Pseudopotential calculations of nanoscale CdSe quantum dots

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A plane-wave semiempirical pseudopotential method with nonlocal potentials and spin-orbit coupling is used to calculate the electronic structure of surface-passivated wurtzite CdSe quantum dots with up to 1000 atoms. The calculated optical absorption spectrum reproduces the features of the experimental results and the exciton energies agree to within ; 0.1 eV over a range of dot sizes. The correct form of Coulomb interaction energy with size-dependent dielectric constant is found to be essential for such good agreement.

One of the best-studied quantum dot systems is CdSe.[1–9] It can be prepared[1] with a narrow size distribution of only 5% rms, and was the subject of detailed spectroscopic studies,[1] thus offering the opportunity for detailed comparison between experiment and theory. We will focus here on ~i! the dependence of exciton energy E_{ex} on the diameter D of the quantum dot;[1,2,5,6,8] ~ii!

results.[16] The predominate feature of quantum dot $\epsilon_2(E)$ is the development of a few strong ''excitonic peaks'' near the threshold shoulder of the bulk $\epsilon_2(E)$.[17,18]

bution to the screening. To include the ionic contribution to the screening, one can define a distance-dependent screening dielectric constant $\epsilon(r_{eh})$ from

$$V(r_{eh}) = 1/\epsilon(r_{eh})r_{eh}, \tag{4}$$

where r_{eh} is the electron-hole distance and $V(r_{eh})$ is the screened electron-hole Coulomb potential. Then the expression of $1/\epsilon(r_{eh})$ derived by Haken[20] for *bulk* exciton screening is

$$\frac{1}{\epsilon^{\text{bulk}}(r)} = \frac{1}{\epsilon_{\infty}^{\text{bulk}}} + \left[\frac{1}{\epsilon_{\infty}^{\text{bulk}}} - \frac{1}{\epsilon_0^{\text{bulk}}}\right]\left[1 - \frac{e^{-2r/r_e} + e^{-2r/r_h}}{2}\right], \tag{5}$$

where $r_e = (2m_e^* \nu_{\text{LO}}/\hbar)^{-1/2}$ and $r_h = (2m_h^* \nu_{\text{LO}}/\hbar)^{-1/2}$. Here, ν_{LO} is the longitudinal-optical–phonon frequency and m_e^* and m_h^* are electron and hole effective masses. For CdSe, $r_e \approx 33$ Å and $r_h \approx 18$ Å. In Eq. (5) and the following, the subscripts ∞ and 0 stand for $\nu = \infty$ (electronic contribution) and $\nu = 0$ (electronic and ionic contributions), respectively, and $\epsilon_0^{\text{bulk}} = 9.7$. To extend Eq. (5) to the case of the quantum dot, we require that the ϵ

$$\frac{1}{e^{\mathrm{dot}}(r,D)} = \frac{1}{\tilde{e}^{\mathrm{dot}}(D)} + \left[\frac{1}{\tilde{e}^{\mathrm{dot}}(D)} - \frac{1}{\tilde{e}^{\mathrm{dot}}(D) + e(\mathrm{ion})}\right] \times \{1 - [e^{-2r/r_e} + e^{-2r/r_h}]/2\}. \quad (6)$$

Substituting Eq. (6) into Eq. (4), and using the electron and hole charge density $\{\sin(2\pi r/D)/(2\pi r/D)\}^2$, we have numerically calculated the Coulomb interaction energies. To present the result in a simple form, we can retain Eq. (3), with the $\tilde{e}^{\mathrm{dot}}(D)$ in Eq. (3) expressed as

$$\frac{1}{\tilde{e}^{\mathrm{dot}}(D)} = \frac{1}{\tilde{e}^{\mathrm{dot}}(D)} + b(D)\left[\frac{1}{\tilde{e}^{\mathrm{dot}}(D)} - \frac{1}{\tilde{e}^{\mathrm{dot}}(D) + e(\mathrm{ion})}\right]. \quad (7)$$

The $b(D)$'s for the four quantum dots from large to small are 0.348, 0.282, 0.212, and 0.139, respectively. Here $b(D)$ indicates how much the ions have participated in the exciton screening. The final calculated exciton energies $E_{\mathrm{ex}}(D)$ using Eqs. (3) and (7) (or, equivalently, from Eqs. (4) and (6)) are shown in Fig. 4(b) as crosses compared with the experimental results (diamonds). Our calculated result agrees very well with the experimental results (the diamonds in Fig. 4(b)) for the range of quantum dot size we have studied. The differences between the calculated and experimental results range from 0.2 eV (the smallest dot) to 0.1 eV (the larger dots). This high degree of agreement demonstrates the quantitative accuracy of the SEPM approach to the electronic structure calculations of nanostructures. Finally, as shown in Fig. 4(b), the Coulomb interaction energy is large. The use of $\tilde{e}^{\mathrm{dot}}(D)$ instead of e^{bulk} is important. However, for the very small quantum dots, the exact formalism of this Coulomb energy via the use of the dielectric constant is far from clear. The ; 0.2 eV error in Fig. 4(b) for the smallest dot might stem from this uncertainty of the calculated Coulomb energy at that small size range. More work needs to be done to get more accurate results of the exciton energy for this very