Optical Properties of Ellipsoidal CdSe Quantum Dots

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The energy spectrum and optical absorption of confined carriers in ellipsoidal CdSe quantum dots are calculated. Our model relies on the effective mass approximation and Fermi's golden rule for the electronic structure and optical properties, respectively. We demonstrate that the electronic structure and the interband optical absorption are highly dependent on the ellipsoid aspect ratio.

Keywords: Optical properties; Ellipsoidal CdSe quantum dots; Effective mass approximation

I. INTRODUCTION

Shape control of CdSe nanocrystals is favoring the development of polarized single-photon sources [1,2], and enlarging their advantages for biological detection and imaging [3,4]. In particular, controlled utilization of semiconductor quantum dots (QDs) asks for a better understanding of their electronic levels, which in turn are rather sensitive to the actual geometrical (QD shape, vertical and lateral sizes) and compositional (interdiffusion profile, stress field) parameters defining the carriers confinement conditions. In fact, even though the existence of quantum confinement effects on the optical response of QDs is nowadays well established, the fine structure of their emission and absorption spectra is still not completely settled [5-9].

Recently, Cantele et al. [8,9] have investigated the optical anisotropy of ellipsoidal quantum dots as a function of the dot aspect ratio. They have obtained that the optical processes significantly depend on the radiation polarization in contrast to non-polarized processes observed for spherical quantum dots. The dot anisotropy was shown to play a fundamental role in determining the dot properties. However, they do not have focused on effects due to high excited transitions in the interband absorption.

The proposal of the present work is to perform an investigation of the electronic states and optical response of ellipsoidal CdSe QDs. The optical absorption CdSe QDs is shown to be highly dependent on the ellipsoid aspect ratio. An increase in the ellipsoidal character of the CdSe QDs can redshift the recombination energy by several tenths of meV.

II. MODELING THE ELLIPSOIDAL CDSE QDS

The ellipsoidal CdSe QD has c=b and a axes along the z, y and x directions, respectively, with the ellipsoid aspect ratio given by β=a/c. QDs with changing volumes are considered, and Schrödinger-like equations with position dependent kinetic energy operator were solved numerically, considering V(r)=0 (∞) inside (outside) the ellipsoidal QD. This assumption is justified by the fact that the QDs investigated in this work are produced through chemical reactions in liquid environments yelding the formation of capping layer covering QDs which prevents chemical reactions with the solution. Even though the use of a position dependent kinetic energy operator makes no sense in a hard wall confinement system, this formalism is general enough to be extended to finite barriers systems. Many-body and thermal fluctuations effects of the occupation number were not considered, as well as the role of phonons in the calculation of the intraband absorption coefficient. The optical properties calculations were based on the Fermi's Golden Rule. The values for the CdSe parameters were taken from the literature.

III. OPTICAL PROPERTIES

It is interesting to see the role of the symmetry change on the energy spectrum and degeneracy scheme of CdSe QDs. For the spherical shape (a = 5 nm), there are several degeneracies which resembles the atomic orbitals. Following the notation of atomic physics, the first twenty states for electrons in spherical CdSe QDs are presented in Fig. 1. They are labeled as 1s, 2p, 3d, 2s, 4f, and 3p, where the orbitals s, p, d and f present 1, 3, 5 and 7 degenerated states, respectively. In the case of elliptic CdSe QDs (a = 50 nm), the degeneracy scheme is broken lifting practically all degeneracies in the range of states presented here. Due to the larger volume, these states are restricted to a much smaller energy range in comparison to the spherical quantum dot. The effect of an increase of the ellipsoid aspect ratio β is the redshift of the electron energy levels, which is also a result valid for holes. This is shown in Fig. 1 for β=1 and β=10. One may think that this redshift is caused by the volume increase. However, for elipsoidal deformations keeping the volume constant (abc=125 nm^3), a redshift of some of the energy levels is also observed. The highest excited states are much more influenced by an increase of β than the lowest ones, what indicates that one can not be restricted to the calculation of the optical properties of ellipsoidal QDs considering only the ground and first few excited states contribution.

The change of confinement symmetry is expected to modify the selection rules of the optical properties. Theses results are depicted in Fig. 2, which exhibits the interband absorption coefficient of spherical (a=5 nm) and elliptic (a = 50 nm) CdSe QDs. In the case of spherical shape, the main transitions are identified as 1s$\rightarrow$1s, 2p$\rightarrow$2p, 3d$\rightarrow$3d, 2s$\rightarrow$2s, 4f$\rightarrow$4f and 3p$\rightarrow$3p, where the initial and final states are in the valence and

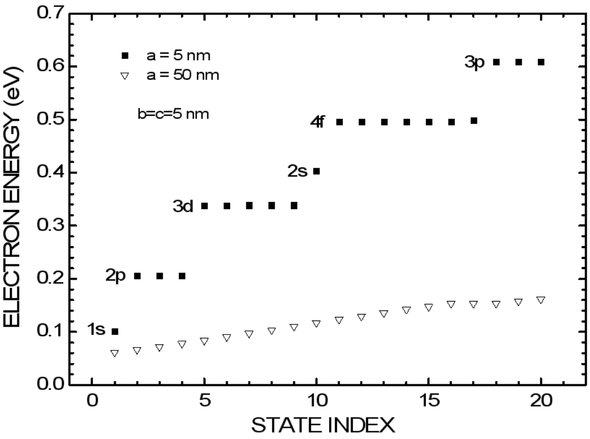

FIG. 1: Electron energy levels of ellipsoidal CdSe QDs as a function of the state index for a changing volume with β=1 (squares) and β=10 (down triangles). The energy states of spherical QDs are labeled using atomic notation.

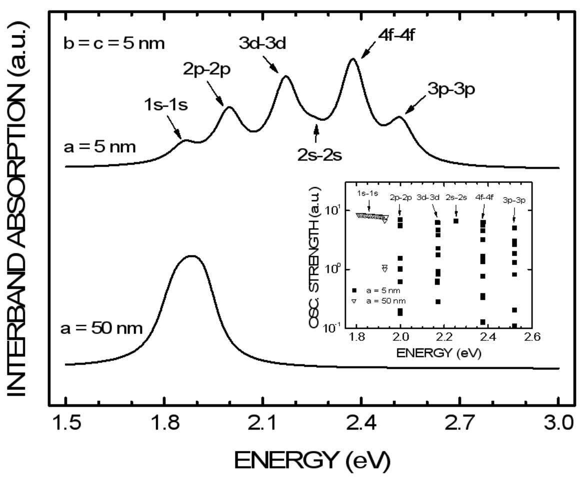

FIG. 2: Interband absorption of spherical (a=5 nm or β=1) and ellipsoidal (a=50 nm or β=10) CdSe QDs. In the inset, the oscilator strenght is presented for both cases to show the role of each transition.

conduction bands, respectively. Due to the spherical symmetry, these are the only possible transitions. The relative peak intensities are explained by the number of degenerated states for each allowed transition.

The absorption coefficient of the elliptic CdSe QDs presents a totally different interband absorption, with several structures. This is a consequence of the new set of transition rules imposed by the change of confinement symmetry. In order to confirm that, the oscillator strength is depicted in the inset graph for both confinement shapes. For simplicity, transitions whose oscillator strengths are too weak to be seen in the absorption spectra are not shown. The discrete nature of the transitions in the spherical quantum dot is very clear, while the elliptic dot exhibits a range of energy for which there is a continuum of allowed transitions. The absence of structures in the interband absorption (several absorption peaks) at high energies for each shape is due to the limitation on the number of calculated states.

IV. CONCLUSIONS

The shape control of QDs is important for a fine tuning of their optical properties emission, which has important applications in the field of biological markers [3,4]. In this work, we describe the role of the deviation from the spherical shape on the energy levels and interband absorption properties of CdSe QDs. Work is on progress to calculate the effects of the ellipsoidal character on the luminescent properties, including the role of light polarization.

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