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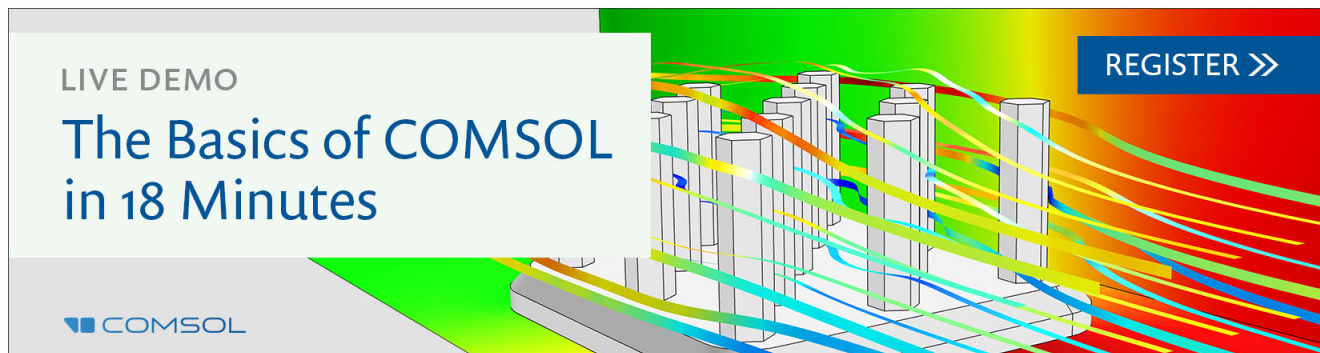
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Addition energies and quasiparticle gap of CdSe nanocrystals

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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 laws 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,¹ single-electron tunneling,² and confocal optical microscopy.^{3,4} In recent single-dot scanning tunneling spectroscopy (STM) experiments,^{5,6} an STM tip is positioned above a specific quantum dot, and the tunneling current-voltage spectrum is acquired by applying a bias V between the STM tip and the substrate. The conductance dI/dV shows, as a function of the voltage V , a series of sharp peaks which correspond (possibly via a scaling factor) to the electron and hole charging energies μ_N . Figure 1 shows a schematic diagram of the conductance/voltage spectrum. The basic physical quantities that can be measured by this method (see Fig. 1) are:

(i) The “*zero-current gap*,” which is the measured difference between the voltage of the first peak in forward bias and the first peak in reverse bias. It corresponds to the difference between the charging energy μ_1 for adding the first electron to the quantum dot and the charging energy μ_{-1} for removing an electron from the dot. This quantity is also called “*quasiparticle gap*,” and will be denoted here as $\varepsilon_{\text{gap}}^{\text{qp}}$. Its *microscopic* meaning is the energy required to remove an electron from the highest occupied orbital h_1 of a neutral dot and place this electron in the lowest unoccupied orbital e_1 of an identical dot located at infinite separation from the first. If $E_N(E_{-N})$ denotes the ground-state total energy of a quantum dot with N electrons in the conduction band (N holes in the valence band), the quasiparticle gap is

$$\varepsilon_{\text{gap}}^{\text{qp}} \equiv \mu_1 - \mu_{-1} = [E_1 - E_0] - [E_0 - E_{-1}]. \quad (1)$$

(ii) The “*intra-doublet spacing*,” which is the measured difference between the voltages of the first and second peaks in forward bias (for electrons) or in reverse bias (for holes). It corresponds to the first addition energy $\Delta_{1,2}^{(e)} \equiv \mu_2 - \mu_1$ for electrons and $\Delta_{1,2}^{(h)} \equiv \mu_{-1} - \mu_{-2}$ for holes. In terms of the total energies E_N , we have

$$\Delta_{1,2}^{(e)} \equiv \mu_2 - \mu_1 = [E_2 - E_1] - [E_1 - E_0]. \quad (2)$$

An analogous equation holds for $\Delta_{1,2}^{(h)}$.

(iii) The “*inter-multiplet spacing*,” which is the measured difference between the second and third peaks in forward bias. It corresponds to the second electron addition energy $\Delta_{2,3}^{(e)} \equiv \mu_3 - \mu_2$, and is given by

$$\Delta_{2,3}^{(e)} \equiv \mu_3 - \mu_2 = [E_3 - E_2] - [E_2 - E_1]. \quad (3)$$

(iv) In addition, optical spectroscopies give access to the “*optical gap*” $\varepsilon_{\text{gap}}^{\text{opt}}$, which is the minimum energy needed to optically excite an *interacting* electron-hole pair in the quantum dot. It is related to the quasiparticle gap via

$$\varepsilon_{\text{gap}}^{\text{opt}} = \varepsilon_{\text{gap}}^{\text{qp}} - J_{h_1, e_1}^{\text{tot}}, \quad (4)$$

where $J_{h_1, e_1}^{\text{tot}}$ is the total electron-hole Coulomb energy.

Our purpose here is to compare the calculated and measured quantities indicated in Eqs. (1)–(4). This will establish a quantitative, microscopic interpretation of the fundamental energetics of quantum dots. If successful, this can be used to predict the scaling laws for such quantities as a function of the quantum dot size. By writing the total energies E_N of Eqs. (1)–(4) in terms of single-particle, Coulomb and polarization energies, and assuming that the single-particle electron and hole levels are occupied in order of increasing single-particle energies, we obtain the following expressions:

$$\varepsilon_{\text{gap}}^{\text{qp}} = \varepsilon_{\text{gap}}^0 + \Sigma_{h_1}^{\text{pol}} + \Sigma_{e_1}^{\text{pol}}, \quad (5)$$

$$\Delta_{1,2}^{(e)} = J_{e_1, e_1}^{\text{dir}} + J_{e_1, e_1}^{\text{pol}} = J_{e_1, e_1}^{\text{tot}}, \quad (6)$$

$$\Delta_{2,3}^{(e)} = (\varepsilon_{e_2}^0 - \varepsilon_{e_1}^0) + (2J_{e_1, e_2}^{\text{tot}} - J_{e_1, e_1}^{\text{tot}}) - K_{e_1, e_2}, \quad (7)$$

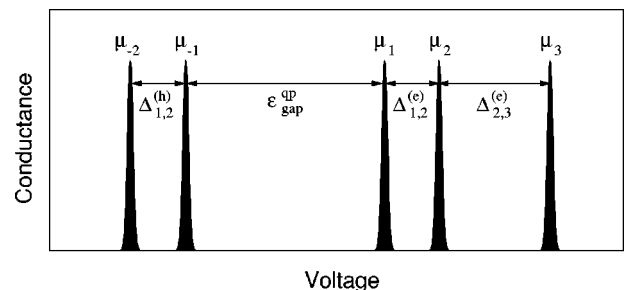


FIG. 1. Schematic diagram of the conductance/voltage spectrum of a semiconductor quantum dot.

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$$\varepsilon_{\text{gap}}^{\text{opt}} = (\varepsilon_{\text{gap}}^0 - J_{h1,e1}^{\text{dir}}) + (\sum_{h1}^{\text{pol}} + \sum_{e1}^{\text{pol}} - J_{h1,e1}^{\text{pol}}) \simeq \varepsilon_{\text{gap}}^0 - J_{h1,e1}^{\text{dir}}. \quad (8)$$

Here $\varepsilon_{\text{gap}}^0 = \varepsilon_{e1}^0 - \varepsilon_{h1}^0$ is the single-particle gap, and $\varepsilon_{e2}^0 - \varepsilon_{e1}^0$ is the splitting between the two lowest electron levels. $\sum_{\alpha}^{\text{pol}}$ is the polarization self-energy of an electron (or a hole) in the single-particle orbital α which occurs due to the dielectric discontinuity between the dot and the surrounding material,⁷ and $J_{\alpha,\beta}^{\text{pol}}$ is the polarization energy arising from the interaction of an electron in the single-particle orbital α and an electron in the single-particle orbital β mediated by the surface polarization charge.⁷ Both $\sum_{\alpha}^{\text{pol}}$ and $J_{\alpha,\beta}^{\text{pol}}$ vanish when $\epsilon_{\text{out}} = \epsilon_{\text{in}}$, and decay monotonically as ϵ_{out} increases. The quantity $J_{\alpha,\beta}^{\text{dir}}$ is the conventional direct Coulomb repulsion between particles in orbitals α and β , while $K_{\alpha,\beta}$ 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

$$[-\nabla^2 + V_{\text{ps}}(\mathbf{r}) + \hat{V}_{\text{nl}}] \psi_{\alpha}(\mathbf{r}, \sigma) = \varepsilon_{\alpha}^0 \psi_{\alpha}(\mathbf{r}, \sigma) \quad (9)$$

in a plane-wave basis set. Here $V_{\text{ps}}(\mathbf{r})$ is the total pseudopotential of the system (nanocrystal+ligands), and \hat{V}_{nl} is a short-range operator that accounts for the nonlocal part of the potential, including spin-orbit coupling. The local pseudopotential $V_{\text{ps}}(\mathbf{r})$ 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 $\psi_{\alpha}(\mathbf{r}, \sigma)$ 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 $\epsilon(\mathbf{r})$ changes smoothly from ϵ_{in} inside the dot to ϵ_{out} outside the dot, with a transition region of the order of the interatomic bondlength. We use a modified Penn model⁹ to calculate $\epsilon_{\text{in}}(D)$, while ϵ_{out} is treated as a parameter. The Coulomb energies $J_{\alpha,\beta}^{\text{tot}}$ are calculated as

$$J_{\alpha,\beta}^{\text{tot}} = e \sum_{\sigma} \int |\psi_{\alpha}(\mathbf{r}, \sigma)|^2 \Phi_{\beta}(\mathbf{r}) d\mathbf{r}, \quad (10)$$

where $\Phi_{\beta}(\mathbf{r})$ satisfies the Poisson equation

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \Phi_{\beta}(\mathbf{r}) = -4\pi e \sum_{\sigma} |\psi_{\beta}(\mathbf{r}, \sigma)|^2. \quad (11)$$

The Coulomb energies $J_{\alpha,\beta}^{\text{tot}}$ can be further decomposed into a direct contribution and a polarization contribution. The polarization self-energies $\sum_{\alpha}^{\text{pol}}$ are calculated as

$$\sum_{\alpha}^{\text{pol}} = \frac{e}{2} \sum_{\sigma} \int \psi_{\alpha}^{*}(\mathbf{r}, \sigma) V_S(\mathbf{r}) \psi_{\alpha}(\mathbf{r}, \sigma) d\mathbf{r}, \quad (12)$$

where $V_S(\mathbf{r}) = \lim_{\mathbf{r}' \rightarrow \mathbf{r}} [G(\mathbf{r}, \mathbf{r}') - G_{\text{bulk}}(\mathbf{r}, \mathbf{r}')]$. Here $G(\mathbf{r}, \mathbf{r}')$ is the Green's function associated with the Poisson Eq. (11),

TABLE I. Quasiparticle gap $\varepsilon_{\text{gap}}^{\text{qp}}$, intra-doublet electron splitting $\Delta_{1,2}^{(e)}$, inter-multiplet splitting $\Delta_{2,3}^{(e)}$, and optical gap $\varepsilon_{\text{gap}}^{\text{opt}}$ (all in eV) of CdSe nanocrystals calculated for a few values of the effective dielectric constant ϵ_{out} . For each nanocrystal, the diameter D , the dielectric constant ϵ_{in} computed at the diameter D (Ref. 9), the single-particle gap $\varepsilon_{\text{gap}}^0$, and the splitting $\varepsilon_{e2}^0 - \varepsilon_{e1}^0$ are given in the first column.

| System | ϵ_{out} | $\varepsilon_{\text{gap}}^{\text{qp}}$ | $\Delta_{1,2}^{(e)}$ | $\Delta_{2,3}^{(e)}$ | $\varepsilon_{\text{gap}}^{\text{opt}}$ |
|---|-------------------------|--|----------------------|----------------------|---|
| $D = 20.6 \text{ \AA}$ | 1 | 4.41 | 1.40 | 1.99 | 2.98 |
| $\epsilon_{\text{in}} = 5.2$ | 3 | 3.42 | 0.56 | 1.14 | 2.83 |
| $\varepsilon_{\text{gap}}^0 = 3.11 \text{ eV}$ | 6 | 3.05 | 0.33 | 0.90 | 2.69 |
| $\varepsilon_{e2}^0 - \varepsilon_{e1}^0 = 0.62 \text{ eV}$ | 12 | 2.77 | 0.21 | 0.77 | 2.53 |
| $D = 29.3 \text{ \AA}$ | 1 | 3.54 | 1.00 | 1.39 | 2.51 |
| $\epsilon_{\text{in}} = 5.9$ | 3 | 2.85 | 0.39 | 0.79 | 2.43 |
| $\varepsilon_{\text{gap}}^0 = 2.62 \text{ eV}$ | 6 | 2.62 | 0.23 | 0.62 | 2.36 |
| $\varepsilon_{e2}^0 - \varepsilon_{e1}^0 = 0.41 \text{ eV}$ | 12 | 2.45 | 0.15 | 0.52 | 2.27 |
| $D = 38.5 \text{ \AA}$ | 1 | 3.06 | 0.77 | 1.06 | 2.27 |
| $\epsilon_{\text{in}} = 6.3$ | 3 | 2.53 | 0.30 | 0.59 | 2.22 |
| $\varepsilon_{\text{gap}}^0 = 2.35 \text{ eV}$ | 6 | 2.36 | 0.18 | 0.45 | 2.17 |
| $\varepsilon_{e2}^0 - \varepsilon_{e1}^0 = 0.30 \text{ eV}$ | 12 | 2.24 | 0.11 | 0.38 | 2.11 |

and $G_{\text{bulk}}(\mathbf{r}, \mathbf{r}')$ is the bulk Green's function. The exchange energies, such as $K_{e1,e2}$ in Eq. (7), are small, and will be neglected in the following.

Table I shows our results for three different sizes and a range of values of ϵ_{out} . We see that:

(i) The quasiparticle gap $\varepsilon_{\text{gap}}^{\text{qp}}$, and the addition energies $\Delta_{1,2}^{(e)}$ and $\Delta_{2,3}^{(e)}$ depend strongly on the effective dielectric constant ϵ_{out} of the environment.

(ii) The optical gap $\varepsilon_{\text{gap}}^{\text{opt}}$ depends weakly on ϵ_{out} . The reason is that as shown in Eq. (8), the terms $\sum_{h1}^{\text{pol}} + \sum_{e1}^{\text{pol}}$ and $J_{h1,e1}^{\text{pol}}$, which depend strongly on ϵ_{out} , nearly cancel each other.

(iii) The formula $\varepsilon_{\text{gap}}^0 = \varepsilon_{\text{gap}}^{\text{qp}} - \Delta_{1,2}^{(e)}$, used by Banin *et al.*⁵ and Alpers *et al.*⁶ to extract the single-particle gap from conductance measurements is incorrect. From Eqs. (5) and (6) we see that

$$\varepsilon_{\text{gap}}^{\text{qp}} - \Delta_{1,2}^{(e)} = (\varepsilon_{\text{gap}}^0 - J_{e1,e1}^{\text{dir}}) + (\sum_{h1}^{\text{pol}} + \sum_{e1}^{\text{pol}} - J_{e1,e1}^{\text{pol}}). \quad (13)$$

The second bracketed term is nearly zero. As a result, $\varepsilon_{\text{gap}}^{\text{qp}} - \Delta_{1,2}^{(e)}$ is *smaller* than $\varepsilon_{\text{gap}}^0$ by approximately the direct Coulomb energy $J_{e1,e1}^{\text{dir}}$. In our calculations we find $J_{e1,e1}^{\text{dir}} = 0.37, 0.24,$ and 0.17 eV for $D = 20.6, 29.3,$ and 38.5 \AA , respectively (where D is the nanocrystal diameter).

In order to compare our results with the experimental data of Alpers *et al.*⁶ we need to know the effective dielectric constant ϵ_{out} of the surrounding material. Table I illustrates our results for $\epsilon_{\text{out}} = 1, 3, 6,$ and 12 . We find that the effective dielectric constant $\epsilon_{\text{out}} \sim 3$ provides a good fit to the measured $\varepsilon_{\text{gap}}^{\text{qp}}$, $\Delta_{1,2}^{(e)}$, and $\Delta_{2,3}^{(e)}$ for the 30-Å-diam nanocrystal (see Table II). We will thus use $\epsilon_{\text{out}} = 3$ in the following

TABLE II. Comparison between calculated and measured properties. The experimental values of $\varepsilon_{\text{gap}}^{\text{qp}}$, $\Delta_{1,2}^{(e)}$, and $\Delta_{2,3}^{(e)}$ are taken from Ref. 6, while $\varepsilon_{\text{gap}}^{\text{opt}}$ is taken from Ref. 10. All values are in eV.

| Dot diameter (Å) | $\varepsilon_{\text{gap}}^{\text{qp}}$ | | $\Delta_{1,2}^{(e)}$ | | $\Delta_{2,3}^{(e)}$ | | $\varepsilon_{\text{gap}}^{\text{opt}}$ | |
|------------------|--|-------|----------------------|-------|----------------------|-------|---|-------|
| | Calc. | Expt. | Calc. | Expt. | Calc. | Expt. | Calc. | Expt. |
| 20 | 3.49 | 3.13 | 0.58 | 0.34 | 1.18 | 1.00 | 2.88 | |
| 30 | 2.81 | 2.88 | 0.38 | 0.33 | 0.77 | 0.85 | 2.40 | 2.54 |
| 45 | 2.41 | 2.44 | 0.25 | 0.22 | 0.50 | 0.50 | 2.14 | 2.24 |

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:

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

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

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

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

where the diameter D is expressed in \AA . Note that (i) In the bulk limit ($D \rightarrow \infty$) the quasiparticle gap and the optical gap approach the bulk band gap (1.83 eV), while the addition energies approach zero. (ii) The optical gap and the quasiparticle gap decay faster than the addition energies.

Using Eqs. (14)–(17) we are able to extrapolate our calculated quantities to the experimentally determined quantum dot sizes.⁶ The results are compared in Table II with the experimental data of Alperon *et al.*⁶ for single nanocrystals, and of Norris and Bawendi¹⁰ for ensembles of nanocrystals. We see from Table II that $\varepsilon_{\text{gap}}^{\text{qp}}$, $\Delta_{1,2}^{(e)}$, and $\Delta_{2,3}^{(e)}$ are in good agreement with the experimental results of Alperon *et al.*⁶ The largest discrepancies occur for the $D = 20 \text{ \AA}$ nanocrystal. The optical gap $\varepsilon_{\text{gap}}^{\text{opt}}$ is somewhat underestimated compared to the results of Norris and Bawendi.¹⁰ We note, however, that the nanocrystal size is difficult to determine experimentally, and is subject to a significant uncertainty.

As shown by Eq. (7), the electron addition energy $\Delta_{2,3}^{(e)}$ depends both on the single-particle energy difference $\varepsilon_{e2}^0 - \varepsilon_{e1}^0$ and on the Coulomb and exchange energies. The $e2 - e1$ splitting cannot be directly measured. Alperon *et al.* estimated the $e2 - e1$ splitting by subtracting $\Delta_{1,2}^{(e)}$ from $\Delta_{2,3}^{(e)}$. For a 30-\AA -diam dot they obtain $\varepsilon_{e2}^0 - \varepsilon_{e1}^0 \approx 0.52 \text{ eV}$. The $e2 - e1$ splitting of CdSe nanocrystals was independently derived by Guyot-Sionnest and Hines¹¹ using infrared spectroscopy. For an ensemble of nanocrystals having a mean diameter of 31.5 \AA they found the first infrared absorption peak at 0.50 eV . If one assumes that the electron-hole Coulomb energy is nearly the same for an electron in the $e1$ state and in the $e2$ state, one can identify the infrared absorption energy with the $e2 - e1$ splitting. This value should be compared with our calculated splitting $\varepsilon_{e2}^0 - \varepsilon_{e1}^0 = 0.41 \text{ eV}$ at $D = 29.3 \text{ \AA}$ (Table I).

Finally, we have calculated the addition energies $\Delta_{N,N+1} \equiv \mu_{N+1} - \mu_N$ of CdSe nanocrystals for N up to 7 electrons (or holes). The electron and hole addition energies of a $D = 29.3 \text{ \AA}$ CdSe nanocrystal calculated for $\varepsilon_{\text{out}} = 3$ are shown in Fig. 2 as a function of N . The pronounced peak in the electron addition spectrum for $N = 2$, corresponding to $\Delta_{2,3}^{(e)}$, is due to the filling of the $e1$ electron shell: adding a third electron to a dot already containing two electrons in the $e1$ shell requires investing the single-particle energy $\varepsilon_{e2}^0 - \varepsilon_{e1}^0$, as shown by Eq. (7). The second electron shell is p like, and consists of three nearly degenerate single-particle levels which can be occupied by up to six electrons. Thus,

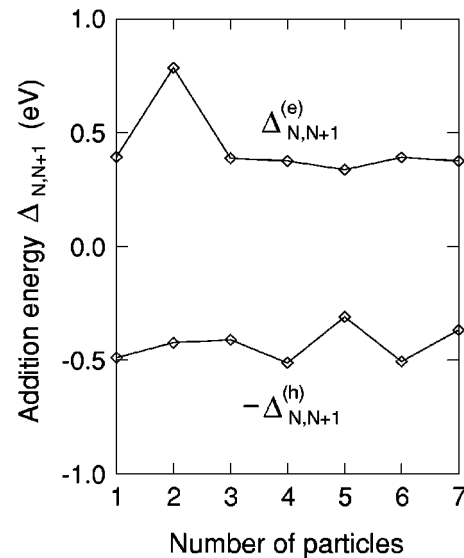


FIG. 2. Electron and hole addition energies of a 29.3-\AA -diam CdSe nanocrystal, as a function of the number of particles N , calculated for $\varepsilon_{\text{out}} = 3$.

the next few addition energies are almost entirely determined by the electron Coulomb repulsion, and depend rather weakly on N . The addition energies of the holes are approximately constant up to $N = 4$. This is due to the fact that the energy difference between the hole single-particle states is relatively small, and is comparable with the variations of the direct Coulomb energies between different hole states.

In conclusion, we have calculated the electron and hole addition energies, the quasi-particle gap, and the optical gap of CdSe quantum dots in the strong confinement regime. Atomistic pseudopotential wave functions are used as input for the calculation of Coulomb and polarization integrals. Our results are compared with recent experimental data obtained by scanning tunneling spectroscopy, and provide a microscopic interpretation of the experimentally measured quantities.

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