Multiple charging of InAs/GaAs quantum dots by electrons or holes: Addition energies and ground-state configurations

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Received 1 November 2005; revised manuscript received 4 January 2006; published 20 March 2006

Atomistic pseudopotential plus configuration interaction calculations of the energy needed to charge dots by

gies, and show how to calculate these quantities in the single-particle pseudopotential plus many-particle CI scheme. In Sec. III, we give detailed results calculated from pseudopotential-CI scheme the single-particle levels, Coulomb integrals and the ground state configurations as well as the addition energies. We contrast these results with the parabolic 2D-EMA model. We summarize in Sec. IV.

II. THEORY OF DOT CHARGING AND ADDITION ENERGIES

A. General equation for dot charging in the configuration-interaction approach

The calculation of the total-energy $E(N)$ of N-particle dot requires obtaining first the single-particle states from an effective Schrödinger equation, and then the many-particle state from a many-particle treatment. The first step is formulated as,

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_{scr}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}), \quad (3)$$

where $V_{ext}(\mathbf{r})$ is the external ("bare") potential experienced by the electrons or holes, and $V_{scr}(\mathbf{r})$ is the screening response. The single-particle orbital ψ_i and energies ε_i are used in the second step to construct the many-particle wave functions Ψ_i and energies (E) from,

$$E(N) = \Psi_N(H)\Psi_N \quad (4)$$

where, the many-body Hamiltonian is,

$$H = \sum_{i,\sigma} \varepsilon_i c_{i\sigma}^{\dagger} c_{i\sigma} + \frac{1}{2}\sum_{i,j,k,l}\sum_{\sigma,\sigma'} \langle ij|kl\rangle\, c_{i\sigma}^{\dagger} c_{j\sigma'}^{\dagger} c_{k\sigma'} c_{l\sigma}, \quad (5)$$

and,

$$\langle ij|kl\rangle = \sum_{\mathbf{s}_1,\mathbf{s}_2}\int\int d\mathbf{r}\, d\mathbf{r}' \frac{\psi_i^*(\mathbf{r},\mathbf{s}_1)\psi_j^*(\mathbf{r}',\mathbf{s}_2)\psi_k(\mathbf{r}',\mathbf{s}_2)\psi_l(\mathbf{r},\mathbf{s}_1)}{\varepsilon(\mathbf{r}-\mathbf{r}')|\mathbf{r}-\mathbf{r}'|}, \quad (6)$$

are the screened Coulomb and exchange integrals. In the above Eqs. (5) and (6), we use $c_{i\sigma}(\mathbf{r}) = A\,\psi_i(\mathbf{r})$ as the field operator, whereas A is a fermion operator, and $\psi_i(\mathbf{r})$ is the single-particle eigenfunction. Here, "σ" is a pseudospin index, i.e., an index of Kramers degenerate states, while "$\mathbf{s}$" is the A electronic spin. For ε_i in InAs/GaAs QDs, the spin-orbit interactions is extremely small and can be neglected. In this case, the pseudospin σ and intrinsic electronic spin $\mathbf{s}$ are equivalent. However, for ε_i, which have a mixture of heavy-, (H) light-hole (LH) and split-off character, an eigenstate of σ has both $\mathbf{s}=\uparrow$ and $\mathbf{s}=\downarrow$ components. The N-particle wave functions can be solved using, e.g., configuration interaction (CI) method,[23] by expanding the N-electron wave function in a set of Slater determinants, $\Phi_{\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_N} = A^{\dagger}_{\varepsilon_1}A^{\dagger}_{\varepsilon_2}\ldots A^{\dagger}_{\varepsilon_N}\Phi_0$, where $A^{\dagger}_{\varepsilon_i}$ creates an electron in the state ε_i. The ith many-particle wave function is then the linear combination of the determinants,

$$\Psi_i^N = \sum_{\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_N} A_i(\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_N)\,\Phi_{\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_N}. \quad (7)$$

Once Ψ_N is known, we can then calculate the corresponding total energies for the ground states as well as excited states using Eq. (4). Once we solve the CI problem, we get the order of total CI energy for various holes or electron configurations, so we can see if Hund's rule or the Aufbau principle or spin-blockade occurs. For example, H ε states that degenerate single-particle levels are occupied with maximum number of unpaired electrons, while the Aufbau principle states, nondegenerate single-particle levels are occupied in order of increasing single-particle energy.

We construct all possible Slater determinants corresponding to N electrons or N holes (i.e., we ignore the excitonic (electron+hole) excitations), using only the bound states of the dots, (i.e., we neglect all continuum states). The underlying electrons that are not considered explicitly by this approach are represented by the dielectric screening function $\varepsilon(\mathbf{r}-\mathbf{r}')$ in Eq. (6).

B. The Hartree-Fock equations for charging and addition energies

$$E_{\mathrm{HF}}(4) = 2\varepsilon + \varepsilon_1 + \varepsilon_2 + J + 2J_1 + 2J_2 + J_{12} - K_1 - K_2 - K_{12},$$

$$E_{\mathrm{HF}}(5) = 2\varepsilon + 2\varepsilon_1 + \varepsilon_2 + J + 4J_1 + 2J_2 + J_{11} + 2J_{12} - 2K_1 - K_2 - K_{12},$$

$$E_{\mathrm{HF}}(6) = 2\varepsilon + 2\varepsilon_1 + 2\varepsilon_2 + J + 4J_1 + 4J_2 + J_{11} + J_{22} + 4J_{12} - 2K_1 - 2K_2 - 2K_{12}. \quad (10)$$

We can then readily calculate the charging energies Eq. (1) in this approximation,

$$\mu_{\mathrm{HF}}(1) = \varepsilon,$$

$$\mu_{\mathrm{HF}}(2) = \varepsilon + J,$$

$$\mu_{\mathrm{HF}}(3) = \varepsilon_1 + 2J_1 - K_1,$$

$$\mu_{\mathrm{HF}}(4) = \varepsilon_2 + 2J_2 + J_{12} - K_2 - K_{12},$$

$$\mu_{\mathrm{HF}}(5) = \varepsilon_1 + 2J_1 + J_{11} + J_{12} - K_1,$$

$$\mu_{\mathrm{HF}}(6) = \varepsilon_2 + 2J_2 + 2J_{12} + J_{22} - K_2 - K_{11}. \quad (11)$$

Similarly, we can calculate the addition energies Eq. (2) as follows,

$$\Delta_{\mathrm{HF}}(1,2) = J,$$

$$\Delta_{\mathrm{HF}}(2,3) = \varepsilon_1 - \varepsilon + 2J$$

$$v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{scr}}(\mathbf{r}) = v_{\mathrm{so}}(\mathbf{r}) + \sum_{n} \sum_{\mathbf{R}_n} v^{\alpha}_{\mathrm{epm}}(\mathbf{r} - \boldsymbol{\tau}_n - \mathbf{R}_n). \quad (14)$$

Here, $v^{\alpha}_{\mathrm{epm}}(\mathbf{r})$ is determined semiempirically. Unlike the classic empirical pseudopotential method,[24] which fitted only to eigenvalues, here we require that when Eq. (3) is applied to the underlying periodic solids containing atom α, $v^{\alpha}_{\mathrm{epm}}$ reproduce the band energies, effective-mass tensors, deformation potentials, and the single-particle wave functions have a large overlap with the corresponding LDA wave functions.[25,26] In Eq. (14), a nonlocal potential $v_{\mathrm{so}}(\mathbf{r})$ is also added to the total potential to represent the spin-orbit interaction. In our approach, the potential of an As atom depends on the number of Ga and In atoms around it as

$$v_{\mathrm{As}}(\mathrm{Ga}_n \mathrm{In}_{4-n}) = \frac{n}{4} v_{\mathrm{As}}(\mathrm{Ga}) + \frac{4-n}{4} v_{\mathrm{As}}(\mathrm{In}), \quad (15)$$

where n is the number of Ga atoms around the As atom. In this atomistic approach, one assume that $v^{\alpha}_{\mathrm{epm}}(\mathbf{r})$ is transferable to different environments. Note that a fixed v is a good approximation if the dot has no surfaces (as is the case in self-assembled dots, where only a strained interface between chemically-similar materials is present). For surface atoms in free-standing dots, a separate $v^{\alpha}_{\mathrm{epm}}(\mathbf{r})$ is fitted[27] to LDA calculations. For InAs/GaAs dots, we use the pseudopotentials of Ref. 19. These pseudopotentials have been tested not only for the InAs and GaAs binaries, but also for alloys and superlattices of the corresponding ternaries.[19]

Once $v^{\alpha}_{\mathrm{epm}}(\mathbf{r})$ is known, one can solve Eq. (3) for the bulk solid, quantum wells superlattices, quantum-wires or quantum dots by adopting a supercell approach where the respective objects are placed. In our case, Eq. (3) is solved using the "linear combination of Bloch bands" (LCBB) method,[28] where the wave functions are expanded as,

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{m} \sum_{\mathbf{k}'} C^{\beta}_{n,\mathbf{k}}(m,\mathbf{k}',\varepsilon) \phi^{\beta}_{m,\mathbf{k}',\varepsilon}(\mathbf{r}). \quad (16)$$

In the above equation, $\phi^{\beta}_{m,\mathbf{k}',\varepsilon}(\mathbf{r})$ are the bulk Bloch orbitals of band index m and wave vector $\mathbf{k}$ of material β (=InAs, GaAs), strained uniformly to strain ε. The inclusion of stain-dependent basis functions improves their variational flexibility. We use $\varepsilon = 0$ for the (unstrained) GaAs matrix material, and an average ε value from valence force field (VFF) method for the strained dot material (InAs). For the InAs/GaAs system, we use $m = 8$ (including spin) for electron states on a 6 6 16 -mesh. Note that the potential $v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{scr}}(\mathbf{r})$ contain full strain effects through the use of atomic positions, in addition to the explicit strain[19] and alloy composition[29] dependence.

In the atomistic approach to the singla8lnr7821Tf0.3330TD(ncluding)259.6(spin)D6(b)lf113(n).s syston(pi4685.7044es1Tf0.59260TD39

are totally determined by J and the single-particle energy spacing δ.

However, real self-assembled quantum dots grown by the Stranski-Krastanov techniques, are not well-described by the single-band particle-in-a-box approaches, despite the great popularity of such approaches in the experimental literatures.[11,15,16,32] The model contains significant quantitative errors[37] and also qualitative errors, whereby cylindrically symmetric dots are deemed to have, by symmetry, no fine-structure splitting, no polarization anisotropy, and no splitting of "twofold degenerate" levels and levels, all being a manifestation of the "farsightedness effect."[30]

III. RESULTS

Using the pseudopotential approach for single-particle and configuration interaction approach for the many-particle step, we studied the electron or hole addition energy spectrum up to 6 carriers in lens-shaped InAs dots embedded in a GaAs matrix. We study dots of three different base size, =20, 25, and 27.5 nm, and for each base size, two heights, =2.5 and 3.5 nm. To study the alloy effects, we also calculated the addition spectrum for alloy dots In_{1-} Ga As/GaAs of / =3.5/25 nm dots, with Ga composition =0, 0.15, 0.3, and 0.5. In this section, we give detailed results of the single particle energy levels and Coulomb integrals, and the addition energy as well as ground state configurations. We also compare the results with what can be expected from the parabolic 2D-EMA model.

A. Single-particle level spacing: Atomistic versus 2D-EMA description

1. E

We depict in Fig. 2 the calculated energy-level diagram of a pure lens-shaped InAs/GaAs quantum dot, with height =2.5 nm and base =20 nm. Figure 2 shows that the electron confinement energy is 230 meV, somewhat larger than the hole confinement energy (190 meV). The levels are split as are the levels, even though the dot has macroscopic cylindrical symmetry (see below).

The pseudopotential calculated electron single-particle energy spacings are summarized in Table I for QDs of different heights, bases, and alloy compositions. Table I gives the fundamental exciton energy E calculated from CI approach for each dot. These exciton energies are between 980 and 1080 meV for pure InAs/GaAs dots, and can be as large as 1297 meV for In_{1-} Ga As/GaAs alloy dots. This range agrees very well with experimental results for these classes of dots, ranging from 990 to 1300 meV.[8,11,38,39]

(a) - - : From Table I, we see that for electrons in the lens-shaped dot, the - energy level spacing =, −, and - energy level spacing =, −, are nearly equal, as assumed by the 2D harmonic model. The energy spacing sp

- energy spacing ranges from 10 to 18 meV for dots of sizes we studied. These energy spacings are considerably smaller than those of electrons. The first confined hole state is found to be about 190 meV above the VBM of bulk GaAs, for the pure, / =2.5/20 nm dot Fig. 2. Unlike the case for electrons, the energy spacing between hole and levels depends strongly on the height of the dots,[40] while being relatively insensitive to the base size of the dots.

b *S* : The well-defined , , shell-

ticles Eq. 12

for holes[11,16,45] 20–25 meV. We plot in Fig. 4 J for electrons and holes versus height for base = 25 nm dots. For flat dots, the electron-electron Coulomb energy J^{ee} is smaller than that of holes J^{hh}. However, J^{ee} is larger than J^{hh} for taller dots. The crossover is at about 2.5 nm for the = 25 nm dots. Note that in our calculation, the two nearly degenerate electron orbitals $_1$ and $_2$, are spatially almost orthogonal to each other. However, in the simple parabolic 2D-EMA model,[16] the two degenerate orbitals $_+ = +_{,y}$ and $_- = -_{,y}$ have same spatial function differing

C. Ground state configurations: Atomistic versus 2D-EMA description

1. G *2D-E* *A*

4. G

We next use $_{1,\ 2}$, $_{2,\ 1}$, and

that for very large electrostatically confined dots, where single-particle energy spacing $\Delta/J \ll 1$ (down-left corner of the phase diagrams of Fig. 6), the ground state mixes large number of configurations, which have no significant leading configurations and are, therefore, in strongly correlated states[47] that are not discussed here.

D. Calculated charging and addition energies

Once we determined the ground state configurations, we can calculate the total energies using Eq. (4). We calculate the ground state total energies for up to 6 electrons/holes for each dot. For electrons, in the CI approach we used 6 single-particle electron levels (s, p_1, p_2, d_1, d_2, f_3) to construct all possible Slater determinants, while for holes, we used 8 single-particle hole levels. The total number of Slater determinants for 6 electrons is 924. For 6 holes, the total number of determinants is 8008. We plot in Fig. 7 the CI total energies for the ground state of 6 carriers versus number of single-particle states included in the CI expansions. The total energies converge to about 1 meV if 6 single-particle states are used for electrons and 8 states are used for holes.

The charging energies and addition energies are calculated using Eqs. (1) and (2). The addition energies calculated (dot-333.06(.7(ha.06()32.06(es)5.06(1Tf0.275.-105.39ive)20d)281.dditio

breakdown of Hund's rule as a consequence of irregular shape of the dots. These results are listed in Table V and compared with our theoretical results. We see that the electron addition energies of an In,GaAs/GaAs dot, with / =3.5/25 nm and Ga composition =0.15, agree very well with the above experimental results, which show 1,2 =20.5 meV, 2,3 =61.2 meV, and the average addition energies between -states of about 16 meV.

The experimental hole addition energies are taken from Ref. 11, which gives 1,2 =23.9 meV, comparable to that of 1,2. However, the addition energy between and orbitals, 2,3 =34.2 meV, is significantly smaller than 2,3 57 meV. This result reflects that the - energy spacing of holes is much smaller than that of electrons. As seen from Table V, our calculated addition energies of pure and flat height=2.5 nm InAs/GaAs dots agree very well with this experiment.

To study trends of addition energies for the electrons and the holes, we depict the electron addition energies for different dot heights Fig. 8a, bases Fig. 8b and alloy compositions

(ii) Electron addition energies decrease with increasing height and base of the dots, and the hole addition energies share the same trend. However, the electron addition energies are more sensitive to the base of the dots and relatively insensitive to the height. In contrast, the hole addition energies are very sensitive to the heights of the dot, and relatively

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