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Polarization effects on spectra of spherical core/shell nanostructures: Perturbation theory against finite difference approach

Asmaa Ibral [a,b], Asmaa Zouitine [c], El Mahdi Assaid [a,b,*], Hicham El Achouby [a,b], El Mustapha Feddi [c], Francis Dujardin [d]

[a] Equipe d'Optique et Electronique du Solide, Département de Physique, Faculté des Sciences, Université Chouaïb Doukkali, B. P. 20 El Jadida principale, El Jadida, Royaume du Maroc, Morocco
[b] Laboratoire d'Instrumentation, Mesure et Contrôle, Département de Physique, Faculté des Sciences, Université Chouaïb Doukkali, B. P. 20 El Jadida principale, El Jadida, Royaume du Maroc, Morocco
[c] Département de Physique, Ecole Nationale Supérieure d'Enseignement Technique, Université Mohammed V Souissi, B. P. 6207 Rabat-Instituts, Rabat, Royaume du Maroc, Morocco
[d] LCPMC, Institut de Chimie, Physique et Matériaux, Université de Lorraine, 1 Bd Arago, 57070 Metz, France

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ABSTRACT

Poisson equation is solved analytically in the case of a point charge placed anywhere in a spherical core/shell nanostructure, immersed in aqueous or organic solution or embedded in semiconducting or insulating matrix. Conduction and valence band-edge alignments between core and shell are described by finite height barriers. Influence of polarization charges induced at the surfaces where two adjacent materials meet is taken into account. Original expressions of electrostatic potential created everywhere in the space by a source point charge are derived. Expressions of self-polarization potential describing the interaction of a point charge with its own image–charge are deduced. Contributions of double dielectric constant mismatch to electron and hole ground state energies as well as nanostructure effective gap are calculated via first order perturbation theory and also by finite difference approach. Dependencies of electron, hole and gap energies against core to shell radii ratio are determined in the case of ZnS/CdSe core/shell nanostructure immersed in water or in toluene. It appears that finite difference approach is more efficient than first order perturbation method and that the effect of polarization charge may in no case be neglected as its contribution can reach a significant proportion of the value of nanostructure gap.

1. Introduction

In the late 1960s, Leo Esaki imagined and realized an alternate stacking of two lattice-matched semiconductors of different gaps where charge carriers revealed bi-dimensional characters [1]. The resulting one-dimensional periodic structure showed outstanding properties such as negative differential conductivity and a series of narrow allowed mini-bands separated by forbidden bands. This original work laid foundations of a rising field of investigation which will be called later '*low-dimensional physics*'.

About one decade later, quantum size effect due to complete confinement in zero-dimensional structures has been described, for the first time, by Ekimov [2] and Brus [3,4]. Since these pioneering works, Quantum Dots (QD's) have been the subject of intensive experimental and theoretical investigations. QD's are semiconductor inclusions with a nanometer-scale size. In the early 1980s, QDs were precipitated by annealing in a glassy host matrix. Now, most of them are synthesized, at low temperature, as colloidal suspensions in organic solutions through soft chemistry methods. QD's are synthetic structures which are at the midway between crystals and atoms. They present spatial order and compactness of bulk crystals, but their spectroscopic properties are similar to those of single atoms. Indeed, charge carriers are deprived of their three degrees of freedom and single-particles envelope wave functions are subjected to additional continuity conditions which lead to quantization of electron and hole energies. As a consequence, QDs absorption edge is blue shifted.

Nowadays, technological advances in soft chemistry based fabrication methods have made it possible to realize quasi-pure and high-quality semiconductor quantum dots with size ranging from few to hundreds nanometers for various fields of applications such as optical encryption [5], combining multiple signals into one signal in a shared channel (multiplexing) [6], solar energy

* Correspondence to: Département de Physique, B. P. 20 El Jadida Principale, El Jadida, Royaume du Maroc, Morocco. Fax: +212 523342187.
E-mail address: eassaid@yahoo.fr (E.M. Assaid).

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harvesting [7], medicine and biology where quantum dots are used in studying intracellular processes at the single molecule level [8,9]. QDs are also used in tumor targeting and in diagnostics [10–13], in long term *in vivo* observation of cell trafficking and in high-resolution cellular imaging [14–17].

In the second half of the 1990s, new types of QD's such as multi-shell, onion-like or core/shell nanostructures have emerged [18]. They are obtained using soft chemistry process of growth by capping a spherical QD of a given semiconductor with a spherical layer of another semiconductor. The outer layer may also be encapsulated by a spherical inorganic or organic thin shell to smooth quantum dot surface and to neutralize dangling bonds.

Core/shell nanostructures are classified according to conduction and valence band edge alignments of semiconductors involved. In type I core/shell nanostructures such as CdSe/CdS [19] or CdSe/ZnSe [20], electrons and holes tend to localize within the core. In inverted type I core/shell nanostructures such as CdS/CdSe [21] or ZnSe/CdSe [22], electrons and holes tend to localize within the shell. In type II core/shell nanostructures such as CdTe/CdSe [23] or CdS/ZnSe [24], electrons and holes tend to localize, respectively, within the core and the shell or vice versa.

Today, semiconducting colloidal core/shell nanostructures from soft chemistry process of growth display outstanding optoelectronic properties. Their electroluminescence spectrum depends on semiconducting materials used, on core size, on shell thickness and also on applied electric field strength. This enables fabrication of quantum dot size-tunable color colloidal solution, the synthesis of colloidal quantum dot light emitting devices (QD-LED) and full-color QD-LED displays driven by an applied electric field [25].

Semiconducting colloidal core/shell quantum dots are often suspended in organic or aqueous host solution (see Fig. 1). As a consequence, their spectroscopic properties depend on double dielectric mismatch at inner and outer surfaces [26].

In the present paper, we solve analytically the eigenvalues equation in cases of an electron from conduction band and a hole from valence band confined in ZnS/CdSe core/shell nanostructure

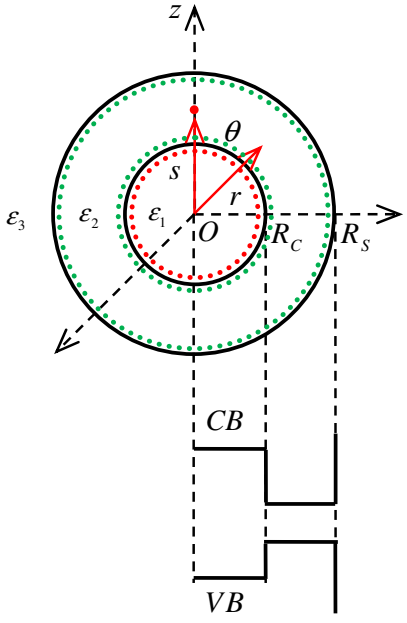

Fig. 1. Sketch of inverted type I ZnS/CdSe core/shell nanostructure immersed in aqueous or organic host solution. According to core radius and shell thickness, the source particle may be in core or in shell. In both cases, the source particle is submitted to effects of: (a) positive charge on internal face of core surface, (b) negative charge on external face of core surface and (c) negative charge on internal face of shell surface.

(see Fig. 1). We determine single-particles ground state energies, wave functions and radial probability densities as functions of core radius and shell thickness. We show that for a fixed dot size R_S, there are two critical values R_{Ce} and R_{Ch} of core radius for which electron ground state energy E_e^{1s} is equal to conduction band offset $V_{0e} = \Delta E_c(0)$ and hole ground state energy E_h^{1s} is equal to valence band offset $V_{0h} = \Delta E_v(0)$ respectively (see Fig. 2(2) and (4)) [27]. As a consequence, there are different single-particles localization regimes according to core radius R_C (or shell thickness ($T_S = R_S - R_C$)). For $0 < R_C < R_{Ce}$, electron and hole tend to localize within nanostructure shell (see Fig. 2(1)) [27]. For $R_{Ce} < R_C < R_{Ch}$, electron tends to localize within nanostructure core while hole tends to localize within nanostructure shell (see Fig. 2(3)) [27]. For $R_{Ch} < R_C < R_S$, electron and hole tend to localize within nanostructure core (see Fig. 2(5)) [27]. To examine the influence of double dielectric constant mismatch, we solve analytically Poisson equation in the case of a point charge placed anywhere in a spherical core/shell nanostructure, immersed in aqueous or organic solution or embedded in semiconducting or insulating matrix (see Appendix A). We take into account the effects of surface densities of image–charge induced at the junctions where two neighboring materials meet. We derive new expressions of the generalized coulomb potential created everywhere in the space by a source point charge placed anywhere in the quantum dot (see Appendix A). We deduce the expressions of self-polarization potential describing the interaction of a confined point charge with its own image–charge (see Appendix A). We calculate the contributions of double dielectric constant mismatch to electron and hole ground state energies and to nanostructure gap using first order perturbation theory and finite difference approach. We determine the variations of electron, hole, gap energies and image–charge contributions as functions of core to shell radii ratio in the case of ZnS/CdSe core/shell nanostructure in vacuum or immersed in water or in toluene. We show that even for a core/shell nanostructure such as ε_{Core} is close to ε_{Shell}, the effect of polarization charge may in no case be neglected as its contribution can reach a significant proportion of the nanostructure gap. We also show that in case of ZnS/CdSe core/shell nanostructure, first order perturbation theory reproduces well the magnitude of image–charge effects even if it only calculates the expectation value of self-polarization potential in ground state of unperturbed Hamiltonian. Unfortunately, to determine first order correction to ground state wave function, this theory becomes unsuitable since it requires long and tedious calculations. However, finite difference approach which is more efficient than first order perturbation theory allows access at the same time, via numerical calculations, to energies and wave functions of the perturbed Hamiltonian.

2. Model and theory

Let us consider an inverted type I core/shell nanostructure (see Fig. 1). It consists of a spherical wide band gap semiconductor crystallite of nanometer-scale radius R_C and dielectric constant ε_1 playing the role of core, over coated with a narrower band gap semiconductor layer of thickness ($T_S = R_S - R_C$) and dielectric constant ε_2 playing the role of shell. The whole nanostructure is immersed in aqueous or in organic solution of dielectric constant ε_3. The minimum of core conduction band is above the minimum of shell conduction band. The maximum of core valence band is below the maximum of shell valence band. Due to this band edge alignments, electron and hole tend to localize in the narrowest band gap semiconductor. Nevertheless, their probabilities of presence in core are not equal to zero. So, the junction between core and shell is modeled by finite height barriers (see Fig. 1).