Pseudopotential calculations of electron and hole addition spectra of InAs, InP, and Si quantum dots

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The electron and hole addition energies, the quasiparticle gap, and the optical gap of InAs, InP, and Si quantum dots are calculated using microscopic pseudopotential wave functions. The effects of the dielectric mismatch between the quantum dot and the surrounding material are included using a realistic profile for the dielectric constant $\epsilon(\mathbf{r}$

The electron and hole charging energies m_N and addition energies $D_{N,N+1}$ can be measured by charging spectroscopies or tunneling spectroscopies.[5,10] Figure 2 shows a schematic diagram of the conductance/voltage spectrum of a quantum dot. The charging energies m_N correspond to the peaks of the charging spectrum, while the addition energies $D_{N,N+1}$ correspond to the spacings between the peaks. Since the polarization energies $S_i^{\rm pol}$ and $J_{i,j}^{\rm pol}$ depend strongly on the dielectric constant $e_{\rm out}$ of the surrounding material, the charging energies m_N and the addition energies $D_{N,N+1}$ depend on the dielectric environment.

(b) Creation of a noninteracting electron-hole pair. Figure 1~b! describes the process of removing an electron from the highest-energy valence-band level h_1 of a neutral quantum dot and placing it into the lowest-energy conduction-band level e_1 of an identical dot located at infinite distance from the first dot. The energy required by this process is the difference between the ionization potential and the electron affinity of the dot and corresponds to the energy of a noninteracting electron-hole pair ~''quasiparticle gap''!. The initial configuration, consisting of the two neutral dots in the ground state, has energy $2E_0$, while the final configuration has energy $E_1@e_1\#+E_{-1}@h_1\#$, where $E_{-1}@h_1\#=E_0-«_{h1}^0+S_{h1}^{\rm pol}$ is the energy of the quantum dot with a hole in the highest occupied orbital h_1. The quasiparticle gap is then

$$«_{\rm gap}^{\rm qp}=E_1@e_1\#+E_{-1}@h_1\#-2\,E_0=«_{\rm gap}^0+S_{e1}^{\rm pol}+S_{h1}^{\rm pol}, \tag{10}$$

where $«_{\rm gap}^0 [«_{e1}^0-«_{h1}^0$ is the *single-particle* gap. For an infinitely large dot the polarization self-energies vanish, and the quasiparticle gap approaches the bulk single-particle gap: $«_{\rm gap}^{\rm qp}\rightarrow«_{\rm gap}^0$. The quasiparticle gap can be measured by tunneling spectroscopy experiments[10] as the difference $«_{\rm gap}^{\rm qp}=m_1-m_{-1}$ between the energy required to load an electron into the quantum dot and the energy required to remove an electron from the quantum dot ~Fig. 2!. We see that the quasiparticle gap depends, via the polarization self-energies $S_{e1}^{\rm pol}$ and $S_{h1}^{\rm pol}$, on the dielectric environment.

(c) Creation of an interacting electron-hole pair via optical excitation. Figure 1~c! describes the process of optically exciting an electron from the highest occupied orbital h_1 to the lowest unoccupied orbital e_1 of a neutral quantum dot.

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ing different dielectric media stems from the fact that, due to the long-range character of the Coulomb interaction and the exponential decay of the wave functions outside the quantum dot, dielectric confinement and quantum confinement can be physically separated. In fact, by changing the dielectric environment *far away* from the dot, while keeping the same barrier material next to the dot, one can control and tailor the electronic properties ~such as $\Delta_{N,N+1}$ and $\alpha_{\mathrm{gap}}^{\mathrm{qp}}$) without affecting quantum confinement ~i.e., the single-particle energies and wave functions!.

II. PREVIOUS CALCULATIONS AND PRESENT OBJECTIVES

There are two basic approaches in the literature for calculations of addition energies. The ''standard model'' of addition spectra of quantum dots is the ''constant capacitance'' model,[11] which assumes that the addition energies $\Delta_{N,N+1}$ are constant and independent of the number of particle N: $\Delta_{N,N+1}=e^2/2C$, where C is the capacitance of the dot. This simple model has been quite successful at describing Coulomb blockade effects in large quantum dots, where the Coulomb energies ~e.g., $J_{e1,e1}$) are much larger that the single-particle energy differences ~e.g., $\alpha_{e2}-\alpha_{e1}$). However, this model fails to properly describe the addition spectrum of smaller quantum dots, where the single-particle energy spacings become comparable with the Coulomb energies.

A second class of models[12–21] treats the interplay between quantum confinement and Coulomb charging using the effective-mass approximation ~EMA

The interparticle Coulomb energies $\overline{J}_{i,j}$ obtained from the solution of Eqs. ~21! and ~22! are screened by the *macroscopic* dielectric constant of the system. The *microscopic* dielectric function $\epsilon(\mathbf{r},\mathbf{r}')$, however, tends to 1 when $\mathbf{r}'\rightarrow\mathbf{r}$. As a result, the short-range interparticle interaction is essentially unscreened. Recent pseudopotential calculations have shown that for wave functions localized in a quantum dot this effect can significantly enhance the electron-hole interaction. Therefore, we calculate the interparticle Coulomb energies $J_{i,j}$ as

$$J_{i,j}=J_{i,j}^{\mathrm{dir}}+J_{i,j}^{\mathrm{pol}}, \qquad \text{~26!}$$

where $J_{i,j}^{\mathrm{pol}}$ is the polarization contribution obtained from Eq. ~25! and $J_{i,j}^{\mathrm{dir}}$

calculated polarization energies are compared in Figs. 3~c! and 3~d! with the results of an EMA calculation assuming ~i! an infinite potential barrier at the surface of the quantum dot, and ~ii! a purely *s*-like envelope function.[9] We see that the EMA calculation agrees well with the pseudopotential calculation, the difference being less than 5 meV across the entire range of values of ϵ_{out}. This suggests that the polarization energies $J_{i,j}^{\text{pol}}$ are rather insensitive to the details of the electron and hole charge distributions.

D. Polarization self-energies

The polarization self-energies S_i^{pol} are given by

$$S_i^{\text{pol}} = \frac{e}{2} \left(\right.$$

be unchanged in this range. For smaller values of ϵ_{out} ~i.e., $\epsilon_{\text{out}} ; 1-4$) the ground-state configuration may be different from the ground-state configuration at $\epsilon_{\text{out}}=\epsilon_{\text{in}}$. However, the difference in the addition energies will be of the order of a few meV, i.e., only a few percent of the addition energies themselves. ~ii! We neglect the contribution of the exchange energies $K_{i,j}$, which are about an order of magnitude smaller than the Coulomb energies $J_{i,j}$.

The addition energies $\Delta_{N,N+1}$ of a few representative dots are shown in Fig. 5 for a few values of the external dielectric constant ϵ_{out}. The following features can be noted: ~i! The electron and hole addition energies depend strongly on ϵ_{out}. This is due to the contribution of the polarization energies $J_{i,j}^{\text{pol}}$ to the addition energies $\Delta_{N,N+1}$ @see, for example, Eqs. ~7! and ~8!#. ~ii! The electron addition energies of InAs and InP quantum dots show a pronounced peak for $N=2$ ~corresponding to $\Delta_{2,3}^{(e)}$). This peak is due to the filling of the *s*-like shell: adding a third electron to a quantum dot that already contains two electrons in the *s*-like shell requires occupying a level of the *p*-like shell, which is about 0.3–0.4 eV higher in energy ~see Table I!. The effect is

The addition energies of InAs nanocrystals have been recently measured by Banin *et al.*[10] using scanning tunneling spectroscopy. In these experiments the dielectric constant of the environment (ϵ_{out}) is an unknown quantity, as it corresponds to an average over the gold contact, the hexane dithiol linking molecules, and the organic passivants.[10] To compare our calculations with the experimental results we first fit our calculated value of the addition energy $\Delta_{1,2}^{(e)}$ for the $D = 30.3$ Å InAs dot with the experimental value $\Delta_{1,2}^{(e)} = 0.22$ eV for the nearest size dot ($D = 34$ Å), finding that $\epsilon_{\text{out}} = 6$ gives a good fit. We then use this value of ϵ_{out} to calculate the addition energies and the quasiparticle gap of InAs nanocrystals as a function of size. The calculated electron and hole addition energies $\Delta_{N,N+1}$ are compared in Fig. 6~a! with the experimental results of Banin *et al.*[10] We see that we have a very good agreement for $\Delta_{1,2}^{(h)}$ and $\Delta_{1,2}^{(e)}$ using a single value of ϵ_{out}. The calculated addition energy for the third electron, $\Delta_{2,3}^{(e)}$, is somewhat smaller than the experimental value. However, the nanocrystal size measured by scanning-tunneling microscopy ~STM! tends to be overestimated,[10] and the actual size of the nanocrystals may be smaller. This would bring our results into even closer agreement with experiment.

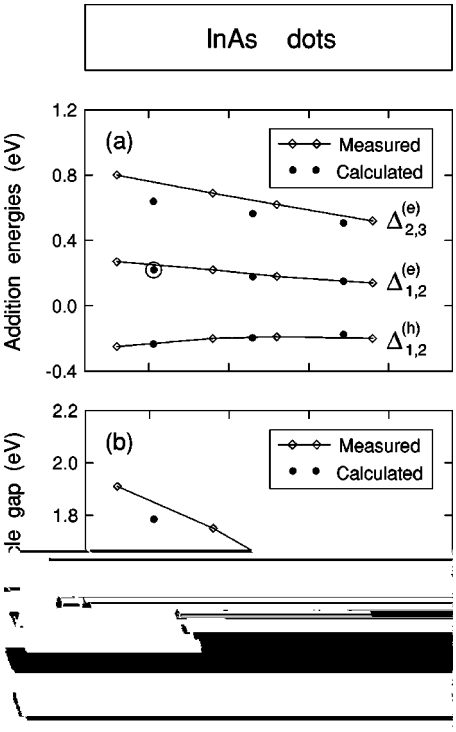

FIG. 6. The electron and hole addition energies @part ~a!# and the quasiparticle gap @part ~b!# of InAs nanocrystals, calculated for $\epsilon_{\text{out}} = 6$, are compared with the experimental data of Banin *et al.* ~Ref. 10! as a function of size. The circle in part ~a! denotes the addition energy used to fit the value of ϵ_{out1}

C. Quasiparticle gap and optical gap

The quasiparticle gap @defined by Eq. ~10!# represents the energy of a *noninteracting* electron-hole pair in a quantum dot, while the optical gap @defined by Eq. ~11!# is the energy of an *interacting* electron-hole pair in the quantum dot.

The quasiparticle gap of Si nanocrystals in vacuum ($\epsilon_{\text{out}} = 1$) was calculated by Öğüt, Chelikowsky, and Louie[42] using density-functional theory in the local-density approximation ~LDA!. They calculated the ground-state total energies E_1^{LDA} and E_{-1}^{LDA} of the charged nanocrystals as well as the ground-state energy E_0^{LDA} of the neutral dot, and obtained the quasi-particle gap as $\alpha_{\text{gap}}^{\text{qp, LDA}} = E_1^{LDA} + E_{-1}^{LDA} - 2E_0^{LDA}$. For a ; 27-Å-diameter Si nanocrystal the LDA-calculated quasiparticle gap was $\alpha_{\text{gap}}^{\text{qp, LDA}}$; 2.5 eV. However, it is well known[43] that in the bulk limit the expression $E_1^{LDA} + E_{-1}^{LDA} - 2E_0^{LDA}$ yields the LDA single-particle gap, which in the case of Si is about 0.68 eV lower than the bulk quasiparticle gap.[42] Therefore, the LDA-calculated quasi-particle gap of Si nanocrystals must also be underestimated.[43] Interestingly, if we estimate the LDA gap error in Si nanocrystals using the *bulk* LDA gap error of 0.68 Å, the quasiparticle gap be-

comes $2.5 + 0.68 \; ; \; 3.2$ eV, which is in good agreement with our calculated value of 3.1 eV.

$$\varepsilon_{\rm gap}^{\rm qp} - \Delta_{1,2}^{(e)} = \varepsilon_{\rm gap}^{0} + \tilde{}\Sigma_{h1}^{\rm pol} + \Sigma_{e1}^{\rm pol} - J_{e1,e1}! \Phi \varepsilon_{\rm gap}^{0}. \quad \tilde{}36!$$

The error is $(\Sigma_{h1}^{\rm pol} + \Sigma_{e1}^{\rm pol} - J_{e1,e1}^{\rm pol}) - J_{e1,e1}^{\rm dir}$; $-J_{e1,e1}^{\rm dir}$. Thus, $\varepsilon_{\rm gap}^{\rm qp} - \Delta_{1,2}^{(e)}$ is *smaller* than $\varepsilon_{\rm gap}^{0}$ by an amount approximately equal to $J_{e1,e1}^{\rm dir}$.

V. SUMMARY

In conclusion, we predict the effects of the dielectric environment on the electron and hole addition energies of semiconductor quantum dots. Atomistic pseudopotential wave functions are used as input for the many-body expansion of the total energy of the charged dots. We find that the the addition energies and the quasiparticle gap depend sensitively on the dielectric constant $\varepsilon_{\rm out}$ of the surrounding material via the self-energies $\Sigma_i^{\rm pol}$ and the polarization energies $J_{i,j}^{\rm pol}$. We compare the calculated addition energies of InAs nanocrystals with recent spectroscopic results,[10] finding excellent agreement for $\varepsilon_{\rm out} = 6$. Our calculations for Si and InP nanocrystals provide predictions for future single-electron charging experiments.

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