Formation of Energy Bands

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Review of Energy Bands

In crystalline solids, the atoms are “assembled” in a *periodical* arrangement, in such a way as to minimize the energy of the system...

Example: NaCl crystal (ionic bound)

In the solid, the separation between the constituting atoms is comparable to the atomic size, so the properties of the individual atoms are altered by the presence of neighbouring atoms.

Energy bands

- Resulting from principles of quantum physics

Discrete energy levels:

More atoms – more energy levels of electrons:

There are so many of them that they form energy bands:

The discrete (allowed) energy levels of an atom become energy bands in a crystal lattice
Energy Bands - Solids

- When atoms approach to form molecules, Pauli’s exclusion principle assumes a fundamental role.

- When two atoms are completely isolated from each other, in a way that there’s no interaction of electrons, they can have identical electronic structures.

- As the space between the atoms becomes smaller, electron superposition occurs.

- As stated previously, Pauli’s Exclusion Principle says that two different electrons cannot be described by the same quantum state; so, an unfolding of the isolated atom’s discrete energy levels into new corresponding levels to the electron pair occurs.
In order to form a solid, many atoms are brought together. Consequently, the unfolded energy levels form, essentially, continuous energy bands.

As an example, the next picture shows an imaginary Si crystal formation from isolated Si atoms.

As the distance between atoms approaches the equilibrium inter-atomic separation of the Si crystal, this band unfolds into two bands separated by an energy gap, $E_g$. 
Semiconductors

- They have an electrical conductivity whose value is in between the metal and the insulators conductivity.

![Diagram showing the conductivity range of metals, semiconductors, and insulators with specific materials like Silica, Diamond, Glass, Si, Ge, Fe, Cu marked on the conductivity scale (Ω cm⁻¹).]
Semiconductors

- Elementary Semiconductors: Si and Ge

- Semiconductors Composites:
  - Binary: ZnO, GaN, SiC, InP, GaAs
  - Ternary: AlGaAs, GaAsP, HgCdTe
  - Quaternarys: InGaAsP, AlInGaP

- Transistors, diodes and ICs: Si and Ge
- LEDs: GaAs, GaN, GaP
- Lasers: AlGaInAs, InGaAsP, GaAs, AlGaAs
- Detectors: Si, InGaAsP, CdSe, InSb, HgCdTe
Semiconductors

- The semiconductor conductivity can be changed through:
  - Temperature
  - Optical Excitation
  - Impurity Doping

- Devices based on semiconductors are fast and consume low energies;
- Semiconductors devices are compact and can be integrated into IC’s;
- Semiconductors devices are cheap.
Both full and empty bands do not partake in electrical conduction.
At low temperatures the valance band is *full*, and the conduction band is empty.

Recall that a full band can not conduct, and neither can an empty band.

At low temperatures, semiconductors do not conduct, they behave like insulators.

The *thermal energy* of the electrons sitting at the top of the full band is much lower than that of the *$E_g$* at low temperatures.
Conduction Electron:

- Assume some kind of energy is provided to the electron (valence electron) sitting at the top of the valence band.

- This electron gains energy from the applied field and it would like to move into higher energy states.

- This electron contributes to the conductivity and this electron is called as a conduction electron.

- At 0\(^0\)K, electron sits at the lowest energy levels. The valance band is the highest filled band at zero kelvin.
When enough energy is supplied to the电子 sitting at the top of the valance band, e\textsuperscript{-} can make a transition to the bottom of the conduction band.

When electron makes such a transition it leaves behind a missing electron state.

This missing electron state is called as a hole.

Hole behaves as a positive charge carrier.

Magnitude of its charge is the same with that of the electron but with an opposite sign.
Doped and undoped Semiconductors

- Holes contribute to current in **valence band** (VB) as e⁻‘s are able to create current in **conduction band** (CB).

- Hole is **not** a free particle. It can only exist within the crystal. A hole is simply a vacant electron state.

- A transition results an equal number of e⁻ in CB and holes in VB. This is an important property of **intrinsic**, or **undoped semiconductors**. For **extrinsic**, or **doped**, semiconductors this is no longer true.
Bipolar (two carrier) conduction

- After transition, the valance band is now no longer full, it is partly filled and may conduct electric current.

- The conductivity is due to both electrons and holes, and this device is called a bipolar conductor or bipolar device.
What kind of excitation mechanism can cause an electron to make a transition from the top of the valance band (VB) to the minimum or bottom of the conduction band (CB)?

- Thermal energy?
- Electrical field?
- Electromagnetic radiation?

Answer:

To have a partly filled band configuration in a semiconductor, one must use one of these excitation mechanisms.
1-Thermal Energy:

Thermal energy = $k \times T = 1.38 \times 10^{-23} \text{ J/K} \times 300 \text{ K} = 25 \text{ meV}$

Excitation rate = constant $\times \exp(-E_g / kT)$

Although the thermal energy at room temperature, $RT$, is very small, i.e. 25 meV, a few electrons can be promoted to the CB.

Electrons can be promoted to the CB by means of thermal energy.

This is due to the exponential increase of excitation rate with increasing temperature.

Excitation rate is a strong function of temperature.
2- Electric field:

- For low fields, this mechanism doesn’t promote electrons to the CB in common semiconductors such as Si and GaAs.

- An electric field of $10^{18}$ V/m can provide an energy of the order of 1 eV. This field is enormous.

So, the use of the electric field as an excitation mechanism is not a useful way to promote electrons in semiconductors.
3- Electromagnetic Radiation:

\[ E = h\nu = \frac{hc}{\lambda} = (6.62\times10^{-34} \text{ J s}) \times (3\times10^8 \text{ m/s} / \lambda(\text{m})) \Rightarrow E(\text{eV}) = \frac{1.24}{\lambda(\text{in } \mu \text{m})} \]

For Silicon, \( E_g = 1.1\text{ eV} \)

\[ \lambda(\mu \text{m}) = \frac{1.24}{1.1} = 1.1\mu \text{m} \]

To promote electrons from VB to CB Silicon, the wavelength of the photons must be 1.1 \( \mu \text{m} \) or less.
- The converse transition can also happen.
- An electron in CB recombines with a hole in VB and generate a photon.
- The energy of the photon will be in the order of $E_g$.
- If this happens in a direct band-gap semiconductor, it forms the basis of LED’s and LASERS.
The magnitude of the band gap determines the differences between insulators, s/c’s, and metals.

The excitation mechanism of thermal is not a useful way to promote an electron to CB even the melting temperature is reached in an insulator.

Even very high electric fields are also unable to promote electrons across the band gap in an insulator.

Wide band gaps between VB and CB.
Metals:

- No gap between valance band and conduction band

These two bands look like as if partly filled bands and it is known that partly filled bands conduct well.

This is the reason why metals have high conductivity.
Semiconductors

![Graph showing gap energy and lattice constant for various semiconductors.](Image)

- **Gap Energy (eV)**
- **Lattice Constant (Å)**

This graph illustrates the relationship between gap energy and lattice constant for different semiconductors.
Ease of achieving thermal population of conduction band determines whether a material is an insulator, metal, or semiconductor.

- **Insulator**: Few electrons, typically in the order of one electron per atom. The energy gap is very large, as seen in SiO₂ with $E_g \approx 8$ eV.
- **Semiconductor**: Moderate number of electrons, typically in the order of $10^{15}$ to $10^{17}$ cm⁻³. The energy gap is moderate, as seen in Si with $E_g = 1.12$ eV.
- **Metal**: High number of electrons, typically in the order of $10^{22}$ cm⁻³. The energy gap is small or nonexistent, as seen in Ge with $E_g = 0.66$ eV.

Thermal excitation is relatively easy in metals and moderate in semiconductors, but much less so in insulators.
Range of conductivities exhibited by various materials.

Metals, Semiconductors, and Insulators

Range of conductivities exhibited by various materials.

- **Insulators**
  - Many ceramics
  - Alumina
  - Diamond
  - Inorganic Glasses
  - Mica
  - Polypropylene
  - PET
  - PVDF
  - Soda silica glass
  - Borosilicate
  - As$_2$Se$_3$
  - Amorphous

- **Semiconductors**
  - Pure SnO$_2$
  - Intrinsic Si
  - Intrinsic GaAs

- **Conductors**
  - Degenerately doped Si
  - Alloys
  - Te
  - Graphite
  - NiCrAg

**Conductivity (Ωm)$^{-1}$**

- $10^{-18}$
- $10^{-15}$
- $10^{-12}$
- $10^{-9}$
- $10^{-6}$
- $10^{-3}$
- $10^0$
- $10^3$
- $10^6$
- $10^9$
- $10^{12}$
Valence band, conductance band

- **Valance band** – these electrons form the chemical bonds
  - almost full
- **Conductance bend** – electrons here can freely move
  - almost empty
Conductors and insulators

For Si: $W_g = 1.12 \text{ eV}$

For SiO$_2$: $W_g = 4.3 \text{ eV}$
Energy Band Formation

- Energy band diagrams.

N electrons filling half of the 2N allowed states, as can occur in a metal.

A completely empty band separated by an energy gap $E_g$ from a band whose 2N states are completely filled by 2N electrons, representative of an insulator.
Allowed electronic-energy-state systems for metal and semiconductors.

States marked with an “X” are filled; those unmarked are empty.
In a metal the various energy bands overlap to give a single band of energies that is only partially full of electrons.

There are states with energies up to the vacuum level where the electron is free.
Electron motion in an allowed band is analogous to fluid motion in a glass tube with sealed ends; the fluid can move in a half-filled tube just as electrons can move in a metal.
Electron Motion in Energy Band

No fluid motion can occur in a completely filled tube with sealed ends.
Energy Band Formation

Energy band diagrams.

Energy-band diagram for a semiconductor showing the lower edge of the conduction band $E_c$, a donor level $E_d$ within the forbidden gap, and Fermi level $E_f$, an acceptor level $E_a$, and the top edge of the valence band $E_v$. 
Electron Motion in Energy Band

- Fluid analogy for a semiconductor

- No flow can occur in either the completely filled or completely empty tube.

- Fluid can move in both tubes if some of it is transferred from the filled tube to the empty one, leaving unfilled volume in the lower tube.
The electron potential energy \([PE, V(x)]\), inside the crystal is periodic with the same periodicity as that of the crystal, \(a\).

Far away outside the crystal, by choice, \(V = 0\) (the electron is free and \(PE = 0\)).
Energy Band Diagram

- *E*-k diagram, Bloch function.

\[ \frac{d^2 \Psi}{dx^2} + \frac{2m_e}{\hbar^2} [E - V(x)] \cdot \Psi = 0 \]

V(x) = V(x + ma) \quad m = 1, 2, 3, ... 

Schrödinger equation

Periodic Potential

\[ \Psi_k(x) = U_k(x) e^{ikx} \]

Periodic Wave function

**Bloch Wavefunction**

- There are many Bloch wavefunction solutions to the one-dimensional crystal each identified with a particular *k* value, say *kn* which act as a kind of quantum number.

- Each \( \phi_k(x) \) solution corresponds to a particular *kn* and represents a state with an energy \( E_k \).
The \( E-k \) curve consists of many discrete points with each point corresponding to a possible state, wavefunction \( \Psi_k (x) \), that is allowed to exist in the crystal.

The points are so close that we normally draw the \( E-k \) relationship as a continuous curve. In the energy range \( E_v \) to \( E_c \) there are no points \( [\Psi_k (x), \text{solutions}] \).
In GaAs, the minimum of the CB is directly above the maximum of the VB, direct bandgap semiconductor.

In Si, the minimum of the CB is displaced from the maximum of the VB, indirect bandgap semiconductor.

Recombination of an electron and a hole in Si involves a recombination center.
Direct and indirect-band gap materials:

- For a **direct-band gap material**, the minimum of the conduction band and maximum of the valance band lies at the same momentum, \( k \), values.

- When an electron sitting at the bottom of the **CB** recombines with a hole sitting at the top of the **VB**, there will be no change in momentum values.

- Energy is conserved by means of emitting a photon, such transitions are called as radiative transitions.
For an indirect-band gap material; the minimum of the CB and maximum of the VB lie at different k-values.

When an $e^-$ and hole recombine in an indirect-band gap s/c, **phonons** must be involved to conserve momentum.

**Phonons**
- Atoms vibrate about their mean position at a finite temperature. These vibrations produce vibrational waves inside the crystal.
- Phonons are the quanta of these vibrational waves. Phonons travel with a velocity of sound.
- Their wavelength is determined by the crystal lattice constant. Phonons can only exist inside the crystal.
The transition that involves phonons without producing photons are called *nonradiative (radiationless) transitions*.

These transitions are observed in an *indirect band gap* semiconductors and result in *inefficient photon producing*.

So in order to have efficient LED’s and LASER’s, one should choose materials having *direct band gaps* such as compound semiconductors of GaAs, AlGaAs, etc...