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Addition energies and quasiparticle gap of CdSe nanocrystals

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Using atomistic pseudopotential wave functions we calculate the quasiparticle gap, the optical gap and the electron and hole addition energies of CdSe nanocrystals. We find that the quasiparticle gap and the addition energies depend strongly on the dielectric constant of the surrounding material, while the optical gap is rather insensitive to the environment. We provide scaling lows for these quantities as a function of the quantum dot size, and compare our results with recent scanning tunneling spectroscopy experiments. © *2000 American Institute of Physics.*
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Recent developments in the spectroscopy of *single* semiconductor quantum dots allow one to obtain resolution-limited spectra by eliminating all sources of inhomogeneous broadening. These experimental techniques include single-dot far-field photoluminescence,

$$^{\mathrm{opt}}_{\mathrm{gap}} = \left(^{0}_{\mathrm{gap}} - J^{\mathrm{dir}}_{h1,e1} \right) + \left(^{\mathrm{pol}}_{h1} + ^{\mathrm{pol}}_{e1} - J^{\mathrm{pol}}_{h1,e1} \right) \simeq ^{0}_{\mathrm{gap}} - J^{\mathrm{dir}}_{h1,e1} . \quad (8)$$

Here $^{0}_{\mathrm{gap}} = ^{0}_{e1} - ^{0}_{h1}$ is the single-particle gap, and $^{0}_{e2} - ^{0}_{e1}$ is the splitting between the two lowest electron levels. $^{\mathrm{pol}}$ is the polarization self-energy of an electron or a hole) in the single-particle orbital which occurs due to the dielectric discontinuity between the dot and the surrounding material,[7] and $J^{\mathrm{pol}}_{,}$ is the polarization energy arising from the interaction of an electron in the single-particle orbital and an electron in the single-particle orbital mediated by the surface polarization charge.[7] Both $^{\mathrm{pol}}$ and $J^{\mathrm{pol}}_{,}$ vanish when $_{\mathrm{out}} = _{\mathrm{in}}$, and decay monotonically as $_{\mathrm{out}}$ increases. The quantity $J^{\mathrm{dir}}_{,}$ is the conventional direct Coulomb repulsion between particles in orbitals and , while $K_{,}$ is the corresponding exchange attraction.

We consider here nearly spherical CdSe nanocrystals having the wurtzite lattice structure. The interatomic bondlength is assumed to be the same as in bulk CdSe, and the surface dangling bonds are passivated using ligandlike potentials. As discussed in Ref. 8, we first solve the single-particle Schrödinger equation

$$\left[- \quad ^{2} + V_{\mathrm{ps}}\ \mathbf{r}) + \hat{V}_{\mathrm{nl}} \right] \quad \mathbf{r}, \ ) = ^{0} \quad \mathbf{r}, \ ) \quad (9)$$

in a plane-wave basis set. Here $V_{\mathrm{ps}}(\mathbf{r})$ is the total pseudopotential of the system nanocrystal+ligands), and $\hat{V}_{\mathrm{nl}}$ is a short-range operator that accounts for the nonlocal part of the potential, including spin-orbit coupling. The local pseudopotential $V_{\mathrm{ps}}(\mathbf{r})$ is calculated from the superposition of screened atomic pseudopotentials, which are fitted to reproduce the measured *bulk* transition energies, deformation potentials, and effective masses, as well as the bulk single-particle wave functions calculated using density-functional theory in the local-density approximation. These pseudopotentials were previously used to calculate the first eight excitonic transitions of CdSe nanocrystals.[8]

The single-particle wave functions $(\mathbf{r}, \ )$ obtained from Eq. 9) are then used to calculate the Coulomb and polarization integrals that occur in Eqs. 5)– 8). We assume that the macroscopic dielectric constant $(\mathbf{r})$ changes smoothly from $_{\mathrm{in}}$ inside the dot to $_{\mathrm{out}}$ outside the dot, with a transition region of the order of the interatomic bondlength. We use a modified Penn model[9] to calculate $_{\mathrm{in}}(D)$, while $_{\mathrm{out}}$ is treated as a parameter. The Coulomb energies $J^{\mathrm{tot}}_{,}$ are calculated as

$$J^{\mathrm{tot}}_{,} = e \sum \int |$$

calculations. We then proceed to determine the scaling laws of the calculated quantities as a function of the quantum dot diameter. Assuming a single power law, we find:

$$^{\mathrm{qp}}_{\mathrm{gap}} = 1.83 + 82.47 \times D^{-1.30}\,\mathrm{eV}, \quad (14)$$

$$\Delta^{(e)}_{1,2} = 11.96 \times D^{-1.01}\,\mathrm{eV}, \quad (15)$$

$$\Delta^{(e)}_{2,3} = 27.93 \times D^{-1.06}\,\mathrm{eV}, \quad (16)$$

$$^{\mathrm{opt}}_{\mathrm{gap}} = 1.83 + 92.75 \times D^{-1.50}\,\mathrm{eV}, \quad (17)$$

where the diameter D is expressed in Å. Note that i) In the bulk limit ($D \rightarrow$) the quasiparticle gap and the optical gap