

CHAPTER 4 : NANO-OPTICS

Study of light-matter interaction at the nanoscale. In other words, how optics phenomena are affected/modified when photons interact with nanoscale objects.

(Reflection, scattering, refraction ($\frac{n_2}{n_1} = \frac{\sin \theta_2}{\sin \theta_1}$), absorption, transmission, diffraction ...)

Is easy to see how nanoscale objects will impose quantum mechanical limits to optical effects. For example, we know the QM diffraction limit due to the Heisenberg uncertainty principle :

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \quad \text{or} \quad \Delta x \Delta k_x \geq \frac{1}{2} \quad (\text{for photons})$$

k is the wave vector

$$\vec{p} = \hbar \vec{k} \quad p = \hbar k = \frac{h\nu}{c} = \frac{h}{\lambda}$$

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

This limit in diffraction has been overcome in advanced optical (microscopy) techniques, such as confocal and near-field microscopy. Raman spectroscopy and multiphoton fluorescence are capable of spatial resolution of 200nm.

4.1. NANOPLASMONICS - SURFACE PLASMONS

In nanoscale clusters (metallic), the number of atoms at the surface is large when compared to the surface/volume ratio in macroscopic objects. In addition, photons mainly interact with electrons which are free (at the surface).

Surface plasmon: The quantum of plasma oscillation, which corresponds to collective oscillations of free electrons at the surface of a metal as a result of their interaction with incident light.

Surface plasmon resonance: when the frequency of oscillation matches the characteristic distance of the nanoparticle, the nanoparticle will resonate, and strong absorption of light will occur.

Size, structure and composition of the nanostructure affects the resonant frequency.

show slides 1

Electric field in an spherical metal nanoparticle surrounded by a dielectric medium (ϵ_0) exposed to light is:

$$E_{\text{sphere}} \propto \left(\frac{\epsilon_m - \epsilon_0}{\epsilon_m + 2\epsilon_0} \right) \lambda$$

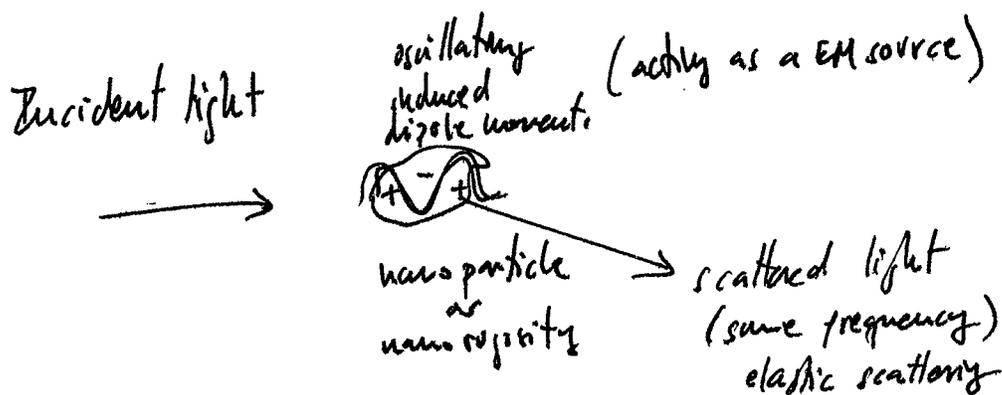
the two is for spherical, and this is the solution from the Drude model (assumes electrons free at the surface, as an electron gas). It is easy to see that when $[\epsilon_m = -2\epsilon_0] \lambda$, the dielectric constant of the metal equals $2\epsilon_0$, the system will be in resonance, i.e., the electric field will be maximum.

This works well for noble metals (Drude is a good approx.) and sizes $< 20\text{nm}$ (above which more complex optics apply)
show slides 2-4

4.2. SCATTERING AT THE NANOSCALE

For larger clusters ($\approx 20 \text{ nm}$), or when the ratio of particle circumference to wavelength is larger than 1, one usually explains scattering through Mie theory. Indeed, scattering phenomena (apart from absorption) gives rise to ~~new~~ new applications of nanomaterials.

For small particles, extinction (of light), is usually ascribed to dipolar oscillations (plasmons), however, as the particle size increases, scattering can also be understood as redirection of light.

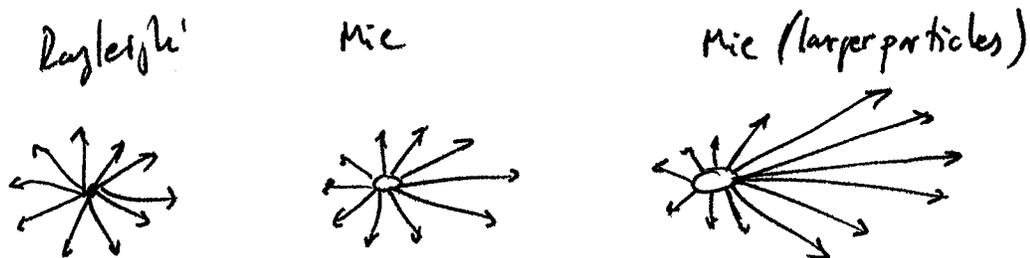


Rayleigh scattering: Molecular phenomena, with size limit $d \leq 0.1 \lambda$. It is elastic (no loss of energy) and the effect is proportional to $1/\lambda^4$ (strongest at high frequencies). Rayleigh scattering is responsible for the blue light of the sky.

This can be used to enhance microscopy techniques. For example, the surface enhanced Raman spectroscopy.

Mie scattering: It dominates when the ~~size~~ size of the particle is large ($d > 1\lambda$)

This scattering produces light patterns like an antenna lobe



Mie theory explains scattering from small to large particles, including Rayleigh scattering and going all the way to classical optics for sufficiently large particles.

4.3. COLORS GENERATED BY NANOMATERIALS show slide 5

* Due to interference: due to constructive interference of waves traveling a given material with small thicknesses.

Example, jewelry made of anodized titanium shows colors due to interference in the oxide coating.

* Due to diffraction: Not need to explain (colors in a CD)

* Due to scattering: sky is blue

* Due to surface plasmons: Lycurgus cup. British museum.
From fifth century Rome. Au and Ag nanoparticles trapped in a some lime NaO glass matrix.

Dichroism: $\begin{cases} \rightarrow \text{reflection} = \text{green} \\ \rightarrow \text{transmission} = \text{red} \end{cases}$

* Due to quantum fluorescence: generated by the size of quantum dots

4.4. QUANTUM DOTS

Although the use of the name has been relaxed and applies to many quantum systems (e.g. gold nanoparticle), formally a quantum dot is a semiconductor of size in the nanoscale. Typically less than 10 nm.

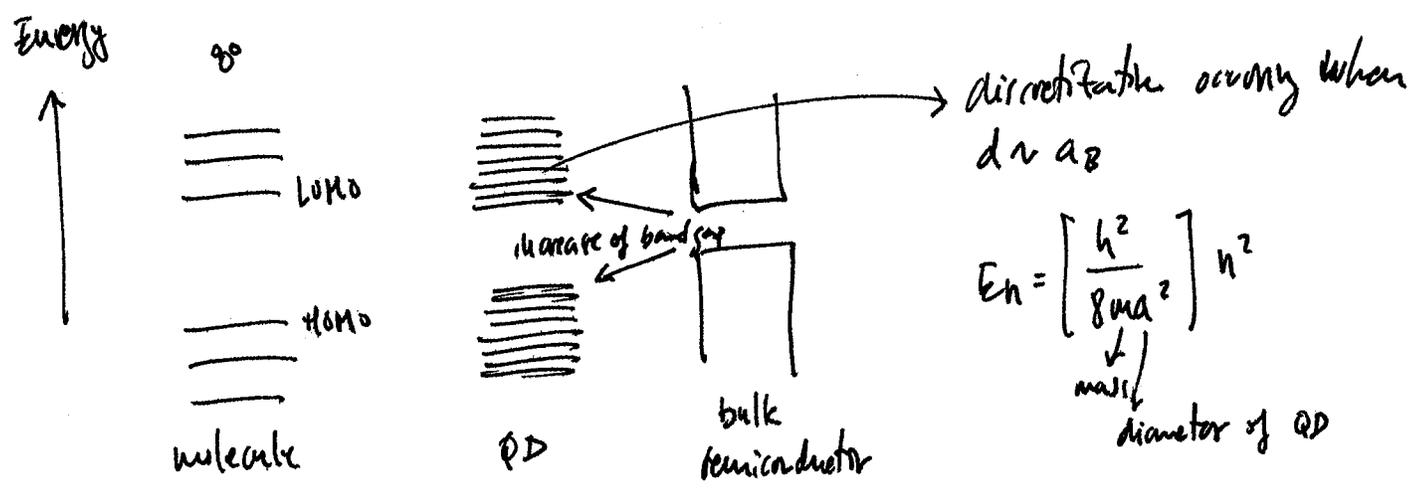
Quantum mechanically, a quantum dot forms when the size of the semiconductor is smaller than the Bohr excitation radius in all three dimensions, such that carriers in the VB and CB are restricted when moving.

The Bohr excitation radius

An exciton in a semiconductor is the quanta of collective hole-electron excitations in the VB and CB. An exciton has an associated spatial separation between the hole and the electron which depends on the material (Bohr exc. radius)

$$a_B = \frac{4\pi\epsilon_0\epsilon_r\hbar^2}{m_0e^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]$$

↓
effective mass of the electron-hole pair



Tuning the gap in a QD

Emission from transitions between levels in the CB to the VB can be easily tuned by varying the size of the quantum dot, from ultraviolet (small dots) to infrared (large dots)

For example,

ZnS (bulk) \rightarrow bandgap = 3.6 eV

ZnS (QD) \rightarrow bandgap up to 4.5 eV (1-4 nm)

Bandgap energy of a QD

$$E_g = E_g(\text{bulk}) + \frac{3\epsilon_0\epsilon_r\hbar^2\pi^2}{2a^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]$$

Dopants can also be used to change the emission frequency

Applications

- Nonlinear optical devices
- Photo- and electro-luminescent materials
- Fluorophores in biolabeling, medical imaging, etc
- Enhanced microscopy

4.5. NANOPHOTONICS

Photonics: "Technology of generating and harnessing light (EM) and other forms of radiant energy whose quantum unit is the photon" therefore, photonics is the study of light-matter interaction, not just the study of light, with the goal of building applications. Started with the invention of the laser and the optic fiber. It is now enormous!

In 1987, Yablonovitch (Bell labs) created an array of 1- μ m holes in a material with refractive index 3.6, which prevented microwaves from propagating in any direction. "Photonic bandgap"

microwaves \sim mm
optical light \sim nm

↓
as electron waves in natural crystals
Therefore, solid state theory should be applicable to "photonic crystals"

[solid state theory: Brillouin zones, reciprocal space, dispersion relations, Bloch wave func.]

Photonic structures in nature: Discuss the blue butterfly morpho, the wing of the butterfly contains veins that are assembled in structures (complicated) of characteristic size \sim 500-600nm. In other words, the color is not dependent on pigments to become visible in animals with so-called "structural interference colors".

[constructive interference]

Photonic crystals: Periodic structures made of dielectric materials that interact with radiation resonantly at wavelengths related to the periodicity of the structure.

Used to control the propagation of light waves (equivalent to semiconductors)

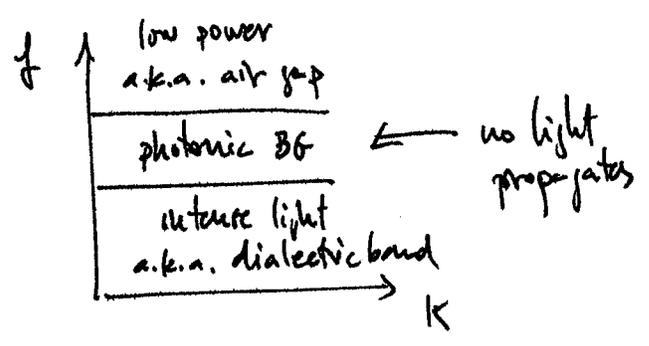
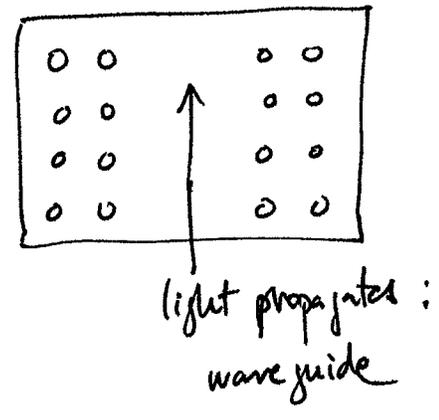
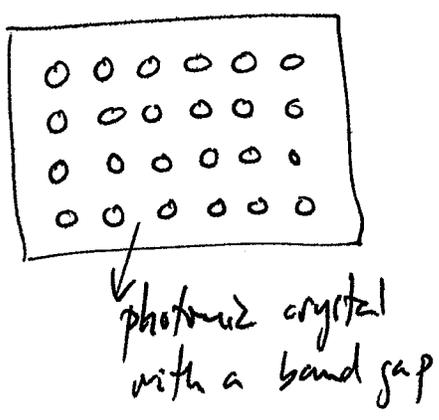
" they share a band gap with semiconductors "

Photonic bandgap: A range of wavelengths within which there is no absorption or propagation of light (EM is forbidden)

The PBG is determined by:

- radius of holes (or other features, like rods...)
- periodicity of holes
- lattice structure
- thickness of material
- Refractive index

show slides 10-13



Applications of photonic crystals

Devices aimed at controlling the flow of radiation.

- dielectric mirrors for antennas
- micro resonators
- controlled miniaturization
- pulse sculpting
- filters
- ~~transparent~~ LEDs