Advanced Reading

*Optical Properties and Spectroscopy of Nanomaterials*

Jin Zhong Zhang

Many of the optical properties are closely related to the electrical and electronic properties of the material. But as we shall see other factors also come into the picture when dealing with optical properties.

When one is talking about optical properties, one is usually referring to the interaction of electromagnetic radiation with matter. The simple picture one can start with is by considering a 'ray' of an electromagnetic wave of a single frequency entering a medium from vacuum. This ray could be reflected, transmitted (refracted) or absorbed.

The reflection could be specular or diffuse.
From a more fundamental perspective, there are only two possibilities (of interaction of a medium with electromagnetic radiation):

(i) scattering &
(ii) absorption

If one considers a wider spectrum of frequencies, then some part of the spectrum could be absorbed while the other frequencies could be scattered.
Absorption essentially involves activating some process in the material to take it to an excited state (from the ground state). These processes are: (i) electronic, (ii) vibrational and (iii) rotational excitations.

Further part of the absorbed energy could be re-emitted.

If the absorbed energy is dissipated as heat, this is called dissipative absorption.
When an electromagnetic wave impinges on an atom (or a material containing an atomic species), the electron cloud is set into oscillation. This situation is like a dipole oscillator, which emits radiation of the same frequency in all directions. This is the process of scattering. Similar to absorption, scattering is also frequency dependent.

There are two possible ways in which transmission can take place:

(i) if the medium is sparse, the ray (wave) could just 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 as transmission in common usage is actually forward scattering).

When a wave is being transmitted form one medium (say vacuum) to another, its frequency remains constant, but its velocity decreases (the wave being slower in the medium). The ratio of the velocities $c/v_{\text{medium}}$ is called the refractive index ($n$):

$$n = \frac{c}{v} = \sqrt{\frac{\varepsilon \mu}{\varepsilon_0 \mu_0}} = \sqrt{K_E K_M}$$

$$K_E = \frac{\varepsilon}{\varepsilon_0}$$

$$K_M = \frac{\mu}{\mu_0}$$

Where, $\varepsilon$ is permittivity of the medium and $\mu$ is the permeability of the medium. The subscript '0' refer to these values in vacuum. $K_E$ is the relative permittivity (dielectric constant) and $K_M$ is the relative permeability of the medium.
- Usually $K_M$ is close to unity. $K_E$ is a function of the frequency of the electromagnetic wave and leads to the phenomenon of dispersion (e.g. dispersion of white light by a prism into 'VIBGYOR' colours).

- Physically, the origin of the dependence of 'n' on frequency is due to three factors:
  (i) orientational polarization
  (ii) electronic polarization
  (iii) ionic polarization
  (iv) space charge.
- Usually the refractive index (n) is greater than one (n > 1), but under certain circumstances it can be less than one (n < 1) or even be negative (n < 0).

- n < 1 implies that light is traveling faster than speed of light which is in 'apparent' contradiction to the theory of Relativity.
  - In cases where n < 1, the velocity which one needs to consider (instead of the 'phase velocity') is the 'group velocity (v_g)' (or in still other cases the 'signal velocity' (v_s)), which will be less than 'c'. [i.e. causality will not be violated!].

- In negative refractive index materials (or typically structures) the refracted beam (in the medium) will be on the other side of the normal.
A special kind of scattering of importance to materials science is diffraction. Diffraction is nothing but 'coherent reinforced scattering' and comes into play in periodic and quasiperiodic structures. The incoming 'coherent beam' (assumed monochromatic for now) energy is redistributed in space as 'transmitted' and diffracted beams. The transmitted beam in this case is a forward diffracted beam. If there are an array of scatters (1D) with spacing 'a', a schematic of dominant regimes of the three possible outcomes which can take place.

Though in our discussions here we have considered EM waves, phenomena such as scattering and diffraction are true for all kinds of waves. Young's double slit experiment performed in a ripple tank (with water as the medium) is a good example of scattering and interference, which does not involve EM radiation.
Colour can arise from various mechanisms as outlined below.

- **Absorption/emission**
  - Atomic electronic transitions can give rise to colour: yellow colour of sodium in flame test

- **Reflection/Transmission**

- **Scattering**
  - Blue sky

- **Dispersion**
  - Prism

- **Interference**
  - Oil films on water, CD, Butterfly wing

- Atomic electronic transitions can give rise to colour: yellow colour of sodium in flame test
Plasmons (akin to phonons for lattice vibrations) are collective oscillations of free electrons. Bulk plasmons are longitudinal oscillations of electrons gas w.r.t. the ion cores. Incoming visible electromagnetic radiation sets up plasmon oscillations and hence is absorbed (bulk metals are opaque in the visible region).
Three (two, sub-divided into three) frequency regimes can be identified for interaction of EM radiation with metals.

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>Pt</th>
<th>Al</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_p \ (10^{15} \text{/s})$</td>
<td>2.18</td>
<td>1.24</td>
<td>3.57</td>
<td>2.18</td>
</tr>
</tbody>
</table>

- $\tau$ → time between two consecutive collisions. $\tau \sim 10^{-14} \text{s}$.
- $1/\tau$ → probability of an electron suffering a collision/unit time

1) Low frequency range ($\omega \tau < 1$) → beam penetrates the metal for a short distance $\delta$ (skin depth) below the surface. (for Cu at $\omega = 10^7 \text{/s}$, $\delta = 100\mu$) → absorbed (& reflected)

2) High frequency range ($\omega \tau >> 1 \rightarrow$ visible and ultraviolet range)
   - a) $\omega < \omega_p$ → reflection
   - a) $\omega > \omega_p$ → metal becomes a non-absorbing transparent dielectric

$\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_{\text{Lattice}} m^*}}$
Ionic crystals show strong absorption and reflection in the IR region (due to interaction of light with optical phonons). Compound semiconductors (GaAs, GaP etc.) have a partial ionic character to their bond and exhibit absorption and reflection in the IR.

If energy of the incoming photon is greater than the band gap then the photon can be absorbed. $\hbar \nu > E_g$ $\nu_0 = E_g / \hbar$ is known as the absorption edge.

As the wave vector of a photon in the optical region is very small (only constant momentum transfers are allowed across the bandgap) → vertical transitions in k-space are allowed (valence to conduction band).

As the bandgap in semiconductors is $\sim 1\text{eV}$ the fundamental edge occurs in the IR.

In indirect bandgap semiconductors both photon and phonon needs to be absorbed (the phonon energy $\sim 0.05\text{eV}$ and can be ignored and hence it can be thought of as contributing only momentum to the electron).
Exciton

- Exciton is a bound state of an electron and hole. The binding is due to electrostatic (Coulomb) attraction → the exciton has lower energy than the unbound electron + hole.
- This brings the energy levels closer to the conduction band (and the Bohr radius increases)
- It is an electrically neutral quasiparticle that exists in insulators and semiconductors.
- The exciton can be considered as an elementary excitation in materials which can transport energy without transporting electric charge (excited state can travel through lattice without transfer of charge). [The free exciton (Mott-Wannier) can move in the crystal. Exciton trapped by an impurity is a bound exciton (has a higher binding energy than free exciton)].

The effective reduced mass of exciton ($\mu$):

\[ \mu_{\text{exciton}}^* = \frac{m_e^* m_h^*}{m_e^* + m_h^*} \]

For GaAs: $\mu_{\text{exciton}}^* = 0.059 m_e$ (this is much smaller than the free electron mass $m_e$)

- $m_e^*$ → effective mass of electron
- $m_h^*$ → effective mass of hole
Photon absorption by a semiconductor can lead to the formation of an exciton. The exciton binding energy for most semiconductors is in the range of few to few 10s of meV (milli-electron volts) \( E_{\text{exciton}}^{\text{(GaAs)}} = 4.6 \text{ meV}, \ E_{\text{exciton}}^{\text{(CdS)}} = 28 \text{ meV} \).

For comparison:
- the binding energy of \( \text{H}_2 \) atom is 13.6 eV and
- \( kT \) at room temperature is 40 meV.

Given the small value of \( E_{\text{ex}} \to \) an exciton can be dissociated by thermal energy at RT.

The exciton spectrum has a sharp line, just below the fundamental edge → usually observed at low temperature where thermal energy is lower than the binding energy.
The exciton diameter can be calculated as:

\[ r_{\text{Exciton}}^{\text{Bohr}} = \frac{\varepsilon r_B m_e [1 + (m_e^*/m_h^*)]}{\varepsilon_0 m_e^*} \]

\[ r_{\text{Exciton}}^{\text{Bohr}} = \frac{\varepsilon_0 \varepsilon \hbar^2}{\pi \mu e^2} \]

- \( r_B \) → Bohr radius in the absence of exciton
- \( \varepsilon \) → dielectric constant of the medium
- \( \varepsilon_0 \) → dielectric constant of free space
- \( m_e \) → mass of free electron
- \( m_e^* \) → effective mass of electron
- \( m_h^* \) → effective mass of hole

Exciton radius has nanoscale dimensions

<table>
<thead>
<tr>
<th>Material</th>
<th>Exciton energy (meV)</th>
<th>Exciton radius (nm)</th>
<th>Band-Gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>4.6</td>
<td>~11.8</td>
<td>1.43</td>
</tr>
<tr>
<td>CdSe</td>
<td>~5</td>
<td></td>
<td>1.74</td>
</tr>
<tr>
<td>CdS</td>
<td>28</td>
<td>~3 (2.4)</td>
<td>2.58</td>
</tr>
</tbody>
</table>

Hydrogen atom ground state: 13.6 eV

- If the dimension of the crystal ~ of the exciton diameter (or less)
  → confinement effects become prominent.
Optical Properties of Nanomaterials
Size effect on optical properties

- Bulk metal samples absorb electromagnetic radiation (say visible region). Thin films of metals may partially transmit, just because there is insufficient material to absorb the radiation. Au films few 10s of nm thick become partially transparent.
- Apart from ‘insufficient material’ effects, there are important phenomena which come into play in nanomaterials.
- These include: dominance of surface plasmons, quantum confinement effects, etc.
- E.g. in semiconductor quantum dots optical absorption and emission shift to the blue (higher energies) as the size of the dots decreases.
- The size reduction is more prominent in the case of semiconductors as compared to metals (i.e. quantum size confinement effects become more important in metals at smaller sizes than semiconductor crystals).
- We have already seen that at very small sizes metal nanoparticles can develop a bandgap (can become a semiconductor or insulator).
On decreasing the size the electron gets confined to the particle (confinement effects) leading to:
(i) increase in bandgap energy and
(ii) band levels get quantized (discrete).
Surface states (trap states), which lie in the bandgap become important → alter the optical properties of nanocrystals.
The energy level spacing increases with decreasing dimension → Quantum Size Confinement Effect
The effective bandgap of particle of radius $R$:

$$
E_g^{\text{effective}}(R) = E_g(\infty) + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\varepsilon R} 
$$

$\Rightarrow$

$R \downarrow \rightarrow E_g^{\text{effective}} \uparrow$

$R \downarrow E_g^{\text{effective}} \uparrow \rightarrow$ this dominates over

$R \downarrow E_g^{\text{effective}} \downarrow$ (Coulombic attraction term)

- $E_g^{\text{effective}} \rightarrow$ effective band gap energy of particle of radius $R$
- $E_g(\infty) \rightarrow$ bulk bandgap
- $\varepsilon \rightarrow$ dielectric constant (bulk)
- $m_e \rightarrow$ mass of free electron
- $m_e^* \rightarrow$ effective mass of electron
- $m_h^* \rightarrow$ effective mass of hole
In nano-GaAs (with size range 7-15 nm) a broad excitonic peak at 526.0 nm (2.36 eV) is seen → energy gap of the nano-GaAs has been blue shifted by 0.93 eV [bulk band gap (1.43 eV)] due to the QSE.

Enhancement of absorbance over the range of wavelengths seen → enhanced oscillator strength (dimensionless quantity to express the strength of the transition).

The excitonic peak is broad due to the size distribution of crystallites.
- With reducing size of the particle the density of states becomes more quantized and the band gap shifts to higher energies (shorter wavelengths) → the absorption spectrum shows a blue shift

Absorption spectra of PbSe nanocrystals

[Graph showing absorption spectra with different sizes (3 nm, 4.5 nm, 5.5 nm, 9 nm) and a blue shift indicated]
Photoluminescence

- In photoluminescence material is excited by EM radiation, followed by relaxation to ground state by emission of photons.
- When the semiconductor relaxes to the ground state by recombination of electron and hole, a photon is emitted.
- If the photon energy lies in the range 1.8 - 3.1 eV the radiation will be in the visible range → luminescence.
- By changing the size of the nanoparticles the frequency of emission can be tailored.
- As the size of the nanoparticles decrease → ‘blue shift’ in frequencies.
Properties of core-shell nanostructures: semiconductor on semiconductor

- The luminescent properties are a characteristic of the core.
- The shell leads to an enhancement of the luminescent properties of the core (the luminescence of nanoparticles are well defined with narrow spectral ranges, which depend on particle size).
- Deposition of a semiconductor with a larger bandgap than that of the core typically results in ‘luminescence enhancement’ due to the suppression of radiationless recombination mediated by surface states.
- E.g. CdS coated with MoS$_4$, ZnSe coated with CdSe, CdSe coated with CdS. Bandgaps tunable in the near-IR, which can be useful as IR biological luminescent markers.
Fluorescence emission of (CdSe)ZnS core-shell quantum dots.

Gold nanoparticles were used as a pigment of ruby-colored stained glass dating back to the 17th century. 1-10 nm sized particles give rise to this colour.

Thin film of Au (~100nm or less) will transmit blue-violet light.

The colour of metallic nanoparticles depends on size in the nanoscale regime.

Bulk Au is ‘golden’ yellow colour. Nanoparticles of gold (colloidal) can have red, purple or blue colour.

The colour depends on the size (& shape) of the particle and the dielectric properties of the medium.

Surface plasmons are excited by incident electromagnetic radiation.

Surface plasmons have lower energy than bulk plasmons which quantize the (or plasma).

MFP of Au, Ag ~50 nm ⇒ for particles smaller than this there will be no scattering within the particle and all the interactions will be with the surface.

In particles with shape anisotropy (e.g. cylinders) more than one type of plasmon absorption peak may be observed.
• For the sphere (d~15nm) only the Transverse plasmon peak is observed (λ~ 520nm).
• If the radius of the sphere is doubled (d~30nm), the transverse plasmon absorption peak will only shift slightly → this is unlike semiconductor nanoparticles where the absorbance is strongly affected by size in the nanoscale.
• For the cylinder both the surface and longitudinal plasmon peaks are observed.
• For the longer cylinder the longitudinal plasmon peak shifts to longer wavelengths.
• Many applications has been envisaged due to large enhancement of surface electric field.
Properties of core-shell nanostructures: metal on dielectric

- In Au shells coated on SiO₂ cores the plasmon band depends on the core radius and on the core to shell ratio.
- Increasing core to shell ratio red-shifts the plasmon resonance band (figure below).

Metamaterials (with negative refractive index)

- Negative index metamaterials (negative index materials) are man made structures where the refractive index has a negative value (typically over some frequency range).
  - So far this has not been discovered in natural materials.
- Metamaterials have been made with negative effective permittivity and permeability.
- A crystal with Magnetic Split Ring Resonator (SRR) as the motif can be used for the construction of a negative refractive index material.
- When the SRR scale is of the order of \( \sim 200 \text{nm} \rightarrow \) negative refractive index can be obtained in the mid-infrared range (100 THz)

\[
n = \pm \sqrt{\varepsilon \mu} \\

n = +\sqrt{(+\varepsilon)(+\mu)} \\

n = -\sqrt{(-\varepsilon)(-\mu)}
\]
SiO₂ shell on various cores have been studied. E.g. Au@SiO₂.

Core shell nanowires have also been prepared. E.g. Ni@TiO₂.

Au@SiO₂: Nanosized gold colloids show a very intense surface plasmon absorption band in the visible (around 520 nm). The exact position of this plasmon band is extremely sensitive both to particle size and shape and to the optical and electronic properties of the medium surrounding the particles. Silica does not exchange charge with the Au particles and hence can be considered inert.

As the shell thickness is increased, there is an increase in the intensity of the plasmon absorption band, as well as a red shift in the position of the absorption maximum (due to the increase in the local refractive index around the particles). At larger shell thicknesses, scattering becomes significant, resulting in a strong increase in the absorbance at shorter wavelengths. This effect promotes a blue shift of the surface plasmon band and a weakening in the apparent intensity of the plasmon band. Eventually at shell thicknesses above 80 nm, the scattering almost completely masks the surface plasmon band.
Properties of core-shell nanostructures: metal on metal

- Examples: Au@Ag, Au@Pb, Au@Sn, Ag@In.
- Metal nanoparticles display very interesting optical and electronic properties.
- These arise due to the collective oscillation of conduction electrons, when interacting with an electromagnetic radiation (of certain frequency).
- Surface plasmon resonance frequency is the relevant property.
- Formation of core-shell structures alters the property of the pure metal.
- E.g.: Pure Au has an plasmon absorption frequency of ~518nm. Silver coating blue shifts and broadens the absorption peak. The peaks shifts to 400nm for sufficiently thick Ag shells.

Coated magnetic nanoparticles

- The shell usually stabilizes the core (also in colloidal form).
- The core gives rise to the relevant properties.
- Fe@Au nanoparticles show superparamagnetic behaviour.
- Fe@Nd shows low coercivities.
Table 2: Included in this table are the plasma frequency $\nu_p$ and the damping frequency $\gamma$ for the Drude model, the measured contact angle $\theta$ and the non-retarded Hamaker constant $H$ between liquid II and the following metallic substrates immersed in liquid I: gold, platinum, silver, aluminium.

From 
**Surface-wetting effects on the liquid–liquid transition of a single-component molecular liquid**

Kenichiro Murata & Hajime Tanaka
*Nature Communications 1*, Article number: 16 | doi:10.1038/ncomms1015

<table>
<thead>
<tr>
<th>Material</th>
<th>$\nu_p (10^{15} s^{-1})$</th>
<th>$\gamma (10^{12} s^{-1})$</th>
<th>$\theta (\circ)$</th>
<th>$H (10^{-22} J)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>2.183</td>
<td>6.46</td>
<td>62±3</td>
<td>18.2</td>
</tr>
<tr>
<td>Platinum</td>
<td>1.244</td>
<td>16.73</td>
<td>76±4</td>
<td>6.97</td>
</tr>
<tr>
<td>Silver</td>
<td>2.18</td>
<td>4.363</td>
<td>76±3</td>
<td>18.1</td>
</tr>
<tr>
<td>Aluminium</td>
<td>3.57</td>
<td>19.79</td>
<td>NW</td>
<td>30.3</td>
</tr>
</tbody>
</table>

Here NW stands for non-wetting.

$\theta$ is the angle between the solid surface and the surface of liquid II.
When an electromagnetic wave impinges on an atom (or a material containing an atomic species), the electron cloud is set into oscillation. This situation is like a dipole oscillator, which emits radiation of the same frequency in all directions. This is the process of scattering. Similar to absorption, scattering is also frequency dependent.

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(i) if the medium is sparse, the ray (wave) could just pass through the particles of the medium (like in vacuum), which essentially means there is no interaction;
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When a wave is being transmitted from one medium (say vacuum) to another, its frequency remains constant, but its velocity decreases (the wave being slower in the medium). The ratio of the velocities $c/v_{\text{medium}}$ is called the refractive index ($n$):

$$\frac{c}{v} = n = \sqrt{\frac{\varepsilon\mu}{\varepsilon_0\mu_0}} = \sqrt{K_E K_M}$$

$$K_E = \frac{\varepsilon}{\varepsilon_0} \quad P = \chi E$$

$$K_M = \frac{\mu}{\mu_0} \quad D = \varepsilon (E + P)$$

$$B = \mu_0 (H + M) \quad \mu = \frac{B}{H}$$

$$\chi = \frac{M}{H}$$

Where, $\varepsilon$ is permittivity of the medium and $\mu$ is the permeability of the medium. The subscript '0' refer to these values in vacuum. $K_E$ is the relative permittivity (dielectric constant) and $K_M$ is the relative permeability of the medium.
- With reducing size of the particle the density of states becomes more quantized and the band gap shifts to higher energies (shorter wavelengths) → the absorption spectrum shows a **blue shift**
- When the particle radius is ~ few times the exciton radius the exciton levels decide the energy levels
- When the dimension of the particle is < exciton radius → exciton ceases to exist.

\[ E_{\text{exciton}} = \left[ -\frac{(13.6 \mu / m_e)}{(\varepsilon / \varepsilon_0)^2 n^2} \right] eV \]

\( n=1 \rightarrow \text{lowest energy ground state} \)

- \( E_{\text{exciton}} \rightarrow \text{exciton binding energy} \)
- \( \varepsilon \rightarrow \text{dielectric constant of the medium} \)
- \( \varepsilon_0 \rightarrow \text{dielectric constant of free space} \)
- \( m_e \rightarrow \text{mass of free electron} \)
- \( m_e^* \rightarrow \text{effective mass of electron} \)
- \( m_h^* \rightarrow \text{effective mass of hole} \)
- \( n \rightarrow \text{quantum number (n = \infty corresponds to unbound state)} \)
Variation of Emission spectra of CdSe quantum dots with size