Addition Spectra of Quantum Dots: the Role of Dielectric Mismatch

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Using atomistic pseudopotential wave functions, we calculate the electron and hole addition energies and the quasi-particle gap of InAs quantum dots. We find that the addition energies and the quasi-particle gap depend strongly on the dielectric constant ϵ_{out} of the surrounding material, and that when

at infinite distance from the first dot). The energy required by this process ("quasi-particle gap") is the difference between the ionization potential and the electron affinity of the dot. The initial configuration, consisting of the two neutral dots in the ground state, has energy $2E_0$, while the final configuration has energy $E_1 + E_{-1}$, where E_{-1} is the energy of the quantum dot with a hole in the highest occupied orbital h1. The quasi-particle gap is then

where $\epsilon_{\mathrm{gap}} \quad \epsilon_{\mathrm{e1}} - \epsilon_{\mathrm{h1}}$ is the single-particle (HOMO−LUMO)

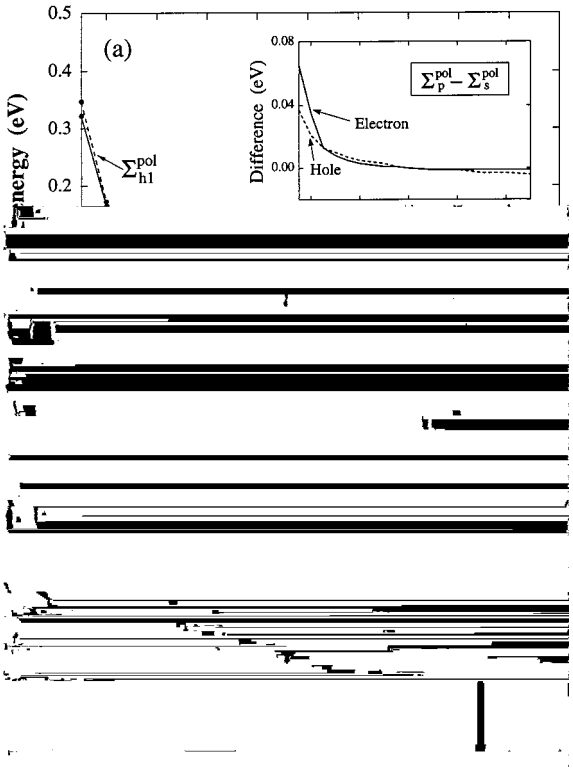

Figure 2. Self-energies Σ^{pol}_{h1} and Σ^{pol}_{e1} (a) and polarization energies $J^{pol}_{h1,h1}$ and $J^{pol}_{e1,e1}$ (b) of an InAs quantum dot (diameter $D = 30.3$ Å) shown as a function of the outside dielectric constant ϵ_{out}. Also shown in (b) are the direct Coulomb energies $J^{dir}_{h1,h1}$ and $J^{dir}_{e1,e1}$. The insets show the differences $\Sigma^{pol}_{p} - \Sigma^{pol}_{s}$ and $J^{pol}_{s,p} - J^{pol}_{s,s}$ as a function of ϵ_{out}. The vertical arrows indicate the value $\epsilon_{out} = \epsilon_{in}$.

We see that (i) both Σ^{pol}_{i} and $J^{pol}_{i,j}$ depend strongly on ϵ_{out} and vanish when $\epsilon_{out} = \epsilon_{in}$ (vertical arrows in Figure 2); (ii) when $\epsilon_{out} > \epsilon_{in}$ the polarization energies $J^{pol}_{i,j}$ become negative, thus acting to diminish the electron−electron interaction; (iii) the dependence of Σ^{pol}_{i} and $J^{pol}_{i,j}$ on the identity of the orbitals i and j (e.g., s or p) is rather weak, as shown in the insets in Figure 2; (iv) there is a critical value of ϵ_{out} ($\epsilon_{critical}$ 4) such that for $\epsilon_{out} < \epsilon_{critical}$ the polarization energies $J^{pol}_{i,j}$ dominate over the direct Coulomb energies $J^{dir}_{i,j}$.

The charging energies $\acute{\imath}_N = E_N - E_{N-1}$, calculated from the total energies E_N given by eq 7, are shown in the central panel of Figure 3 as a function of ϵ_{out}. The vertical arrow at the bottom of the figure denotes the value $\epsilon_{out} = \epsilon_{in}$, which divides the behavior into two domains: (i) In the weak screening regime ($\epsilon_{out} \ll \epsilon_{in}$) the charging energies are widely spaced, and their value depends strongly on ϵ_{out}. (ii) In the strong screening regime ($\epsilon_{out} \geq \epsilon_{in}$) the charging energies are closely spaced and do not depend significantly on ϵ_{out}. The calculated charging spectrum is shown in Figure 3 for $\epsilon_{out} = 1$ (left-hand side) and $\epsilon_{out} = 20$ (right-hand side), illustrating these two limiting behaviors.

The electron and hole addition energies $\Delta_{N,N+1}$ (spacings between peaks in the charging spectra of Figure 3), the quasiparticle gap ϵ^{qp}_{gap}, and the optical gap ϵ^{opt}_{gap} are summarized in Table 1 for a few values of ϵ_{out}.

Electron Addition Energies. We see from Table 1 that the addition energy of the third electron $\Delta^{(e)}_{2,3}$ is significantly larger than the addition energy of the second electron $\Delta^{(e)}_{1,2}$. This can be explained by noting from eqs 4 and 5 that while $\Delta^{(e)}_{1,2}$ measures only the interelectronic repulsion, $\Delta^{(e)}_{2,3}$ includes also the single-particle gap $\epsilon_{e2} - \epsilon_{e1}$ between the s-like state e1 and the p-like states e2, e3, and e4. We find $\epsilon_{e2} - \epsilon_{e1} = 400$ meV for the 30.3 Å diameter nanocrystal and 360 meV for the 42.2 Å diameter nanocrystal. The addition energies of the remaining electrons (up to $N = 8$) are approximately constant, as a consequence of the fact that the p-like states e2, e3, and e4 are nearly degenerate. The addition energy of the ninth electron, $\Delta^{(e)}_{8,9}$, is slightly larger, and reflects the single-particle gap between the p-like shell and the next (d-like) shell.

Hole Addition Energies. The addition energies of the holes are approximately constant. This is due to the fact that the energy difference between the h1, h2 and the h3, h4 single-particle states is relatively small (38 meV in the 30.3 Å diameter nanocrystal and 14 meV in the 42.2 Å diameter nanocrystal) and is comparable with the variations of the direct Coulomb energies $J^{dir}_{i,j}$ between different hole states. Banin et al.[1] found

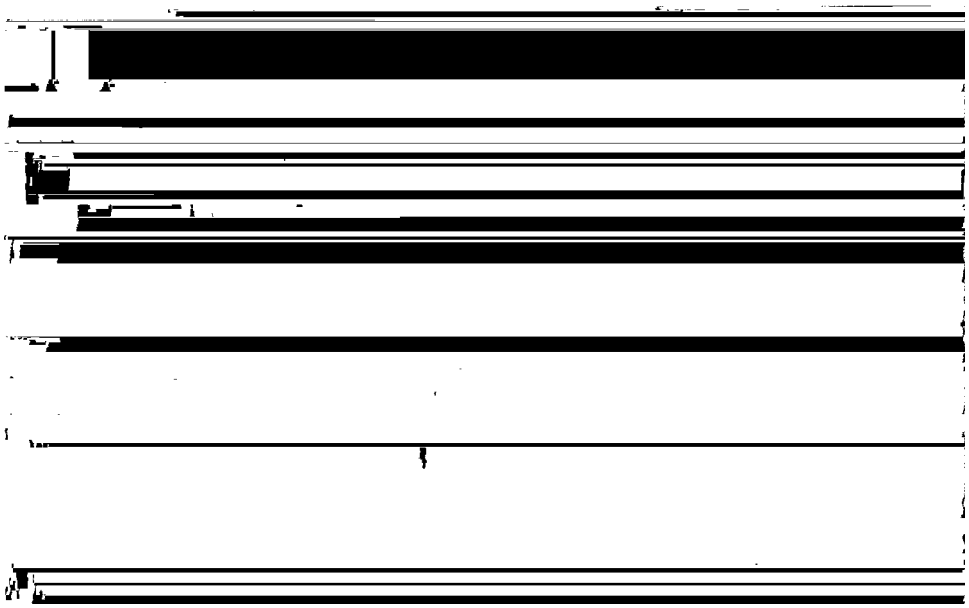

Figure 3. (middle panel) Dependence of the electron and hole charging energies on the outside dielectric constant ϵ_{out}. The vertical arrow indicates the value $\epsilon_{out} = \epsilon_{in}$. The side panels show the calculated charging spectrum in the case $\epsilon_{out} = 1$ (left-hand panel) and $\epsilon_{out} = 20$ (right-hand panel). The zero of the energy scale corresponds to the highest-energy valence state.

TABLE 1: Addition Energies $\Delta_{N,N+1}$, Quasi-Particle Gap ϵ_{gap}^{qp}, and Optical Gap ϵ_{gap}^{opt} of InAs Nanocrystals (in eV) for Different Values of the Dielectric Constant ϵ_{out}

$D = 30.3$ Å, ϵ	

two distinct multiplets in the hole addition spectrum, which they denoted as 1_{VB} and 2_{VB}. They attributed the 2_{VB} multiplet to tunneling of holes into the $2S_{3/2}$ valence-band level. We find that the $2S_{3/2}$ level is significantly lower in energy than the h1−h4 levels, so we do not consider hole injection into the $2S_{3/2}$ level. Our calculations show that charging of the h1−h4 levels produces a rather featureless spectrum, and that the first multiplet in the hole addition spectrum (1_{VB}) consists of at least eight nearly equally spaced peaks. The fact that Banin et al.[1] do not observe such a high multiplicity suggests that some of the hole charging peaks may be missing.

Quasi-Particle and Optical Gap. As shown in Table 1, the quasi-particle gap ϵ_{gap}^{qp} depends strongly on ϵ_{out}, while the optical gap $\epsilon_{gap}^{opt} = \epsilon_{gap}^{qp} - J_{h1,e1}$ does not. This is so because the terms $(\Sigma_{h1}^{pol} + \Sigma_{e1}^{pol})$ and $J_{h1,e1}^{pol}$ tend to cancel, so $\epsilon_{gap}^{opt} \approx (\epsilon_{e1} - \epsilon_{h1}) - J_{h1,e1}^{dir}$.

Table 1 provides clear predictions for the addition energies and the quasi-particle gap of InAs nanocrystals. To compare with the experimental measurements of Banin et al. (ref 1), in which ϵ_{out} is an unknown quantity, we first fit our calculated $\Delta_{1,2}^{(e)}$ for the smaller dot with the experimental value $\Delta_{1,2}^{(e)} = 0.22$ eV, finding that $\epsilon_{out} = 6$ gives a good fit (Table 1). This value of ϵ_{out} should be viewed as the "effective" dielectric constant of the environment, which accounts for the presence of metal electrodes as well as organic ligands. Using $\epsilon_{out} = 6$, we then predict for $D = 30.3$ Å (experimental data in parentheses for $D = 34$ Å) $\epsilon_{gap}^{qp} = 1.78$ (1.75), $\Delta_{1,2}^{(h)} = 0.23$ (0.20), $\Delta_{2,3}^{(h)} = 0.26$ (0.22), $\Delta_{2,3}^{(e)} = 0.64$ (0.71), and $\Delta_{3,4}^{(e)} = 0.24$ (0.23). Using the same value of ϵ_{out}, our predictions for $D = 42.2$ Å (experimental data in parentheses for $D = 44$ Å) are: $\epsilon_{gap}^{qp} = 1.38$ (1.38), $\Delta_{1,2}^{(h)} = 0.18$ (0.20), $\Delta_{2,3}^{(h)} = 0.15$ (0.17), $\Delta_{1,2}^{(e)} = 0.15$ (0.14), $\Delta_{2,3}^{(e)} = 0.51$ (0.52), and $\Delta_{3,4}^{(e)} = 0.15$ (0.14). We see that we can achieve a very good agreement with experiment using a single value of the parameter ϵ_{out}.

Our theory can be further used to decompose the experimentally measured quantities into distinct physical contributions. For example, for $D = 30.3$ Å the quasi-particle gap $\epsilon_{gap}^{qp} = 1.78$ eV includes [eq 6] the single-particle gap $\epsilon_{e1} - \epsilon_{h1} = 1.71$ eV and the polarization self-energy contribution $\Sigma_{h1}^{pol} + \Sigma_{e1}^{pol} = 0.07$ eV. The addition energy for the third electron $\Delta_{2,3}^{(e)} = 0.64$ eV includes [eq 5] the single-particle contribution $\epsilon_{e2} - \epsilon_{e1} = 0.40$ eV, the direct Coulomb contribution $2J_{e1,e2}^{dir} - J_{e1,e1}^{dir} = 0.17$ eV, the polarization contribution $2J_{e1,e2}^{pol} - J_{e1,e1}^{pol} = 0.07$ eV, and a negligible self-energy contribution $\Sigma_{e2}^{pol} - \Sigma_{e1}^{pol}$. The exchange contribution $K_{e1,e2}$ is smaller than 0.02 eV, and can be neglected.

In conclusion, we predict the effects of the dielectric environment on the electron and hole charging energies and on the addition spectrum of semiconductor quantum dots. We find that the charging energies and the addition energies depend sensitively on the dielectric constant ϵ_{out} of the surrounding material via the self-energies Σ_i^{pol} and the polarization energies $J_{i,j}^{pol}$. Our calculations for InAs nanocrystals are in excellent agreement with recent spectroscopic results[1] for $\epsilon_{out} = 6$, and provide a quantitative prediction of how single-electron tunneling in quantum dots can be tuned by changing the dielectric environment.

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