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Electric field effect on the third-order nonlinear optical susceptibility in inverted core–shell nanodots with dielectric confinement

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ABSTRACT

Third-order nonlinear optical processes associated with the interlevel transitions in ZnS/CdSe core–shell quantum dots under electric fields are theoretically investigated. Taking into account the dielectric mismatch with the surrounding matrix, the electronic structure of the dots is obtained within the effective mass and parabolic band approximations. It is shown that large applied electric fields break the symmetry of the confinement potential and lead to a significant blue-shift of the peak positions in the nonlinear optical spectrum. The size effect is also discussed and it is proved that large nonlinear susceptibility can be obtained by increasing the thickness of the nanocrystal shell. Our results suggest that external factors such as the applied electric field and orientation of the incident light polarization can be used – in addition to spatial confinement – to improve the performances of the optical devices.

1. Introduction

Colloidal semiconductor nanocrystals with their excellent photoelectronic properties are now widely used for various technologies such as biomedical fluorophores, light emitting diodes (LEDs), and photovoltaic devices [1–6]. Quantum confinement of carriers in these systems leads to the formation of discrete energy levels, which can be tailored by changing the dot size and shape, the surrounding environment and/or external applied fields. Moreover, quantum size effects are responsible for large optical nonlinearities associated with intersubband transitions. Significant changes of these quantities are expected if the symmetry of a system is broken, for example in asymmetric nanostructures and low-dimensional systems under external electric fields. There are a number of theoretical investigations on the nonlinear optical properties in semiconductor quantum dots (QDs), including the effects of external perturbations like electric and magnetic fields, hydrostatic pressure and impurities and excitonic states [7–14].

In the last decade, the use of multicomponent semiconductor heterostructures has provided interesting opportunities for changing electronic properties of materials via the control of confinement energies as well as by adjusting the spatial distributions of electronic wave functions. Among these, the core–shell structures seem to be very attractive for their optical and photovoltaic properties. Successful syntheses of core–shell QDs have been reported for various combinations of CdSe/ZnS, CdSe/CdTe, ZnTe/ZnSe, and PbSe/CdSe [15–20].

There are also reports about experimental and theoretical predictions of large optical nonlinearities associated with the intersubband transitions in such multi-shell semiconductor nanocrystals. The third-order nonlinear optical properties of CdSe/ZnS core–shell nanodots in toluene solution were studied over a spectrum ranging from 450 to 680 nm by using 225-fs pulses [20]. Several techniques, including the Z-scan method by using the Nd:YAG laser second harmonic radiation [21] and the photoluminescence of CdSe/ZnS QDs dispersed on a glass surface [22] have been used to study the structure design effect on the nonlinear optical properties. Within the density matrix formalism, the size-dependent quadratic electro-optic effects in CdSe/ZnS spherical QDs [23] and cylindrical quantum dot–quantum wells [24] have been also theoretically investigated. For CdSe/ZnS/CdSe quantum structures Bahari and Moghadam [25] have found that the intensity and position of the third order nonlinearity susceptibility peak may be strongly tuned by changing the nanoshells thicknesses.

In recent papers [26,27] we have shown that the dielectric confinement and the electric field action significantly modify the electronic states in CdSe/ZnS core–shell QDs. The present work is concerned with the theoretical study of the quadratic electro-optic effect and the electro-absorption process in nanocrystals under the combined effects of the electric applied field and dielectric mismatch with the surrounding medium. We have investigated an inverted ZnS/CdSe nanodot, in which a wide-gap semiconductor core is over-coated with a shell of a narrower gap material. Such nanocrystals can exhibit either type-I or type-II behaviors, depending on the core radius and the shell thickness [28]. As far as

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we know, a theoretical investigation of the third-order nonlinear optical susceptibility in dielectric modulated core–shell QDs under applied electric fields was not performed yet.

The paper is organized as follows. In Section 2 the theoretical framework is described. Section 3 is dedicated to the results and discussion, and finally, our conclusions are given in Section 4.

2. Theoretical framework

The system consists of a spherical core with inner radius R_1, coated by a spherical shell with R_2 radius, which is further embedded in a dielectric material. We have assumed the same value of the static dielectric constant in the two semiconductors. The appropriate dielectric constant of the QD is taken to be $\varepsilon_1 = \sqrt{\varepsilon_{ZnS}\,\varepsilon_{CdSe}}$ [29], whereas ε_2 denotes the dielectric constant of the surrounding matrix. As we consider nanocrystallites surrounded by a wide-band dielectric, for all the structures under study we treat the outside barrier as infinitely high.

The Hamiltonian for an electron in a core–shell nanodot under an electric field $\vec{F}$ has the form

$$H_0 = -\frac{\hbar^2}{2}\nabla\left(\frac{1}{m^*(r)}\nabla\right) + U(r) + W(r) + e\vec{F}\cdot\vec{r} \tag{1}$$

where the first term is the Hermitian kinetic energy operator for a position dependent mass:

$$m^*(r) = \begin{cases} m_{core}, & r \le R_1; \\ m_{shell}, & R_1 < r \le R_2 \end{cases}, \tag{2}$$

and $U(r)$ represents the step-like confining potential

$$U(r) = \begin{cases} V_0, & r \le R_1 \\ 0, & R_1 < r \le R_2 \\ \infty, & r > R_2 \end{cases}. \tag{3}$$

Table 1
Parameters used in the numerical simulations.

Material	m_e^*/m_0	$\varepsilon/\varepsilon_0$	E_g (eV)	ΔE_c (eV) $= V_0$
CdSe	0.13	9.3	1.75	
ZnS	0.28	8.1	3.75	0.9

In Eq. (1) $W(r)$ describes the electron self-polarization potential which originates from the interaction of the electron with its image-charge. According to Ref. [30], for this step-like profile with an abrupt change of the dielectric constant at the dot boundary the self-energy is given by

$$W(r) = \frac{e^2(\varepsilon_1 - \varepsilon_2)}{8\pi\varepsilon_1 R_2}\sum_{k=0}^{\infty}\frac{k+1}{k\varepsilon_1 + (k+1)\varepsilon_2}\frac{r^{2k}}{R_2^{2k}}. \tag{4}$$

After the calculation of the wave functions and the eigenvalues associated with the electron Hamiltonian (Eq. (1)), the nonlinear optical susceptibility $\chi^{(3)}$ corresponding to optical mixing between two incident light beams with frequencies ω_1 and ω_2 can be obtained under the density matrix approach. In the second-order perturbation theory, this quantity is given by [31]

$$\begin{aligned}\chi^{(3)}&(-2\omega_1 + \omega_2, \omega_1, \omega_1, -\omega_2) \\ &= \frac{-2iN\mu^4/\varepsilon_0}{[i\hbar(\omega_0 - 2\omega_1 + \omega_2) + \hbar/\tau][i\hbar(\omega_2 - \omega_1) + \hbar/\tau]} \\ &\quad\times\left(\frac{1}{i\hbar(\omega_0 - \omega_1) + \hbar/\tau} + \frac{1}{i\hbar(\omega_2 - \omega_0) + \hbar/\tau}\right)\end{aligned} \tag{5}$$

where

$$\mu = \langle \Psi_i | e\vec{r} | \Psi_j \rangle \tag{6}$$

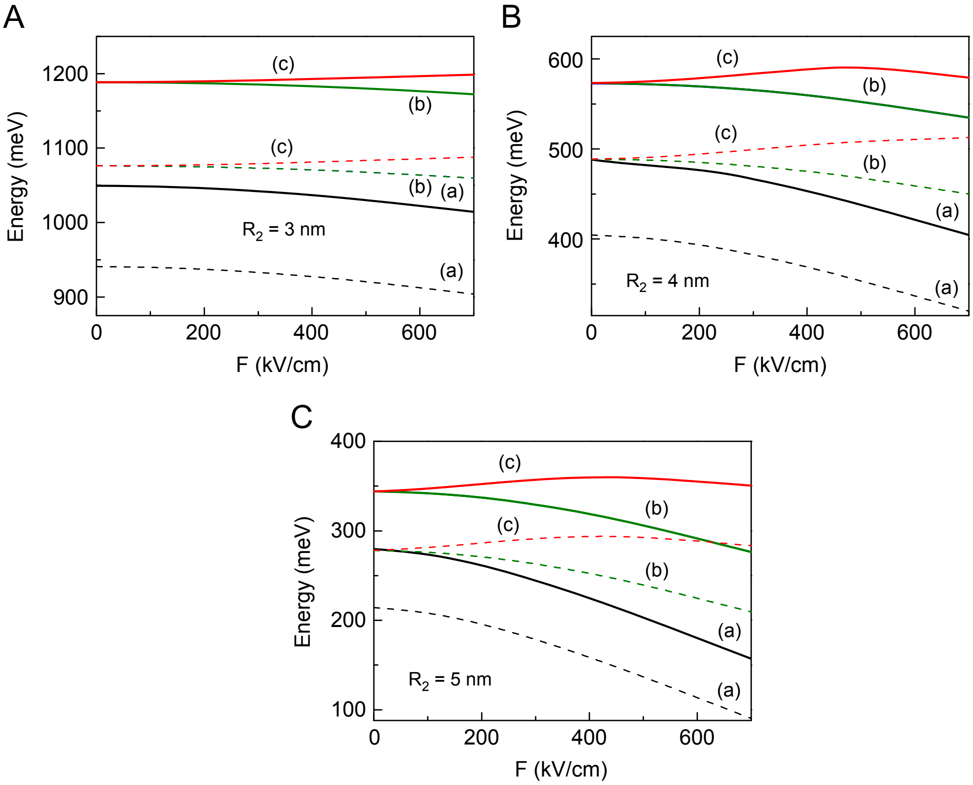

Fig. 1. The electric field dependence of lowest energy levels in ZnS/CdSe QDs taking into account (solid lines) and neglecting (dashed lines) the dielectric confinement effect. Notations (a), (b) and (c) stand for 1 s (black), 2p$_\pm$ (dark green) and 2p$_0$ (red) states, respectively. The results are for fixed R_1=2 nm and a variable outer radius: R_2=3 nm (A); R_2=4 nm (B), and R_2=5 nm (C), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)