Electron and hole addition energies in PbSe quantum dots

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We calculate electron and hole addition energies of PbSe quantum dots using a pseudopotential configuration-interaction approach. We find that (i) the addition energies are nearly constant for the first eight carriers occupying the -like shell. (ii) The charging sequence of the first eight carriers is non-Aufbau, but filling of the -like single-particle states takes place only after the -like states are filled. (iii) The charging spectrum shows bunching-up of all lines as the dielectric constant ε_{out} of the material surrounding the dot increases. At the same time, the addition energies are significantly reduced. (iv) The calculated optical gap shows a rather weak dependence on ε_{out}, reflecting a cancellation between electron-hole interaction energies and surface polarization self-energies.

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I. INTRODUCTION

PbSe quantum dots have been the subject of intense research in recent years, primarily because of efficient carrier multiplication rates[1,2] and relatively slow intraband relaxation rates.[3–5] In this paper, we focus on another unique property of PbSe quantum dots: the high multiplicity of the band-edge states, and its consequence on dot charging. In PbSe,[6] both the valence-band maximum (VBM) and the conduction-band minimum (CBM) are located at the point of the fcc Brillouin zone, and hence are fourfold degenerate (eightfold degenerate including Kramer's degeneracy), on account of the fourfold degeneracy of the valleys. Correspondingly, in PbSe , the first, -like electron and hole confined states are eightfold degenerate. This degeneracy is split (by 4–7 meV in a dot of radius =30.6 Å, and by 16–35 meV in a dot of =15.3 Å) by intervalley couplings induced by the lack of translational symmetry.[7] The manifold of -like electron states is separated from the next group of -like states by a few hundred meV, whereas for the holes the - separation is a few tens of meV, as obtained by recent pseudopotential calculations[7,8] and by scanning tunneling measurements.[9] Because of the near-degeneracy of the band-edge -like states, up to eight electrons or eight holes can be injected into these low-lying states. In this work, we study theoretically such charging effects.

Depending on the relative rates of carrier injection into the dot and carrier escape from the dot, one might be either in "accumulation mode"[10] (the th injected carrier encounters −1 pre-existing carriers) or in "tunneling mode"[10] (the dot has but one carrier at a time). In accumulation mode, the charging energy $\mu(\ )$ is the energy required to add a carrier to the dot that is already loaded with −1 carriers[11]:

$$\mu(\ ) = (\ ) - (\ -1), \tag{1}$$

where $(\ )$ is the ground-state total energy of the -carrier dot. The addition energy $\Delta(\ ,\ -1)$ is the difference between the charging energy of the th carrier and that of the −1 carrier:

$$\Delta(\ ,\ -1) = \mu(\ ) - \mu(\ -1) = (\ ) - 2\ (\ -1) + (\ -2). \tag{2}$$

Measurements of charging energies and addition energies by resonant tunneling spectroscopy were previously reported for colloidal nanocrystals such as InAs,[12] CdSe,[10] and ZnO.[13–15] Analysis of such measurements affords determina-

$$ \text{int}_{\text{PT}}(\quad) = \sum_{\quad} \varepsilon_{\quad}^{0} + \frac{1}{2}\sum_{\quad} [\ \text{int}_{\quad\quad} - \ \text{int}_{\quad\quad}], \tag{4} $$

where $\varepsilon_{\quad}^{0}$ are the single-particle energies, $\text{int}_{\quad\quad}$ ($\text{int}_{\quad\quad}$) are the Coulomb direct (exchange) integrals, the subscripts $\quad,\quad,\quad,\quad$ denote the collective index of orbital and spin states, and the sum runs over the occupied states. The general form of the Coulomb and exchange integrals $\text{int}_{\quad\quad}$ is

$$ \text{int}_{\quad\quad} = \sum_{\sigma} \int \psi_{\quad}^{*}(\mathbf{r},\sigma)\psi_{\quad}(\mathbf{r},\sigma)\Phi_{\quad}^{\text{int}}(\mathbf{r})\, \mathbf{r}, \tag{5} $$

where $\{\psi_{\quad}(\mathbf{r},\sigma)\}$ are the single-particle wave functions (which depend on the spatial variable $\mathbf{r}$ and the spin variable σ), and $\Phi_{\quad}^{\text{int}}(\mathbf{r})$ is the solution of the Poisson equation

$$ \varepsilon(\mathbf{r})\nabla^{2}\Phi_{\quad}^{\text{int}}(\mathbf{r}) = -4\pi\quad^{2}\sum_{\sigma} \psi_{\quad}^{*}(\mathbf{r},\sigma)\psi_{\quad}(\mathbf{r},\sigma). \tag{6} $$

Here $\varepsilon(\mathbf{r})$ is the $\quad\ \quad\ \quad$, position-dependent dielectric constant.

The surface-polarization energy $\text{pol}_{\text{PT}}(\quad)$, due to the dielectric constant mismatch between the quantum dot and its surrounding material, is

$$ \text{pol}_{\text{PT}}(\quad) = \sum_{\quad} \Sigma_{\quad}^{\text{pol}} + \frac{1}{2}\sum_{\quad} [\ \text{pol}_{\quad\quad} - \ \text{pol}_{\quad\quad}], \tag{7} $$

where $\Sigma_{\quad}^{\text{pol}}$ is the surface-polarization self-energy of a carrier in the single-particle state $\quad$, and $\text{pol}_{\quad\quad}$ ($\text{pol}_{\quad\quad}$) are the Coulomb direct (exchange) integrals arising from the interaction of one carrier with the image charge of other carriers across the dielectric discontinuity at the dot surface. The surface polarization self-energy is given in first-order perturbation theory by

$$ \Sigma_{\quad}^{\text{pol}} = \sum_{\sigma} \int |\psi_{\quad}(\mathbf{r},\sigma)|^{2}\Sigma(\mathbf{r})\, \mathbf{r}, \tag{8} $$

where $\Sigma(\mathbf{r})$ is the surface polarization potential

$$ \Sigma(\mathbf{r}) = \frac{1}{2}\lim_{\quad'\to}\{\ \ _{\text{dot}}(\mathbf{r},\mathbf{r}') - \ \ _{\text{bulk}}(\mathbf{r},\mathbf{r}')\}. \tag{9} $$

Here $\ _{\text{dot}}(\mathbf{r},\mathbf{r}')$ is the screened Coulomb potential of the quantum dot at point $\mathbf{r}$ due to a point charge located at $\mathbf{r}'$

C. Quasiparticle band gap

The quasiparticle gap $\varepsilon_{\mathrm{gap}}^{\mathrm{qp}}$ is the minimum energy necessary to remove an electron from the valence band of one dot and place it into the conduction band of another dot at infinite distance from the first dot. Thus the electron and the hole do not interact. In first-order perturbation theory, the quasiparticle gap is given by

$$\varepsilon_{\mathrm{gap}}^{\mathrm{qp}} = [\varepsilon_{\sim 1}^{0} - \varepsilon_{\cdot,1}^{0}$$

dielectric function transition from ε_{in} to ε_{out}. A similar behavior of $\Sigma(\mathbf{r})$ is also observed for the 15.3-Å dot, but the value of $\Sigma(\mathbf{r})$ inside the dot is larger than that for the 30.6-Å-radius dot, because of the closer proximity of the dot surface.

Table I summarizes our calculated surface polarization self-energies Σ^{pol} for several band-edge electron ( ) and hole ( ) single-particle states, and for a few different dielectric function profiles. The effect of ε_{out} on Σ^{pol} is strong, as exemplified by the state of the =15.3-Å dot whose surface polarization energy decreases from ~374 meV for $\varepsilon_{out}=1$ to ~5 meV for $\varepsilon_{out}=20$. For a given ε_{out}, the value of Σ^{pol} depends rather weakly upon the single-particle state. However, some single-particle states, such as and , have considerably larger Σ^{pol} (by as much as 87 meV for $\varepsilon_{out}=1$) than the other states. In general, states that have a relatively large weight just outside the dot boundary have smaller Σ^{pol} than states that are more localized inside the dot, because $\Sigma(\mathbf{r})$ becomes negative outside the dot boundary (Fig. 1). This Σ^{pol} difference among single-particle states is sufficiently large to determine a change in the ordering of the levels in the single-particle energy ladder.

B. Charge distribution of the injected carriers

It is interesting to consider the spatial distribution of the loaded carriers. In a classical electrostatic model where the carriers are described by point charges that are free to move inside a dielectric sphere,[21] Coulomb repulsion leads to localization of the injected carriers near the surface of the quantum dot. In our quantum-mechanical calculations, carrier localization is determined by the spatial localization of the single-particle wave functions and by the mixing of different configurations via configuration interaction. Because of the relatively large splitting between and levels and the large dielectric constant of PbSe (which effectively screens carrier-carrier interactions), configuration mixing beyond the -like manifold is small. In the absence of surface states near the band edges, the first eight injected carriers will occupy -like, quantum-confined states, and their charge distribution will be largely localized in the dot interior. However, the inorganic ligand shell surrounding the PbSe quantum dots can hardly passivate all surface anions and cations, resulting in localized surface states. In that case, part of the injected carriers will reside at the surface of the quantum dots.

C. Charging spectrum and addition energies

Figures 2 and 3 show the charging spectrum and the addition energies $\Delta(, -1)$ obtained by diagonalizing the CI many-body Hamiltonian for $\varepsilon_{out}=1, 2.1, 20$. Figures 2(a) and 3(a) show the charging spectra of the =15.3-Å and =30.6-Å dots, respectively. The position of the peaks corresponds to the calculated charging energies, while the intensity of the peaks is normalized to unity. We see that as the dot size increases, the span of the charging energies corresponding to loading eight electrons or eight holes decreases considerably. Furthermore, as the dielectric constant ε_{out} of the environment increases, the charging spectrum shows bunching of the peaks, because the separation between the charging peaks becomes smaller as ε_{out} increases. In Figs. 2(a) and 3(a) $\mu=0$ is the chemical potential of the electron reservoir. Thus for $\mu<0$ electrons are attracted to the quantum dot, while for $\mu>0$ electrons are repelled. We see from the charging spectra of Figs. 2(a) and 3(a) that only a limited number of electrons (corresponding to the peaks with $\mu\leq 0$) can be loaded into the quantum dot. The number of electrons that can be injected into the dot becomes smaller as the dielectric constant of the environment decreases. For example, in the case of the =15.3-Å dot, up to six electrons can be loaded into the dot if $\varepsilon_{out}=2.1$, but only three electrons if $\varepsilon_{out}=1$ [Fig. 2(a)].

Figures 2(b) and 3(b) show that the addition energies depend only weakly on the number of carriers within the shell. This behavior of $\Delta(, -1)$ can be recovered by reformulating Eq. (16) under the following approximations: (i) The single-particle energy levels $(\varepsilon^0+\Sigma^{pol})$ are the same for the first few single-particle states, (ii) the correlation energy Δ_{corr}

The successive application of approximations (i) and (iii) leads to

$$\Delta(\ ,\ -1) = A\ , \tag{27}$$

which describes the trend in the numerical results. Thus the value of $\Delta(\ ,\ -1)$ can be interpreted as an indirect measure of the Coulomb repulsion between carriers, independent of under the aforementioned approximations. When the small spacings between the quasiparticle energy levels are taken into account, however, $\Delta(\ ,\ -1)$ is more pronounced for

states, and therefore $\Delta(\ ,\ -1)$ is nearly constant up to $=12$ (Ref. 11

of $\Sigma^{\mathrm{pol}}_{\tilde{1}}+\Sigma^{\mathrm{pol}}_{\cdot 1}$ against $\langle \cdot 1_{\tilde{1}}\tilde{1};\cdot 1_{\tilde{1}}\tilde{1}\rangle$ in Eq. (20). As a result, $\varepsilon^{\mathrm{opt}}_{\mathrm{gap}}$ is close to the single-particle gap $\varepsilon^{0}_{\tilde{1}}-\varepsilon^{0}_{\cdot 1}$, and shows a rather weak dependence on $\varepsilon_{\mathrm{out}}$. This cancellation is not particular to PbSe dots, and a similarly weak dependence of $\varepsilon^{\mathrm{opt}}_{\mathrm{gap}}$ on $\varepsilon_{\mathrm{out}}$ was previously reported for InAs, InP, and Si quantum dots.[11]

V. SUMMARY

In summary, we have calculated the electron and hole addition energies of PbSe quantum dots using a pseudopotential configuration-interaction approach. We have decomposed the addition energies into physically distinct contributions. This has revealed peculiar features of the charging spectrum of PbSe quantum dots: (i) The addition energies are nearly constant for the first eight carriers occupying quantum-confined $\cdot$-like states. (ii) While the charging sequence of the first eight carriers is non-Aufbau, filling of the -like single-particle states takes place only after the $\cdot$-like states are completely filled. We also found general features of the charging spectrum that are not specific to PbSe dots. (iii) The charging spectrum shows bunching-up of all lines as the dielectric constant $\varepsilon_{\mathrm{out}}$ of the material surrounding the dot increases. (iv) The calculated optical gap shows a rather weak dependence on $\varepsilon_{\mathrm{out}}$, reflecting a cancellation between electron-hole Coulomb interaction energies and surface polarization self-energies.

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[1] R. D. Schaller and V. I. Klimov, Phys. Rev. Lett. **92**, 186601 (2004).
[2] R. J. Ellingson, M. C. Beard, J. C. Johnson, P. Yu, O. I. Micic, A.