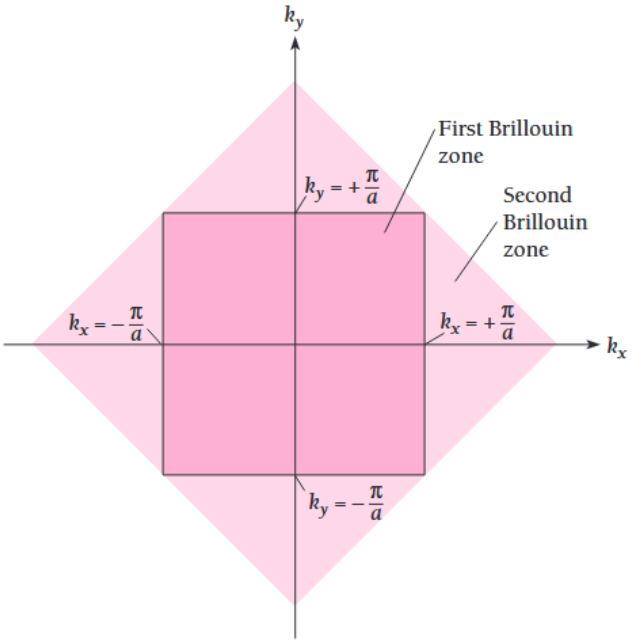


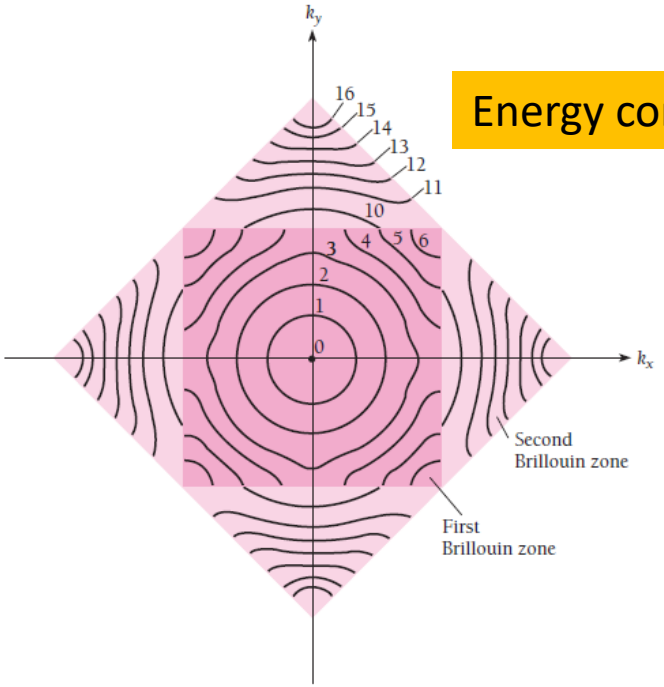
The region in k-space that low-k electrons can occupy without being diffracted is called the first Brillouin zone.

In the case of an electron in a crystal for which $k << \pi/a$, there is practically no interaction with the lattice $\rightarrow$ Free electron

Energy $E = p^2/2m = \hbar^2k^2/2m$

Band theory of solids





Energy contour diagram

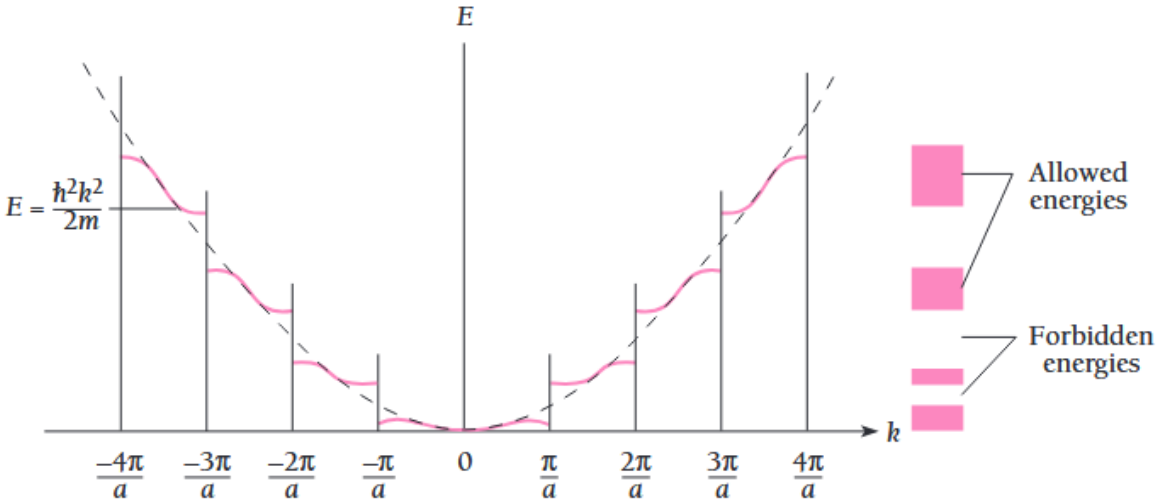
For k << π/a (nearer to center of BZ), constant-energy contour lines are circles.

- there is practically no interaction with the lattice
- Free electron, Energy $E = p^2/2m = \hbar^2k^2/2m$

With increasing *k* the constant-energy contour lines become progressively closer together and also more and more distorted. WHY?

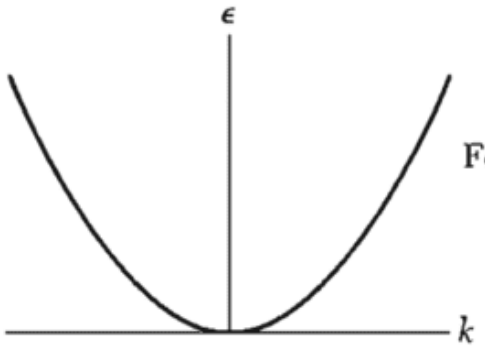
Band theory of solids

How E varies with k (in the x direction)

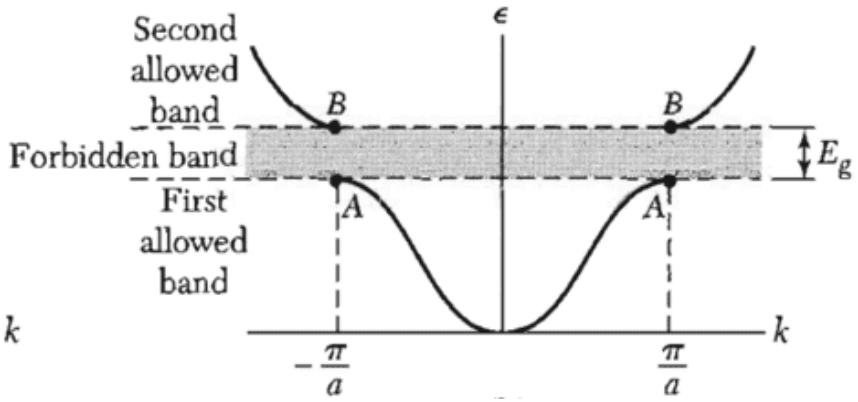


- In the case of an electron in a crystal for which $k << \pi/a$, there is practically no interaction with the lattice. Energy $E = p^2/2m = \hbar^2k^2/2m$
- As k approaches π/a, E increases more slowly than $\hbar^2k^2/2m$, the free-particle figure.
- At $k = \pi/a$, E has two values, the lower belonging to the first Brillouin zone and the higher to the second zone. There is a definite gap between the possible energies in the first and second Brillouin zones which corresponds to a forbidden band.
- The same pattern continues as successively higher Brillouin zones are reached.

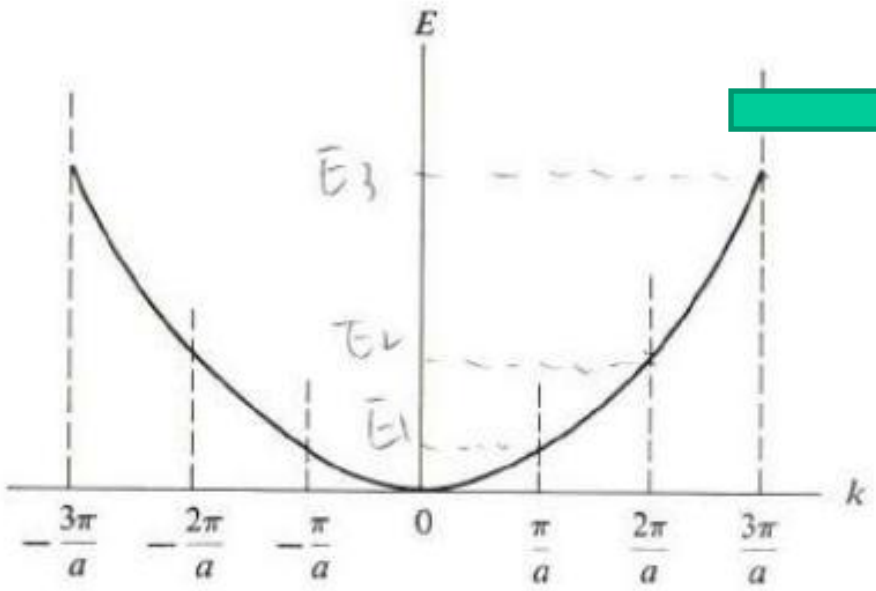
Band theory of solids

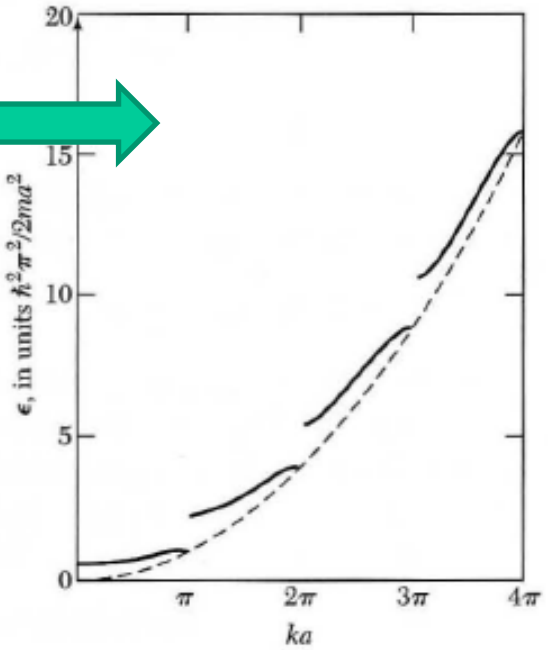


Free electron model



Electron in a periodic potential





Band theory of solids

- The wave functions at k = ± π/a are not the traveling waves $e^{i\pi x/a}$ or $e^{-i\pi x/a}$ of free electrons.
- At these special values of k, the wave functions are made up of equal parts of waves traveling to the right and to the left.
- When the Bragg reflection condition k = ± π/a is satisfied by the wave vector, a wave traveling to the right is Bragg-reflected to travel to the left, and vice versa.
- Each subsequent Bragg reflection will reverse the direction of travel of the wave.
- A wave that travels neither to the right nor to the left is a standing wave: it doesn't go anywhere.
- So solutions can be of form

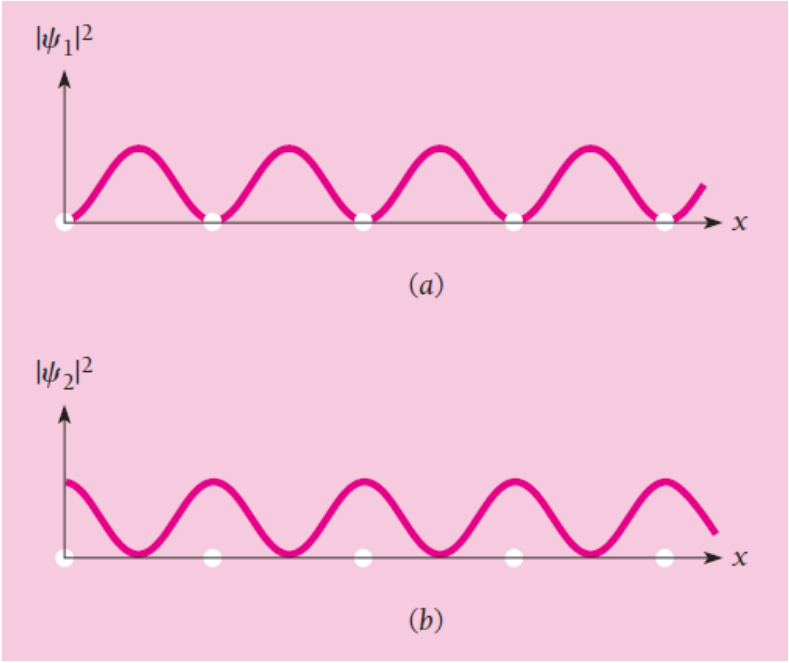
$$\psi_1 = e^{i\pi x/a} + e^{-i\pi x/a} = 2\,cos(\pi x/a)$$

$$\psi_2 = e^{i\pi x/a} - e^{-i\pi x/a} = 2i\,sin(\pi x/a)$$

Both standing waves are composed of equal parts of right- and left-directed traveling waves.

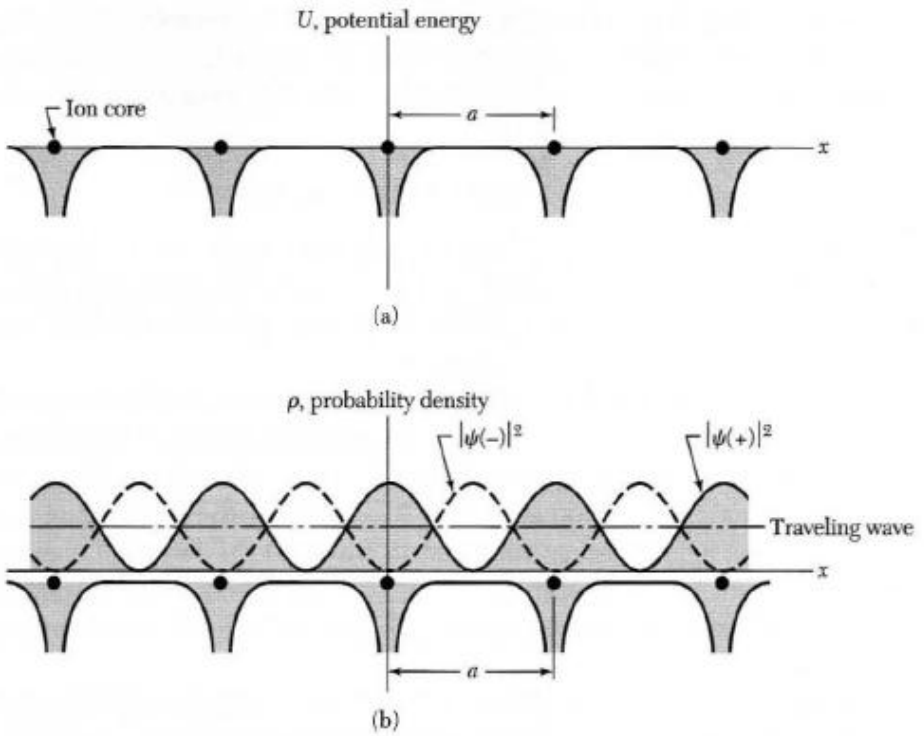
Band theory of solids

- Probability density of a particle $\rho = |\psi|^2$
- For a traveling wave, $\rho = e^{i\pi x/a} e^{-i\pi x/a} = 1$, charge density is constant/uniform across lattice.
- Charge density is not constant for standing waves:
  - $|\psi_1|^2 \propto \cos^2(\frac{\pi x}{a})$, $|\psi_2|^2 \propto \sin^2(\frac{\pi x}{a})$



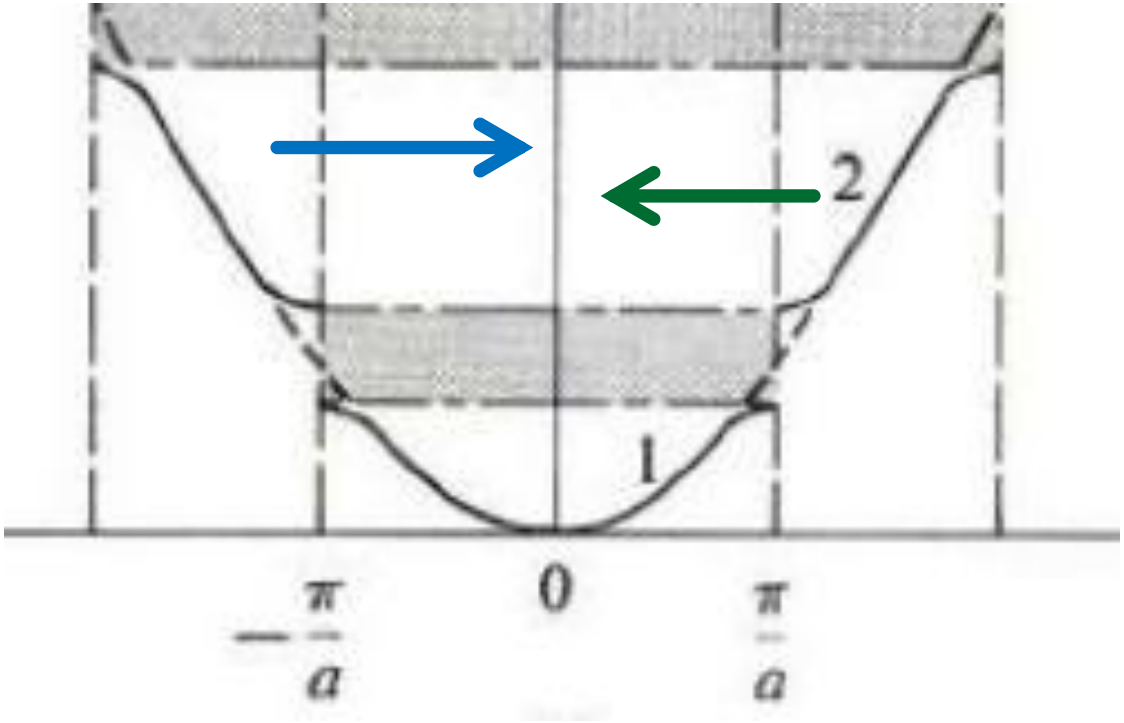
Band theory of solids

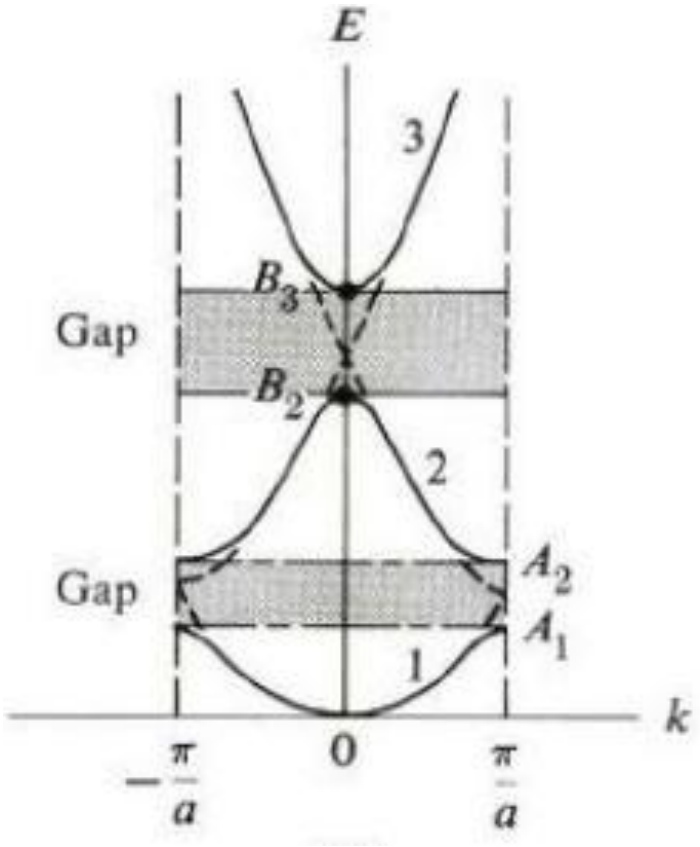
- Probability density or charge density for ψ_1 is concentrated ***between*** positive ions
- Probability density or charge density for ψ_2, it is concentrated ***at*** the positive ions.
- The potential energy of an electron is ***highest*** at the ***midway*** between each pair of ions and ***least at the ions*** themselves,



- ***The electron energies E_1 and E_2 associated with the standing waves ψ_1 and ψ_2 are different.***
- ***No other solutions are possible when $\pm \pi/a$ and accordingly no electron can have an energy between E_1 and E_2.***

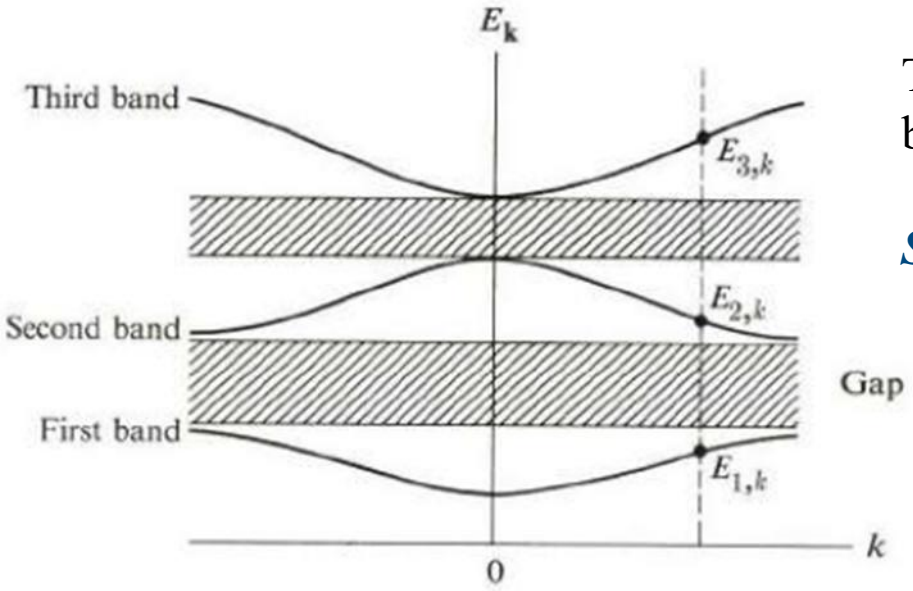
Band theory of solids





We study only the FBZ

Band theory of solids



Energy bands and gaps

The Energy Gaps exists because of the interaction between the electrons and the ionic cores.

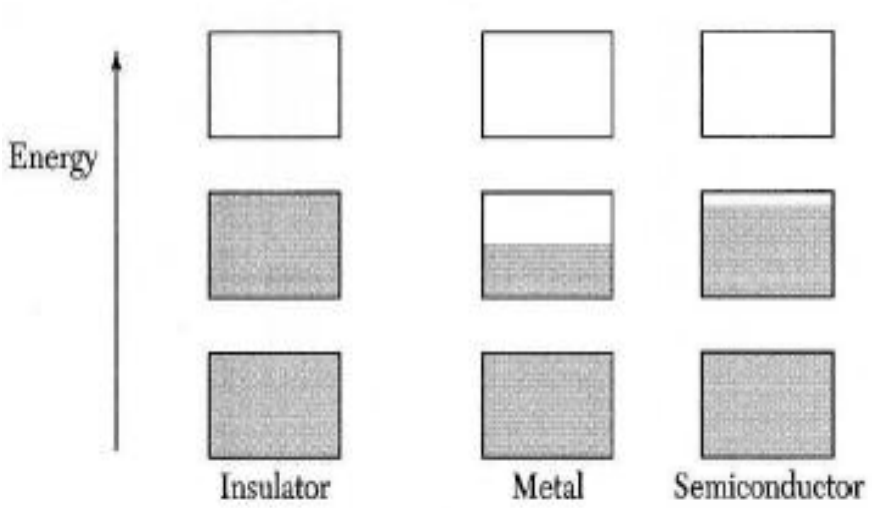
So Energy gap value depends on this interaction

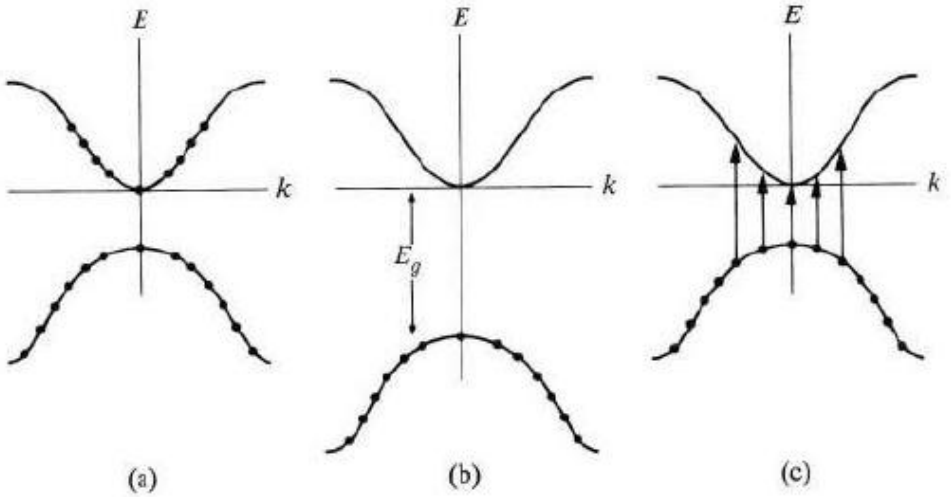
Energy Band Diagram is a graphical representation of the energy levels of electrons in the valence band and conduction band, determining the conductivity properties of the material.

Only the top-most filled level (Valence Band) and the next highest band (Conduction Band) **Matter*!***

Completely filled band contributes no current in the presence of electric field.

Band theory of solids





Conductor Insulator Semi-Conductor

For metal the conduction and the valence bands are the same since the valence band is partially filled so the electrons can conduct electricity/energy.

For semiconductors band gap is small enough (≤ 3-5 eV) for the electron to be excited thermally.

Band theory of solids

Number of electrons accommodated in a band are 2 N (N is total number of primitive unit cells)

A substance with an odd number of valence electrons per unit cell is always a metal, as it takes an even number of electrons to fill a band. In contrast, a substance with an even number of valence electrons can be either a metal or an insulator, depending on whether the energy bands are separate or overlapping.

Band theory of solids

An electron in a crystal interacts with the crystal lattice; its response to an external electric field is not the same as that of a free electron.

All the most important results of the free-electron theory of metals can be incorporated in the more realistic band theory merely by replacing the electron mass m by an average **effective mass** m^*.

effective mass $m^*$of an electron in a solid: the mass the electron appears to have due to the influence of the surrounding crystal lattice.

Table 10.2 Effective Mass Ratios m^*/m at the Fermi Surface in Some Metals

Metal		m^*/m
Lithium	Li	1.2
Beryllium	Be	1.6
Sodium	Na	1.2
Aluminum	Al	0.97
Cobalt	Co	14
Nickel	Ni	28
Copper	Cu	1.01
Zinc	Zn	0.85
Silver	Ag	0.99
Platinum	Pt	13

The electrical behavior of a solid depends on the degree of occupancy of its energy bands as well as on its band structure