

Chapter 1: Fundamentals Properties of Nanomaterials

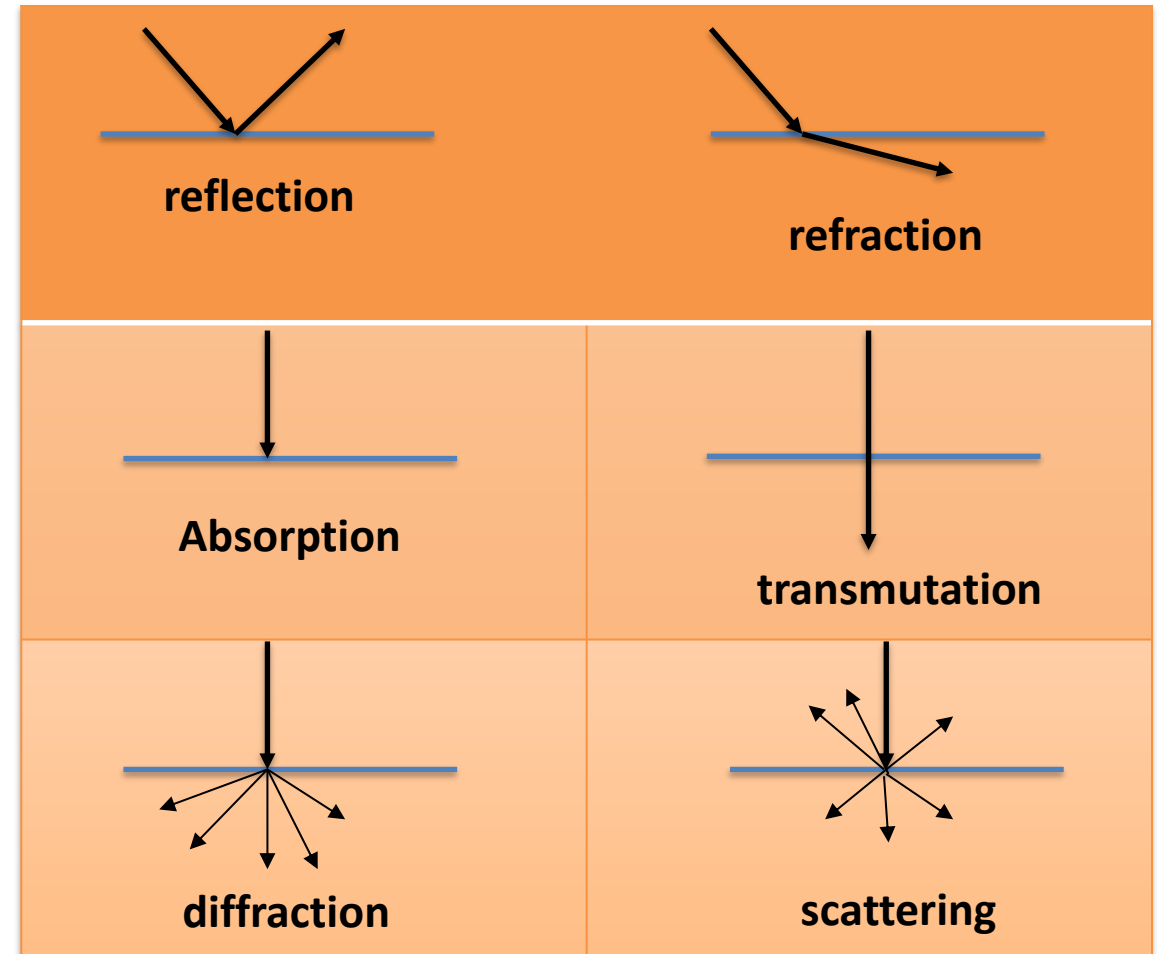
By

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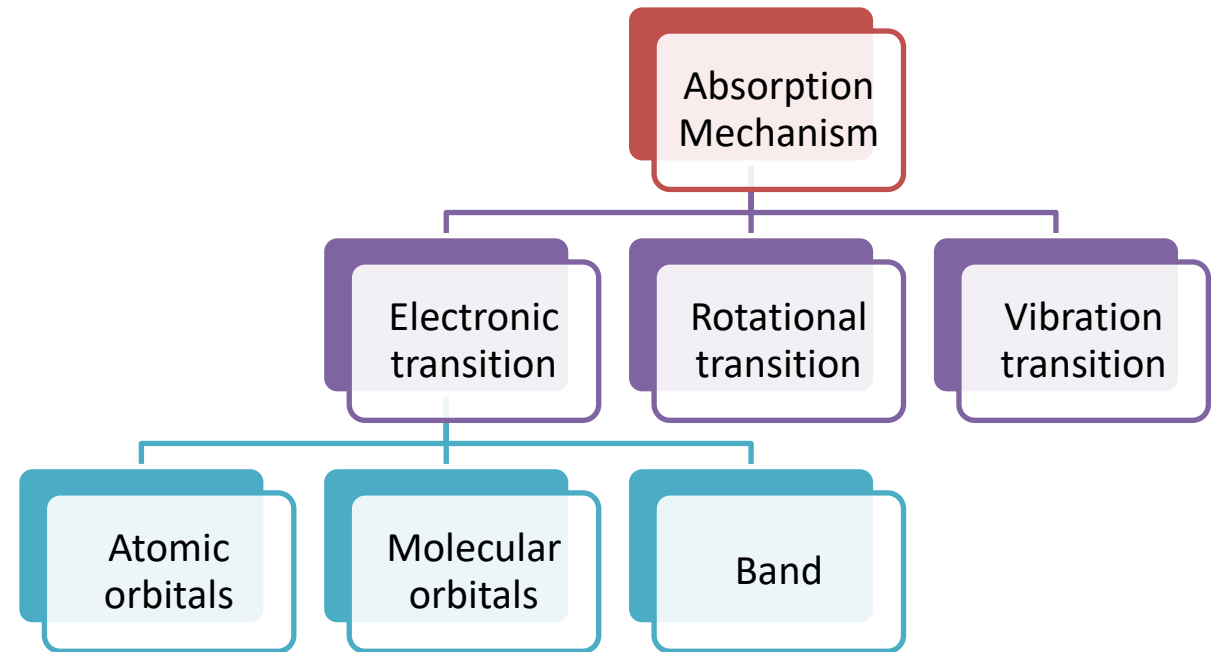
Optical properties of Nanomaterials

- A strong relationship exists between the optical properties and the electrical and electronic characteristics of the material. However, other variables also emerge when addressing optical characteristics. Optical qualities often pertain to the interaction between electromagnetic radiation and matter. One can start with a simple picture by considering a 'ray' of an electromagnetic wave of a single frequency entering a medium from the vacuum. This light may be reflected, transmitted (refracted), or absorbed. The reflection may be either specular or diffuse.



Optical properties of Nanomaterials

- **Absorption** fundamentally entails initiating a process within the material that elevates it to an **excited state** from its **ground state**. The processes include:
(i) electronic, (ii) vibrational, and (iii) rotational excitations.



Optical properties of Nanomaterials

- **Transmission** can occur in two distinct manners:

- I. if the medium is sparse, the ray (wave) could pass through the particles of the medium (like in vacuum), which essentially means there is no interaction.
- II. but the more common mechanism for 'denser media' is 'forward scattering' (i.e. what we call transmission in common usage is forward scattering).

- When a wave transitions from one medium (such as a vacuum) to another, its frequency remains unchanged while its velocity diminishes (the wave travels more slowly in the medium). The ratio of the velocities c to v medium is referred to as the refractive index (n):

$$n = \frac{c}{v} = \sqrt{\frac{\epsilon\mu}{\epsilon_0\mu_0}} = \sqrt{K_E K_M}$$

Here, ϵ denotes the permittivity of the media, while μ signifies the medium's permeability. The subscript 'o' denotes these values in a vacuum. K_E denotes the relative permittivity (dielectric constant), while K_M represents the relative permeability of the medium.

$$K_E = \frac{\epsilon}{\epsilon_0}, \quad K_M = \frac{\mu}{\mu_0}$$

Optical properties of Nanomaterials

- Typically, K_M approximates unity. Kinetic energy is a function of the frequency of the electromagnetic wave and results in dispersion phenomena.
- The dependence of 'n' on frequency originates from three factors:
 - (i) **orientational polarization**
 - (ii) **electronic polarization**
 - (iii) **ionic polarization**
 - (iv) **space charge**
- The refractive index (n) is typically more than one ($n > 1$), but it can, under specific conditions, be less than one ($n < 1$) or even negative ($n < 0$).
- In negative refractive index materials (or typically structures) the refracted beam (in the medium) will be on the other side of the normal.

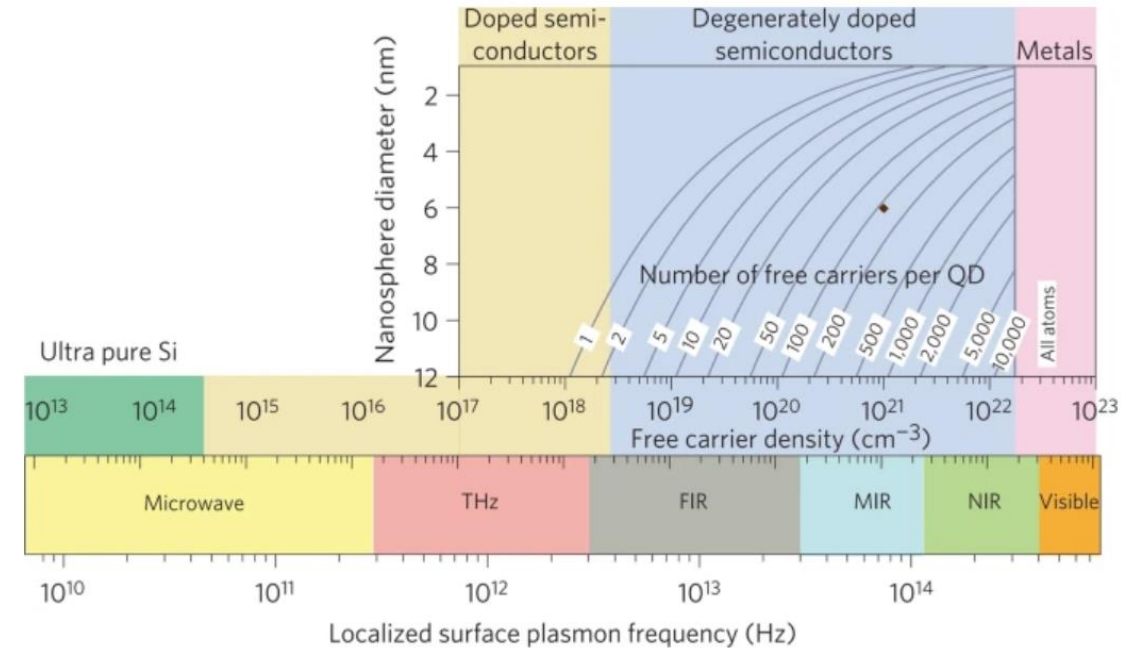
Optical properties of Nanomaterials

- **Diffraction** is an important type of scattering relevant to materials research. Diffraction is defined as 'coherent reinforced scattering' and occurs in periodic and quasiperiodic formations. The incoming 'coherent beam' (now believed to be monochromatic) redistributes its energy in space as 'transmitted' and diffracted beams. The emitted beam, in this instance, is a forward-diffracted beam.
- While our discussions have focused on electromagnetic waves, phenomena like **scattering and diffraction** apply to all wave types. Young's double slit experiment conducted in a ripple tank (utilising water as the medium) exemplifies scattering and interference, excluding electromagnetic radiation.

Optical properties of Nanomaterials

- **Absorption in metals**

- ❑ The interaction between conduction electrons in a metal and incoming photons generates **plasmons**.
- ❑ A plasmon is defined as a quantum oscillation of the free electron cloud relative to the stable positive ions in a metal, whereas those limited to surfaces and exhibiting strong interactions with light are referred to as surface plasmons.



Yu et al., npj Computational Materials volume, 45 (2019)

Optical properties of Nanomaterials

- **Absorption in semiconductors**

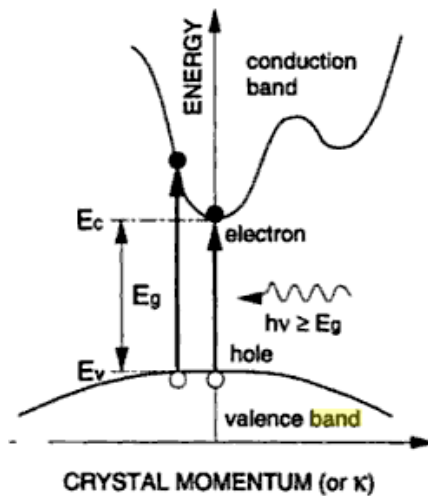
Semiconductors have several optical absorption processes, such as:

- ❖ fundamental absorption
- ❖ free carrier absorption
- ❖ absorption by the energy levels in the band gap.
- When light with more energy than the band gap shines on a semiconductor, it absorbs light fundamentally. This moves electrons from the valence band into the conduction band. Holes are made during the process.

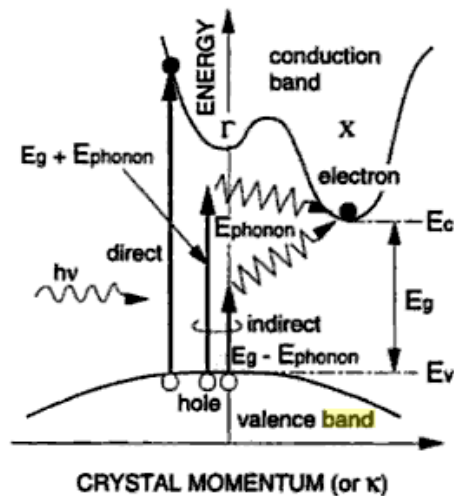
- Because of the amount of impurities inside the band gap, other types of absorption happen. During this process, electrons move from one impurity level to another, from a donor level to the conduction band, from a valence level to an acceptor level, and so on.
- Large absorption and reflection in the infrared range are seen in ionic crystals. This is because light interacts with optical phonons. IR waves can be absorbed and reflected by compound semiconductors like GaAs, GaP, and others. Their bonds are partly ionic. If the photon's energy is higher than the band gap, it can be taken in.

Optical properties of Nanomaterials

- There are two types of absorption in semiconductors: **direct and indirect**.
- In **indirect** bandgap semiconductors, photons and phonons must absorb the phonon energy $\sim 0.05\text{eV}$. They can be ignored; hence, they can be thought of as contributing only momentum to the electron.



direct



Indirect

Optical properties of Nanomaterials

- The band gap in the optical band
The following relationships can be used to estimate the E_g of both direct and indirect semiconductors:

$$\alpha = A(h\nu - E_g)^{1/2}$$

$$\alpha = B(h\nu - E_g \pm E_{phonon})^2$$

- where A and B are constants, $h\nu$ is the energy of the illuminating photon, and E_{phonon} is the phonon energy. For the direct band gap, E_g , which can be calculated from the linear portion of the curve, is extrapolated to $(\alpha h\nu)^2 = 0$ when $(\alpha h\nu)^2$ is plotted as a function of $h\nu$.

Optical properties of Nanomaterials

- **Exciton**

It is a state in which an electron and a hole are joined together. The binding happens because of electrostatic (Coulomb) pull; the exciton has less energy than the electron-hole that is not bound. The Bohr radius increases as this gets the energy levels closer to the conduction band. This kind of quasiparticle doesn't carry electricity and can be found in insulators and semiconductors.

- The exciton is a basic form of excitement in materials that can move energy without moving electric charge.
- The free exciton (Mott-Wannier) can move in the crystal. An exciton trapped by an impurity is a bound exciton (which has a higher binding energy than a free exciton).

Optical properties of Nanomaterials

- The effective reduced mass of exciton ($\mu_{exciton}^*$):

$$\mu_{exciton}^* = \frac{m_e^* m_h^*}{m_e^* + m_h^*}$$

Where $m_e^* m_h^*$ are effective mass of electron and hole, respectively.

- The exciton binding energy for most semiconductors is in the range of few to few 10s of meV.

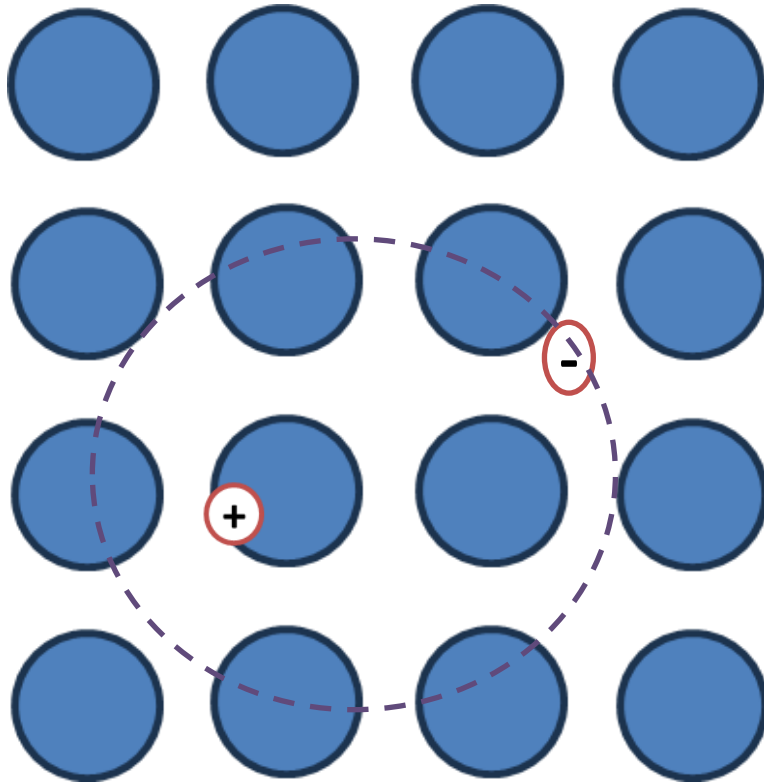
□ Exciton has a small energy value and is dissociated by thermal energy at RT. Exciton diameter can be calculated as:

- $$r_{Bohr}^{Exciton} = \frac{\epsilon r_B m_e [1 + (m_e^*/m_h^*)]}{\epsilon_0 m_h^*}$$
- $$r_{Bohr}^{Exciton} = \frac{\epsilon \epsilon_0 h^2}{\pi \mu e^2}$$

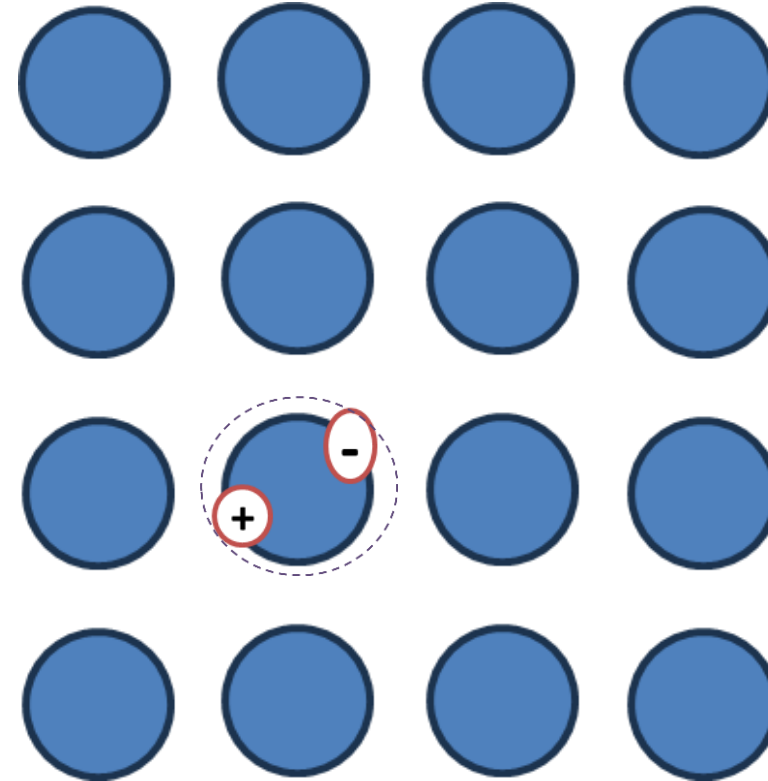
Where r_B , ϵ , ϵ_0 , m_e are Bohr radius in the absence of exciton, dielectric of constant in medium and at free space and mass of free electron, respectively

Optical properties of Nanomaterials

Types of Excitons



Wannier-Mott excitons



Frenkel excitons

THANK YOU

