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DSE3T (Nano Materials and Applications)

Topic – Optical Properties (Part – 3)

We have already discussed part 2 of this e-report.

Now let us continue part 3 of it.

Radiative Processes, General Formulation:

In this e-report, we describe the general basis to calculate the optical properties and the radiative processes of nanostructures when their electronic structure is known. If the formalism of the electron-photon interaction in condensed matter is well-known and has been subject of considerable body of literature, our aim here is to insist on difficulties which are specific to nano-size objects. Taking into account that the diversity of possible physical situations does not allow to make a synthetic review of the problems, we consider in the following the particular case of semiconductor nanocrystals embedded in a dielectric matrix (Fig. 1), which is a common experimental situation. If the host material is a good insulator with a large optical gap, the study of the optical properties of the composite material within the insulator gap allows probing transitions between quantized levels of the nanocrystals. The main tools of optical characterization are absorption, emission and photoluminescence experiments.

Optical Absorption and Stimulated Emission:

We consider an optical absorption experiment made on the sample depicted in Fig. 1. A beam of monochromatic light and of intensity I_0 is irradiated perpendicularly to the sample surface which is supposed to be flat and one measures the intensity I_t of the transmitted light. The electromagnetic field inside the nanocrystals induces the transition of electrons to excited levels by absorption of a photon (Fig. 2(a)). The transition of electrons from excited states to states with lower energy can be non-radiative, (which is not a part of this

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syllabus), or radiative by stimulated emission (Fig. 2(b)) or spontaneous emission (Fig. 2(c)).

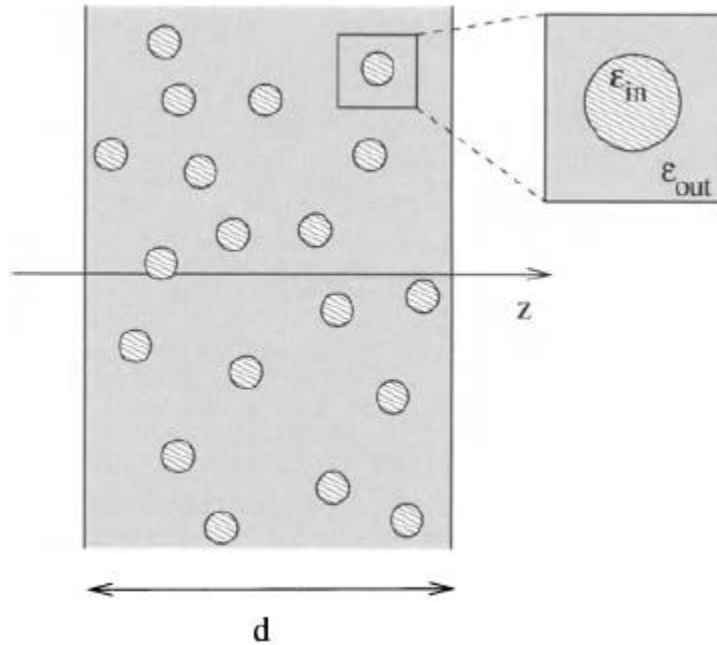


Fig. 1

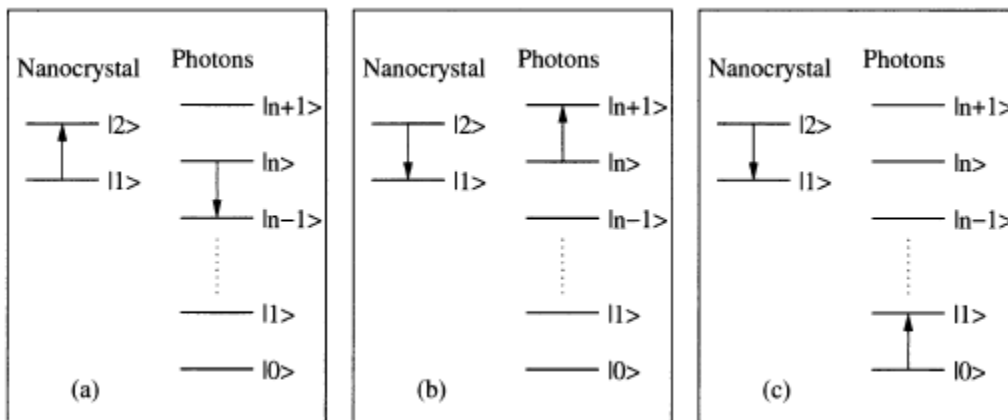


Fig. 2

In absorption, and in stimulated emission, the electronic transitions between the energy levels directly result from the interaction of the electrons with the electromagnetic field in the system. These effects can be treated using a semi-



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classical model, which we present hereafter. The probability of transition of an electron is thus proportional to the intensity of the electromagnetic field inside the nanocrystal. But the field inside a particle is not equal to the field in the surrounding medium of different (and usually smaller) dielectric constant. Local-field effects due to the dielectric confinement may strongly influence the optical properties of the quantum dots. In the general case, there is no simple analytical form to describe the distribution of the field in the system. However, because the size of the nanocrystals is small compared to the photon wavelength ($> 100 \mu\text{m}$), we can define a macroscopic electromagnetic field as an average over a volume large compared to the heterogeneities. With respect to this average field, the composite material is seen as a homogeneous and isotropic material characterized by an effective dielectric constant ϵ_M . Thus it remains to calculate the optical absorption for the macroscopic material as a function of ϵ_M and to relate ϵ_M to the electronic structure of the nanocrystals.

Local-Fields and Density Matrix Formulation. The macroscopic dielectric constant can be calculated using the Maxwell-Garnett effective medium theory. One difficulty is to describe the distribution of the field in the system. However, for some geometrical shapes of crystallites, such as ellipsoids or spheres, the field inside the nanocrystal is uniform (using the fact that the size of the particles is much smaller than the wavelength of the electromagnetic wave) and proportional to the field outside. It is then possible to define a local-field factor F , such that $\vec{E}_{in} = F\vec{E}_{out}$. For simplicity, we consider in the following that all the nanocrystals are spherical and identical. In that case, we have $F = \frac{3\epsilon_{out}}{\epsilon_{in} + 2\epsilon_{out}}$ where ϵ_{in} is the frequency-dependent dielectric constant of a nanocrystal and ϵ_{out} the dielectric constant of the host material (Fig. 1).

The average electric displacement \vec{D} and the average electric field \vec{E} in the composite medium are given by

$$\vec{D} = p\vec{D}_{in} + (1 - p)\vec{D}_{out}$$

$$\vec{E} = p\vec{E}_{in} + (1 - p)\vec{E}_{out}$$

where p is the volume fraction of nanocrystals in the composite medium.

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Near the optical threshold, ε_{out} is real and constant, $\varepsilon''_M \ll \varepsilon'_M$ (where $\varepsilon'_M = n_{op}^2 - K_{op}^2$ and $\varepsilon''_M = 2n_{op}K_{op}$ are the real and imaginary parts of the complex dielectric constant ε_M , with n_{op} as the real refractive index of the sample and K_{op} as the extinction coefficient), so that $n_{op} \approx \sqrt{\varepsilon'_M}$ and the absorption coefficient (α) in the composite medium can be shown as

$$\alpha = \frac{2\omega K_{op}}{c} = \frac{\omega}{cn_{op}} \varepsilon''_M \approx \frac{\omega}{cn_{op}} p F^2 \varepsilon''_{in}$$

It remains to calculate ε_{in} . One conceptual difficulty is how to define a dielectric constant in a nano-size object. We have seen that it is sometimes interesting to define an average quantity over the nanocrystal volume. Here we will work in the same spirit, extending this approximation to non-zero frequency. Once again, we use the fact that the dimensions of the nanostructures are small compared the electromagnetic wavelength. The electric field \vec{E} inside the nanocrystal polarizes the system leading to a total dipole moment \vec{p}_{dip} . Thus we can define the average polarization as $\vec{P} = \frac{\vec{p}_{dip}}{\Omega}$ where Ω is the volume of the nanocrystal and we can deduce the dielectric constant using $\vec{P} = (\varepsilon_{in} - 1)\varepsilon_0\vec{E}$.

The dipole moment \vec{p}_{dip} is induced by the transitions of electrons between the discrete levels of the nanocrystal. To characterize this system, we calculate the statistical density matrix ρ_{ij} in the basis of the eigenstates of the electronic Hamiltonian H_0 in absence of electromagnetic field. In this formulation, a diagonal element ρ_{ii} gives the probability to find the system in the state $|i\rangle$. To simplify the problem, we first consider the case of a nanocrystal with only two electronic levels, the ground state $|1\rangle$ of energy E_1 and the excited state $|2\rangle$ of energy E_2 (Fig. 2). In the presence of the electric field $\vec{E}(t) = \vec{E}_0 e^{-i\omega t}$, the Hamiltonian becomes $H = H_0 + W(t)$ where the perturbation is written in the usual dipolar form $W(t) = e\vec{r} \cdot \vec{E}_0 e^{-i\omega t}$

Using these equations, by the method of density matrix theory, one can obtain the expression of the absorption coefficient. For small values of the volume fraction p , we get

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$$\begin{aligned}\alpha(\omega) &= pF^2 \sum_{i,j} \frac{\pi\omega e^2 |\langle i|\vec{r}\cdot\vec{e}|j\rangle|^2}{cn_{op}\epsilon_0\Omega} \delta(\hbar\omega - \hbar\omega_{ji}) [f_i - f_j] \\ &= C(\omega) [f_i - f_j]\end{aligned}$$

where \vec{e} is the polarization vector of the electric field.

We can also rewrite the previous equation in the following form

$$\alpha(\omega) = C(\omega)f_i(1 - f_j) - C(\omega)f_j(1 - f_i)$$

where the first term correspond to the transition from $|i\rangle$ to $|j\rangle$ (absorption) and the second one to the transition from $|j\rangle$ to $|i\rangle$ (stimulated emission). The strength of the optical coupling between two levels $|i\rangle$ and $|j\rangle$ is often described by a quantity without dimension, the oscillator strength

$$f_{ji} = \frac{2m_0}{\hbar} \omega_{ji} |\langle i|\vec{r}\cdot\vec{e}|j\rangle|^2$$

It is sometimes interesting to write $|\langle i|\vec{r}\cdot\vec{e}|j\rangle|^2$ in terms of the matrix elements of the momentum \vec{p} instead of those of \vec{r} using the relation

$$|\langle j|\vec{p}\cdot\vec{e}|i\rangle| = im_0\omega_{ji} |\langle j|\vec{r}\cdot\vec{e}|i\rangle|$$

Luminescence:

In the previous part, we have seen that the optical absorption and the stimulated emission are induced by the electromagnetic field. In contrast, the spontaneous emission occurs even when there is no photon in the system. It is not described in the previous calculation because the electromagnetic field is treated *classically*. In the following, we shall relate the spontaneous emission to the absorption through the Einstein relationships, which will allow to take into account the local-field effects in a simple manner.

We consider the composite material as a system of two levels in thermal equilibrium in an optical cavity of volume V . The number of photons per unit of energy $\hbar\omega$ in the cavity is given by the *Planck formula* for the black body

$$N = \frac{8\pi(\hbar\omega)^2 n_{op}^3 V}{h^3 c^3} (e^{\hbar\omega/kT} - 1)^{-1}$$

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The effective rate of transition from $|1\rangle$ to $|2\rangle$ per photon and per unit time, i.e. the balance between the absorption and the stimulated emission, is given by

$$P_{12} = \alpha(\omega) \frac{c}{n_{op}}$$

The effective number of transitions from $|1\rangle$ to $|2\rangle$ in the cavity per unit of energy is NP_{12} . At equilibrium, they must be compensated by spontaneous transitions from $|2\rangle$ to $|1\rangle$ whose number per unit of energy is proportional to the mean occupancy f_2 of the level $|2\rangle$. Therefore $NP_{12} = Af_2$.

This relation must be verified at any temperature. At equilibrium, we have

$$\frac{f_2}{f_1} = e^{-\hbar\omega/kT}$$

From this, we obtain $A = \frac{8\pi(\hbar\omega)^2 n_{op}^2 V}{h^3 c^2} C(\hbar\omega)$

To calculate the spontaneous recombination rate $\Gamma_{sp} = \frac{1}{\tau_{sp}}$, we must divide A by the number of nanocrystals in the volume V and we must integrate over the energy, leading to

$$\Gamma_{sp} = \frac{1}{\tau_{sp}} = \frac{\omega_{21}^3 F^2 e^2 |\langle 1|\vec{r}\cdot\vec{e}|2\rangle|^2 n_{op}}{\pi c^3 \epsilon_0 \hbar}$$

In this calculation, we have implicitly assumed that the absorption is isotropic.

Optical Properties of Heterostructures and Nanostructures:

In this section, we deal with the optical absorption of systems with reduced dimensionality based on direct gap semiconductors, particularly for quantum wells. We mainly describe the systems in the effective mass approximation for the envelope functions, considering one-particle and excitonic transitions. We only consider the effects of the electronic structure, discarding all the proportionality constants such as the local-field factor etc.

We write the absorption coefficient as

$$\alpha(\omega) \propto \frac{1}{\omega} \sum_{i,f} |\langle i|\vec{e}\cdot\vec{p}|f\rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

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where the sum is over the (final) empty states $|f\rangle$ and the (initial) occupied states $|i\rangle$ ($T \rightarrow 0$ K). Here the wave function of the initial state has the following form $\psi_i(\vec{r}) = u_{b_i}(\vec{r})\phi_i(\vec{r})$ where $u_{b_i}(\vec{r})$ is the periodic part of the *Bloch functions* at the Brillouin zone centre for the band b_i and $\phi_i(\vec{r})$ is the envelope function. A similar expression holds for the final state as well. The optical matrix element is given by

$$\langle i|\vec{e}\cdot\vec{p}|f\rangle \approx \vec{e}\cdot\langle u_{b_i}|\vec{p}|f u_{b_f}\rangle \int \phi_i^* \phi_f d\vec{r} + \delta_{b_i b_f} \vec{e}\cdot \int \phi_i^* \vec{p} \phi_f d\vec{r}$$

In the following, we consider two categories of optical transitions:

- (1) *Interband transitions* that occur between states originating from different bands ($b_i =$ valence, $b_j =$ conduction) where the optical matrix element reduces to the first term in the previous equation.
- (2) *Intraband transitions* ($b_j = b_i$) involving the dipole matrix elements between envelope functions, the second term in the previous equation.

Interband Transitions:

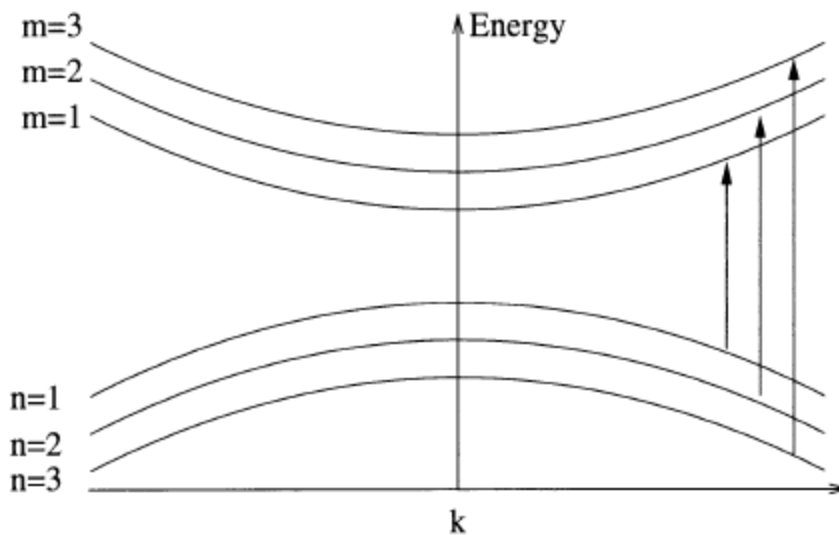


Fig. 3



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Interband Transitions in Quantum Wells. We start with transitions between single particle states. We have seen in that the confinement in the z direction leads to the formation of subbands starting at discrete energies and having a free dispersion in the x and y directions (Fig. 3). The envelope function for the initial state (hole state, with superscript h) is

$$\phi_i(\vec{r}) \propto e^{i\vec{k}^{(h)} \cdot \vec{p}} \chi_n^{(h)}(z)$$

with the same expression holding for the final state (electron state with superscript e). Once again, only vertical transitions are possible, therefore $\vec{k}^{(h)} = \vec{k}^{(e)}$. Thus the optical matrix element becomes approximately

$$\vec{e} \cdot \langle u_v | \vec{p} | u_c \rangle \langle \chi_n^{(h)} | \chi_n^{(e)} \rangle$$

The first term $\langle u_v | \vec{p} | u_c \rangle$ determines the polarization selection rules which depend on the valence band (v) under consideration i.e. heavy holes, light holes and split-off. For simplicity, we will neglect this dependence in the following, replacing $\langle u_v | \vec{p} | u_c \rangle$ by the average value M_{vc} . The second term gives selection rules on the envelope function quantum numbers. In the case of symmetric wells, we can deduce from the parity of the wave functions that the overlap $\langle \chi_n^{(h)} | \chi_n^{(e)} \rangle$ is non zero only if $n + m$ is even. In the case of infinitely deep barriers, the envelope functions both for the electron and the hole reveal that the transition is allowed only if $n = m$. In the general case, it is observed that transitions with $n \neq m$ are always much less efficient than those with $n = m$.

Intraband Transitions:

Intraband Transitions in Quantum Wells. For carriers confined in the z direction and free to move in x and y directions, one must consider two situations for the optical absorption depending on the polarization of the light. With polarizations along x and y , the problem is the 2D analogue of the free-carrier absorption in bulk semiconductors. Direct transitions are not allowed and scattering mechanisms induced by phonons are necessary. With a z polarization corresponding to a wave propagating within the well, direct transitions are

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allowed between different subbands (Fig. 4), provided that the in-plane wavevector of the carrier is conserved.

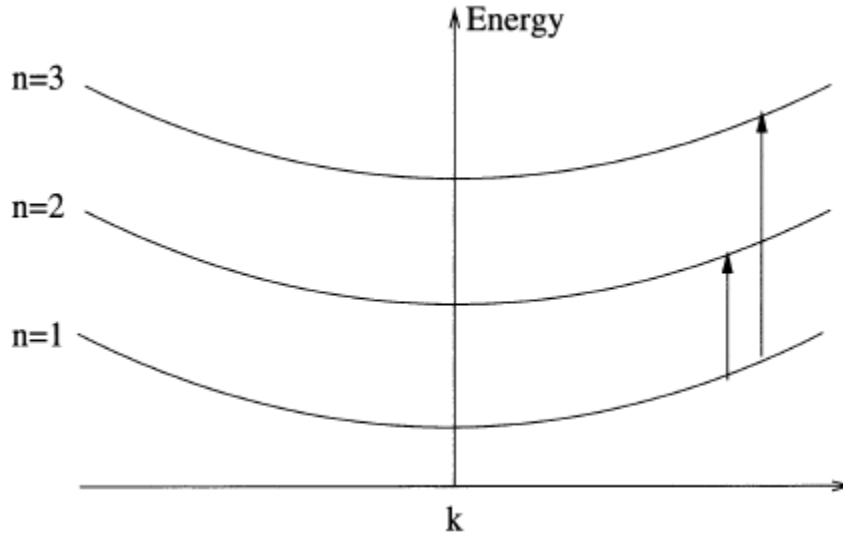


Fig. 4

Using the wavefunctions $\phi_i(\vec{r}) \propto e^{i\vec{k}^{(i)} \cdot \vec{\rho}} \chi_n(z)$ and $\phi_f(\vec{r}) \propto e^{i\vec{k}^{(f)} \cdot \vec{\rho}} \chi_m(z)$ for the initial and final states, respectively, the optical matrix element becomes

$$\delta_{\vec{k}^{(i)}, \vec{k}^{(f)}} \langle \chi_n | p_z | \chi_m \rangle$$

In order to estimate the magnitude of the transitions, we consider the case of a well with infinite barriers. It can be shown that the total oscillator strength for all vertical transitions from the subband n to the subband m

$$f_{nm} = \frac{2^6}{\pi^2} \frac{n^2 m^2}{(m^2 - n^2)^3} \text{ if } n - m \text{ is odd}$$

$$f_{nm} = 0 \text{ otherwise}$$

Let us consider now that only the subband $n = 1$ is populated in the initial state. We see that the amplitude of the optical matrix element quickly decreases with m . The absorption spectrum is a sum of delta functions due to the exact parallelism of the subbands in the effective mass approximation. Using more elaborate calculations, the bands would not be perfectly parabolic and each line in the optical spectrum would acquire a finite width.



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Reference:

**Nanostructures: Theory and Modeling, C. Delerue & M. Lannoo,
Springer**

(All the figures have been collected from the above mentioned reference)