

## Optical properties of semiconductor nanospheres: exciton effect

M. BOUSTIMI

Department of physics, College of Science, University Umm Al-Qura,  
PO Box 715, Makkah, Saudi Arabia  
mohamed.boustimi@gmail.com

**ABSTRACT.** Recent advances in the synthesis of semiconductor clusters, nanospheres and quantum dots open a doorway for the systematic study of size-dependent cluster properties in the condensed phase. This article focuses on the size effect on the optical properties of semiconductor nanospheres. We first introduce fundamental concepts and then compare to experimental results on copper-chloride nanospheres embedded in glass. These results exhibit the quantum size dependence together with a dielectric confinement effect.

### 1 Introduction

Recently a lot of theoretical and experimental works has been dedicated to individual or array nano-systems such as nanospheres, nanowires ... This interest is growing because industrial applications (in nano-electronics, biology, telecommunications, medical science...). Among nano-objects, nanospheres are particularly interesting and have been the object of attention by many scientists [1]. Optical properties of nanospheres are studied by different methods in a quantum mechanical view [2] or by semi-classical treatments [3]. The important role of Excitons in nano-semiconductor optical response has been studied by [4-5]. Our goal in this paper is to study the optical properties of semiconductor nanospheres by means of the susceptibility method, already used by London to calculate the van der Waals forces between two distant atoms [6-7]. In part II, I present the principle of the method and determine the electric potential in a sphere submitted to an

external electric excitation. In part III, I determine the electric non-local response of the nanosphere and the dipolar induced polarization. In part IV, the special case of copper-chloride nanospheres is considered and it is shown that the optical response involves exciton effects.

## 2 Electric potentials inner and outer the nanosphere

Consider a semiconductor nanosphere of radius  $a$  (see Fig.(1)) submitted to an electric field  $\mathbf{E}$  given in a complex form by:

$$\mathbf{E} = (E_0(\omega) e^{i\omega t} + E_0(\omega) e^{-i\omega t}) \hat{\mathbf{z}} \quad (1)$$

where  $\hat{\mathbf{z}}$  is the unit vector along the direction of polarization (Z-axis). In this work, the retardation effect will be neglected because the wavelength of the electric field is much larger than the sphere radius. The external field is then related to the electric potential by:

$$\Phi_0(\mathbf{r}, t) = -E_0(\omega) r \cos\omega t \cos\theta \quad (2)$$

where  $r, \theta, \varphi$  are spherical coordinates. Because of the symmetry, any function  $G(\mathbf{r}, t)$  describing a physical quantity inside the sphere is separable in radial and angular functions as:

$$G(\mathbf{r}, t) = g(r, t) Y_1^0(\theta, \varphi) \quad (3)$$

$Y_1^0$  being the only spherical harmonic involved here. The radial function can be expanded over first-order spherical Bessel functions [7]

$$g(r, t) = \sum_k B_k j_1(kr) \tilde{g}(k, t) \quad (4)$$

Where  $\tilde{g}$  is the Fourier transform of  $g$  and

$$B_k = \frac{1}{\sqrt{\int_0^a dr r^2 j_1(kr)}}$$

The wave number  $k$  obeys the so-called additional boundary condition [7]

$$\left( \frac{dj_1(x)}{dx} \right)_{x=ka} = 0 \quad (5)$$

According to the relations mentioned above, the induced electronic charge density  $\rho_{ind}$  inside the sphere can be expressed (in the Random-Phase Approximation) in term of the electric potential  $\Phi_1$  inside the sphere as

$$\rho_{ind}(r, \omega) = \sum_{k'} \chi(k, k', \omega) \Phi_1(k', \omega) \quad (6)$$

where

$$\chi(k, k', \omega) = \frac{1}{B_k B_{k'}} \iint d\mathbf{r} d\mathbf{r}' j_1(kr) j_1(k'r') Y_1^0(\theta, \varphi) Y_1^0(\theta', \varphi') \chi(\mathbf{r}, \mathbf{r}', \omega) \quad (7)$$

$\Phi_1$  can be derived from the second Green identity and Poisson equation

$$\Phi_1(\mathbf{r}, \omega) = \frac{2}{a} \Phi_1'(a, \omega) Y_1^0(\theta, \varphi) \sum_{k, k'} B_k B_{k'} j_1(kr) j_1(k'a) / \mathfrak{E}(k, k', \omega) \quad (8)$$

This relation connects the inner potential to its normal derivative at the surface. All physical properties of the nanosphere are represented by the dielectric function  $\frac{\mathfrak{E}(k, k', \omega)}{k^2}$  where [8]

$$\mathfrak{E}(k, k', \omega) = k^2 \delta_{k, k'} - 4\pi \chi(k, k', \omega) \quad (9)$$

The potential  $\Phi_2$  outside the sphere is the sum of the response potential and the source potential (generated by the external electric field). From the boundary conditions at the surface of the nanosphere electric potentials are expressed as

$$\Phi_1(\mathbf{r}, \omega) = -\frac{3 a E_0(\omega) f(r, \omega) \cos\theta}{a+2f(a, \omega)} \quad (10a)$$

and

$$\Phi_2(\mathbf{r}, \omega) = \frac{a^3 E_0(\omega) [a-f(r, \omega)] \cos\theta}{r^2 [a+2f(a, \omega)]} \quad (10b)$$

where

$$f(r, \omega) = \frac{2}{a} \sum_{k, k'} B_k B_{k'} j_1(kr) j_1(ka) \mathfrak{E}^{-1}(k, k', \omega) \quad (11)$$

The polarization induced in the sphere, is derived from the latter expressions of the potentials

$$P(\omega) = \frac{a^3 E_0(\omega) \epsilon_s [a-f(a,\omega)]}{[a+2 \epsilon_s f(a,\omega)]} \quad (12)$$

This formula takes in account both the dispersion and the non-locality effects in the sphere embedded in a medium with a relative permittivity  $\epsilon_s$ .

### 3 Optical response of an homogeneous semiconductor nanosphere

Here as an application of the previous treatment the optical absorption of a semiconductor nanosphere submitted to infrared radiations is calculated. In an homogeneous case, the susceptibility is diagonal and related to Lindhard bulk dielectric constant  $\epsilon(k,\omega)$  by [7]

$$\mathfrak{E}(k, \omega) = k^2 \epsilon(k, \omega) \quad (11)$$

The nonlocal effect is introduced *via* the hydrodynamic dielectric constant  $\epsilon(k, \omega)$ , in the vicinity of an excitonic transition frequency [9-10]

$$\epsilon(k, \omega) = \epsilon_s + \frac{\omega_p^2}{\omega_E^2 + D^2 k^2 - \omega(\omega + i\gamma)} \quad (12)$$

$\epsilon_s$  is the relative permittivity of the surrounding medium (glass),  $\gamma$  is the damping constant,  $\omega_p$  is the measure of an oscillator strength and  $D$  depends on both the effective mass  $M$  of the exciton and the transition frequency  $\omega_T$ :

$$D = \frac{\hbar \omega_T}{M}$$

Under the conditions defined above, the function  $f(a, \omega)$  simplifies into

$$f(a, \omega) = a \frac{\alpha}{\beta} + \frac{a \left(1 - \frac{\epsilon_s \alpha}{\beta}\right) I_{3/2}(a\sqrt{\beta})}{a\sqrt{\beta} I'_{3/2}(a\sqrt{\beta}) - \frac{1}{2} I_{3/2}(a\sqrt{\beta})} \quad (13)$$

Where  $\alpha = \frac{(\omega_T^2 - \omega^2 - i\gamma\omega)}{\epsilon_s D}$  and  $\beta = \frac{\epsilon_s (\omega_T^2 - \omega^2 - i\gamma\omega) + \omega_p^2}{\epsilon_0 D}$

The optical response of semiconductor nanosphere is then calculated as the imaginary part of the polarization, by inserting the expression (11) in the equation (13).

#### 4 Conclusion and discussion

The present numerical results deal with copper-chloride nanospheres embedded in glass, the radius of which ranges from 2.5 to 10 nm. Absorption peaks of three nanospheres are calculated (in fig.2) in the region called “Z3 exciton”, where the radius of the sphere is much larger than the Bohr radius (*i.e.* the sum of electron and hole radii). The parameters used are [11]:  $\hbar\omega_L = 3.2079 \text{ eV}$ ,  $\hbar\omega_T = 3.2022 \text{ eV}$ ,  $M = 2.3 m_e$ ,  $\epsilon_0 = 5.59$  and the damping term  $\gamma = 0.002\omega_T$ . As expected a blue shift of the main absorption peak is observed when the radius is about a few nanometers.

The size dependence of excitonic absorption is calculated by our treatment and compared to the measurements performed by Ekimov *et al.* [12]. In the present range of radii, where the susceptibility of the sphere is based upon the excitonic confinement, the calculated absorption peak positions are in quite good agreement with experimental data. In fig.3, the mean absorption peak position is plotted as a function of  $1/a^2$ . The dependence is clearly linear, with a slope which agrees well with the expected value  $\frac{\hbar^2\pi^2}{2M}$ . The susceptibility formalism then takes in account both the quantization of the excitonic motion and the blue shift. Indeed the energy position of the absorption peak is expressed as[13]

$$\hbar\omega = \hbar\omega_T + \frac{\hbar^2\pi^2}{2Ma^2}$$

To conclude, the present treatment appears to be adequate for sphere radii larger than 2 nm. However its validity for smaller radii is questionable and a pure quantum treatment becomes necessary.

#### REFERENCES

- [1] M.Dekker “Semiconductor and Metal Nanocrystals: Synthesis and Electronic and Optical” Edited by V. I. Klimov, New York, (2003)
- [2] Yuanchang Sun, Hiroshi Ajiki and Gang Bao. Comm. In Comput. Physics, 4, 1051 (2008)

- [3] D. Ricard, P. Roussignol and Flytzanis, *Opt. Lett.* **10**, 511 (1985)
- [4] R. Ruppin, *J. Phys. Chem. Solids* **50**, 877 (1989)
- [5] H. Zhou, M. Wissinger, J. Fallert, R. Hauschild, F. Stelzl, C. Klingshirn, and H. Kalt, *Appl. Phys. Lett.* **91**, 181112 (2007)
- [6] B. Labani, C. Girard and Maghezzi, *Molecular Phys.* **69**, 85 (1990)
- [7] C. Girard and F. Hache, *Chem. Phys.* **118**, 249 (1987)
- [8] D. M. Newns, *Phys. Rev. B* **1**, 3304 (1970)
- [9] J.J. Hopfield and D.G. Thomas, *Phys. Rev.* **132**, 563 (1963)
- [10] A.A. Maradudin and D.L. Mills, *Phys. Rev.* **B7**, 2787 (1973)
- [11] T. Mita, K. Sotome and M. Ueta, *Solid State Commun.* **33**, 1135 (1980)
- [12] A.I. Ekimov, A.L. Efros and A.A. Onushchenko, *Solid State Commun.* **56**, 921 (1985)
- [13] A.I. Efros and A.L. Efros, *Soviet Phys. Semicond.* **16**, 772 (1982)

*(Manuscrit reçu le 21 septembre 2010)*

## FIGURES

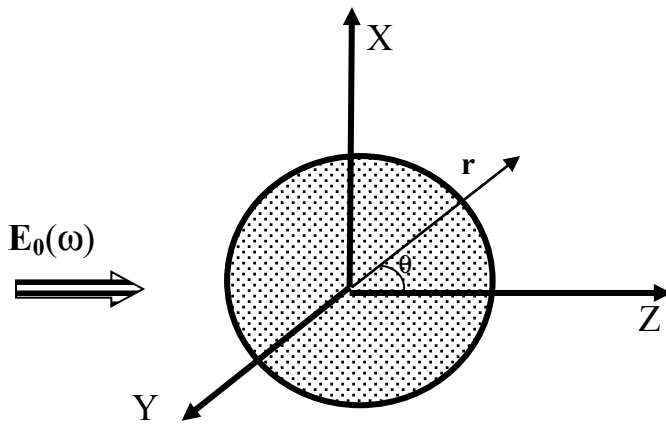


Fig.1: Geometry of a semiconductor nanosphere experiencing an infrared light wave polarized along Z-axis.

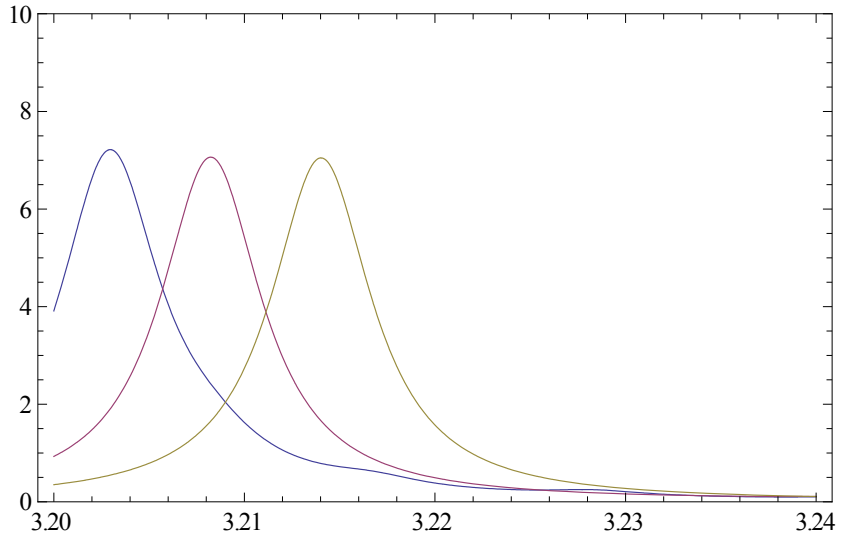


Fig.2: Optical response of CuCl nanospheres embedded in glass (arbitrary unit) with different radii (blue curve for  $a=10$  nm, red curve for  $a=3.5$  nm and  $a=2.5$  nm for the last curve).



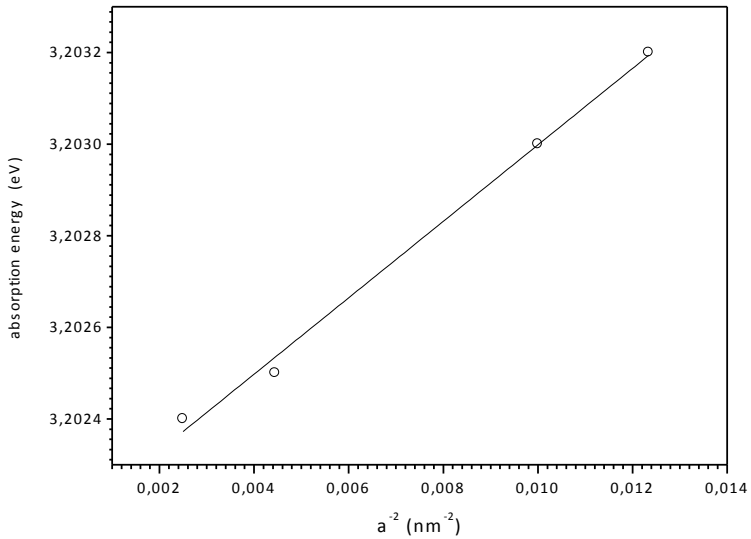


Fig.3: Calculated size-dependence of the location of the excitonic absorption peak of CuCl nanospheres (full line). A linear dependence in  $a^{-2}$  is seen, as expected in the present range of radii. It is in rather good agreement with experimental data (open circles).