



Research paper

Optical properties of colloidal semiconductor quantum dots in dielectric media: A natural potential well approach

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ABSTRACT

Colloidal quantum dots exhibit size-dependent optical properties due to quantum and dielectric confinements at the semiconductor/solvent boundary. To consider both confinement effects, we take a natural potential well approach that assumes separate potential wells for electron and hole which are surrounded by dielectric media. The potential well depths for electron and hole are set by the band offsets at the semiconductor/solvent heterojunction. The kinetic energy is calculated using an effective mass approximation and the electron-hole interaction energy is obtained by taking image charges into account. For cadmium chalcogenides, resulting transition energies agree well with size-dependent optical bandgaps from experiments.

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1. Introduction

Recent advances in colloidal synthesis allow the preparation of a wide variety of semiconductor quantum dots that can be used as emissive materials [1]. The quantum confinement in nanoscale results in size-dependent optical properties, and the size and shape of colloidal quantum dots (CQDs) vary with the growth chemistry. As most CQDs are prepared in organic solvent and covered with stabilizing ligands, their optical absorption and emission spectra are typically taken in liquid solution. When an electron-hole pair is formed in CQDs upon absorption of light, both the electron and hole are confined by the semiconductor/solvent heterojunction, and the dielectric mismatch at the semiconductor/solvent boundary induces image charges of electron and hole. Hence, both the semiconductor/solvent heterojunction and dielectric boundary affect the optical properties of CQDs dispersed in solvent.

Various theoretical methods have been used to study the optical properties of QDs, but mostly without considering the dielectric boundary [2–10]: The multiband effective mass theory was used to calculate various properties of CdSe and InAs QDs [2]. A tight-binding model was utilized to investigate the energy levels of CdS and CdSe QDs [3,4]. A pseudopotential method was employed to examine the electronic structure of CdSe QDs [5]. Both the multiband effective mass theory and the tight-binding method were applied to compare optical properties of CdS nanocrystals [6]. The variational calculation was carried out for CuCl QDs [7]

assuming an infinite potential well for both electron and hole, and for CdS QDs [8] using a semi-finite potential well. The finite potential well model, which has the same depth for both electron and hole, was used to calculate the optical properties of CdS [9], CdE (E = S, Se, Te) and InP QDs [10]. Meanwhile, the dielectric effect was examined in combination with the quantum confinement effect in some cases [11–18]: Brus [11] reported the electronic energy of CdS QDs using an infinite potential well model by considering the high frequency dielectric solvation. Bányai et al. [12] used the Hartree–Fock method to describe the electron-hole interactions in a finite potential well with a dielectric boundary between CdS QDs and surroundings. Takagahara [13] utilized the variational method to examine the dielectric confinement effects on electron-hole interactions in an infinite potential well. However, the calculation of self-polarization energy between charge and self-image charge was problematic due to the singularity at the boundary. Recently, Bolcatto and Proetto [14,15] proposed a smooth dielectric profile between CQDs and surroundings to avoid the divergence and calculated the energy levels of GaAs and CdSe CQDs using a semi-finite potential well model. More recently, the smooth dielectric profile was adopted in numerical calculations of the electronic states of CQDs assuming the same finite potential well for both electron and hole with a dielectric boundary [16,17]. Most recently, it was combined with the tight-binding method to calculate the self-energies of electron and hole in colloidal CdSe nanoplatelets surrounded by dielectric ligand/solvent [18].

In this work, we take a natural potential well approach that assumes different potential wells for the conduction band electron

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and the valence band hole, which are surrounded by dielectric media. Potential wells and the dielectric boundary are depicted in Fig. 1. The potential well depths for the electron (V_e) and hole (V_h) are determined by the band offsets at the semiconductor/solvent heterojunction. The dielectric constant of QD is treated to be size-dependent, varying between optical (ϵ_∞) and static (ϵ_0) dielectric constants, as proposed by Haken [19]. For the calculation of self-polarization energy, a cosine function is used to smooth the dielectric discontinuity. Of the semiconductors, cadmium chalcogenides (CdE, E = S, Se, Te) having a zinc-blende (ZB) structure are chosen for this study because numerous experimental data are available on their size-dependent optical properties and the effective mass approximation assuming a simple parabolic band structure can be applied to both the conduction and valence bands. We compare the bandgaps of CdE CQDs from experiments with theoretical results.

2. Computational details

The kinetic energy of a particle is calculated using an effective mass approximation. The Hamiltonian for an electron–hole pair can be expressed, as given in Eq. (1).

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_e^2 + V_e - \frac{\hbar^2}{2m_h} \nabla_h^2 + V_h + V(|\mathbf{r}_e - \mathbf{r}_h|), \quad (1)$$

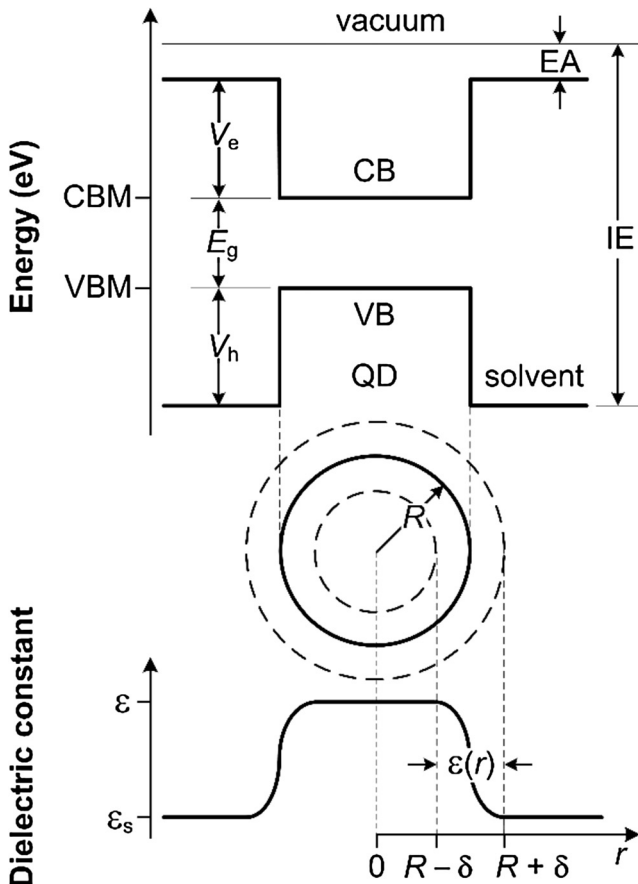


Fig. 1. A schematic of the natural potential well model: the energy level (top) and the dielectric constant profile (bottom). EA and IE are the electron affinity and ionization energy of solvent, respectively. CBM and VBM are the conduction band minimum and valence band maximum of a bulk material, respectively. E_g is the bulk bandgap. V_e and V_h are the well depths for electron and hole, respectively. ϵ is the size-dependent dielectric constant of QD, ϵ_s is the dielectric constant of solvent, and $\epsilon(r)$ is the smooth dielectric profile that varies between ϵ and ϵ_s as a function of distance r ($R - \delta \leq r \leq R + \delta$). R is the radius of QD and δ is the range parameter.

where \hbar is the Planck's constant, m_e and m_h are the effective mass of electron and hole, respectively, V is the interaction energy between electron and hole, and $|\mathbf{r}_e - \mathbf{r}_h|$ is the distance between electron and hole, where \mathbf{r}_e and \mathbf{r}_h are the position vector of electron and hole, respectively. The Schrödinger equation for a particle, either electron or hole, is given in Eq. (2).

$$\left(-\frac{\hbar^2}{2m_i} \nabla_i^2 + V_i - E_i \right) \varphi(r_i) Y(\theta_i, \phi_i) = 0; \quad i = e, h \quad (2)$$

where E_i is the kinetic energy of a particle, $\varphi(r_i)$ is the radial part of the wave function and $Y(\theta_i, \phi_i)$ is the angular part of the wave function. V_i is either V_e or V_h outside the QD ($r_i > R$) and zero inside QD ($0 < r_i \leq R$). We treat the interaction energy V in Eq. (1) as a perturbation and evaluate it to the first order [9,12].

Since the transition occurs between the lowest energy state of electron ($1S_e$) in the conduction band and the ground state of hole ($1S_h$) in the valence band, we employ the radial wave functions for the $1S_e$ and $1S_h$ states with the spherical harmonics $Y(\theta_i, \phi_i) = 1/4\pi$ for orbital angular momentum $l = 0$. The radial wave function is given in Eq. (3) [9].

$$\begin{aligned} \varphi_{in}(r_i) &= A_i \frac{\sin(\alpha_i r_i)}{\alpha_i r_i}, \quad \alpha_i = \frac{\sqrt{2m_i E_i}}{\hbar} \text{ for } 0 < r_i \leq R; \\ \varphi_{out}(r_i) &= B_i \frac{\exp(-\beta_i r_i)}{\beta_i r_i}, \quad \beta_i = \frac{\sqrt{2m(V_i - E_i)}}{\hbar} \text{ for } r_i > R; \quad i = e, h \end{aligned} \quad (3)$$

where A_i and B_i are the normalization constants for $\varphi_{in}(r_i)$ and $\varphi_{out}(r_i)$, respectively. $\varphi_{in}(r_i)$ is the spherical Bessel function of the zeroth order and $\varphi_{out}(r_i)$ is the spherical Hankel function of the first kind of order zero. Inside the potential well, the electron and hole have the effective mass of m_e and m_h , respectively. Outside the potential well, both the electron and hole have the mass of electron m . To determine α_i , β_i and the kinetic energy E_i , we apply the boundary conditions (i) and (ii) [20], as given in Eq. (4).

$$\begin{aligned} \text{i)} \quad & \varphi_{in}(r_i = R) = \varphi_{out}(r_i = R); \\ \text{ii)} \quad & \frac{1}{m_i} \frac{\partial \varphi_{in}(r_i)}{\partial r_i} \Big|_{r_i=R} = \frac{1}{m} \frac{\partial \varphi_{out}(r_i)}{\partial r_i} \Big|_{r_i=R}; \quad i = e, h \end{aligned} \quad (4)$$

The resulting Eq. (5) is numerically solved to find a set of α_i and β_i that satisfies $F(\alpha_i, \beta_i) = 0$ at $r_i = R$, which results in the kinetic energies of electron (T_e) and hole (T_h) [9].

$$F(\alpha_i, \beta_i) = \frac{\alpha_i R}{\tan(\alpha_i R)} + \left(\frac{m_i}{m} - 1 \right) + \frac{m_i}{m} \beta_i R; \quad i = e, h. \quad (5)$$

The size-dependent dielectric constant of QD (ϵ) and the mean distance between electron and hole (r_0) inside QD are calculated using the Haken equation [19], as given in Eqs. (6) and (7), respectively.

$$\begin{aligned} \frac{1}{\epsilon} &= \frac{1}{\epsilon_0} + \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \left[\frac{\exp(-r_0/\rho_e) + \exp(-r_0/\rho_h)}{2} \right]; \\ \rho_i &= \left(\frac{\hbar}{2m_i \omega_{LO}} \right); \quad i = e, h \end{aligned} \quad (6)$$

$$\begin{aligned} r_0 &= \langle \varphi_{in}(r_e) \varphi_{in}(r_h) \| \mathbf{r}_e - \mathbf{r}_h \| \varphi_{in}(r_e) \varphi_{in}(r_h) \rangle \\ &= \int_0^R \int_0^R \int_0^\pi \sqrt{r_e^2 + r_h^2 - 2r_e r_h \cos \theta} |\varphi_{in}(r_e)|^2 |\varphi_{in}(r_h)|^2 r_e^2 r_h^2 \sin \theta d\theta dr_e dr_h \end{aligned} \quad (7)$$

where ω_{LO} is the longitudinal optical frequency and θ is the angle between \mathbf{r}_e and \mathbf{r}_h .

The electron–hole interaction energy (V) includes the charge–charge (V_{charge}) [12], charge–image charge ($V_{image\ charge}$) [12] and

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