Pseudopotential study of electron-hole excitations in colloidal free-standing InAs quantum dots

A. J. Williamson and Alex Zunger

dot ~Secs. II A and II B!. Then we solve the ''two-particle'' problem by calculating the energy of the electron-hole excitations of the system ~Sec. II C!.

A. Single-particle calculation

We use a pseudopotential Hamiltonian to model the single-particle electronic structure of the system

$$\hat{H} = -\frac{1}{2}\nabla^2 + \sum_{a,n} v_a(\mathbf{r} - \mathbf{R}_{an}) + v_a$$

$$\hat{H}_{\mathbf{G},\mathbf{G}'} = \frac{1}{2}\mathbf{G}^2 \delta_{\mathbf{G},\mathbf{G}'} + V_{local}(\mathbf{G}-\mathbf{G}') + V_{nonlocal}(\mathbf{G},\mathbf{G}'). \quad (4)$$

The spin-orbit interaction is represented by a nonlocal pseudopotential, $V_{nonlocal}(\mathbf{G},\mathbf{G}')$, which is evaluated in real space using the linearly scaling small box method from Ref. 22. This method applies the nonlocal pseudopotential to each atom in turn. For each atom, a new wave function $c_{box}(\mathbf{r}) = c_i(\mathbf{r})$ is defined within a small box around the atom. $c_{box}(\mathbf{r})$ is periodically repeated and then fast Fourier transforms are used to generate $c_{box}(\mathbf{G})$. The non-local pseudopotential is then applied by

$$f_i(\mathbf{G}) = \sum_{\mathbf{G}'} V_{nonlocal}(\mathbf{G},\mathbf{G}')\, c_{box}(\mathbf{G}'). \quad (5)$$

The InAs dots, surrounded by barrier material, form a supercell that is periodically repeated. Sufficient barrier atoms are used, to ensure that the interactions between an InAs dot and its periodic images are negligible. The total number of atoms (In, As, and barrier) in the largest supercell is 25 000 atoms, which is too large for the Hamiltonian in Eq. (1) to be solved by conventional diagonalization methods. We thus use the ''folded spectrum method,''[23,24] in which one solves for the eigenstates of the equation

$$(\hat{H} - \varepsilon_{ref})^2 c_i = (\varepsilon - \varepsilon_{ref})^2 c_i, \quad (6)$$

where ε_{ref} is a reference energy. By placing ε_{ref} within the equation

$$F\sim F+1!=\left\langle \left(\right.\right. \quad u_{n,\mathsf{G}}f_n^{(i)}|\sim\hat{F}_u+\hat{F}_f!$$

separated by $r = 6 - 8$ Å, $e(r)$ approaches the particular

$$\overline{I}\sim E,\hat{}R\&!=\int \quad ,$$

This difference can be attributed to the fact that the pseudopotential calculated hole states are derived from a mixture of the bulk heavy and light hole states.

B. The nature of the single particle wavefunctions

The results of the single-particle wave-function analysis from Eqs. ~8!–~10! is given for the 42.2 Å diameter dot in Table V. Details of the analysis for the other dot sizes are given at Ref. 35. Only the states which contribute to the excitonic peaks discussed in Sec. II C are listed in the table. For each state, the fraction of the wave function derived from the bulk Γ-like split off, heavy (Γ_{8v}) and light hole (Γ_{7v}) and lowest conduction band (Γ_{6c}) states is given ~see Fig. 1!. For each of these bulk states, the fraction of the total wave function derived from envelope functions with *s*, *p*, and *d* symmetry is also given. The significant contributions to each state are marked in bold. Contributions less than 0.01 have been set to zero. For example, the highest energy hole state has a fraction of $0.0+0.02+0.02=0.04$ derived the bulk split-off band, $0.50+0.29+0.09=0.89$ derived from the bulk heavy and light hole bands and $0.0+0.02+0.0=0.02$ derived from the lowest bulk conduction band. The remaining 0.05 fraction is derived from bulk bands further from the band gap, and from higher angular momentum envelope functions.

Analysis of the results in Table V and those for the other size dots reveals several interesting properties of the single particle wavefunctions:

~1! The origin of the lowest lying electron states in the dot follows qualitatively the predictions of single-band effective mass theory. For example, the lowest electron state of the 42.2 Å diameter dot ~see Table V! is 69% derived from the bulk conduction band edge state (Γ_{6c}) with an *s*-like envelope function. The next two highest electron levels are 64% derived from the same bulk Bloch state, but with a *p*-like envelope functions.

~2! As a result of the small band gap of bulk InAs, there is a strong coupling between the electron and hole states. Approximately 20% of the weight of the lowest energy *electron states* in the dot is derived from the split-off, heavy and light hole ($\Gamma_{8v}+\Gamma_{7v}$) bulk states. This valence-conduction mixing explains why the 6×6 $k\cdot p$ method, which ignores such coupling, fails to describe these states in InAs dots.

~3! The highest energy hole states in the dot have significant weight from both the *s* and *p* envelope functions from both heavy- and light-hole bulk states. They therefore cannot be described, even qualitatively, by a single-band model. The VBM of the 42.2 Å diameter dot ~see Table V! has 50% *s* and 29% *p* character. Similarly, the lowest electron state in the dot has 27% non-*s* character, originating from valence bands. Such an *s*-*p* mixing is largely absent in current theoretical descriptions of InAs dots via the $k\cdot p$ method.[11]

~4! The order of the electron and hole states changes with size. This reflects different size scaling of the quantum con-

8~a!–8~d!. The identities of each of the major peaks in the spectra were determined by examining the nature of the initial and final single-particle states contributing to each peak.

conduction state is the same as in peak ~a!. In the approximate $k \cdot p$ language this transition is closest to the $P_{5/2}$ to $S_{1/2}$ transition.

~d! ''peak d'' is a transition with very weak intensity. For the largest dot with 42.2 Å diameter this transition merges with ''peak c'' and is no longer distinguishable. The initial valence state associated with this peak is a doubly degenerate hole states with a mix of mostly *s* and *d* character. It is derived from the bulk heavy- and light-hole states. This initial state has a total angular momentum that ranges from 2.48 to 3.25. The final conduction state is the same as in peak ~a!. In the approximate $k \cdot p$ language this transition is closest to the $S_{5/2}$ to $S_{1/2}$ transition.

~e! ''peak e'' has a similar origin to ''peak d'' and also has a very weak intensity. It also merges with ''peak c'' in the largest dot with 42.2 Å diameter. The initial valence state associated with this peak is a singly degenerate hole state with a mix of *s*, *d*, and some *g* character. It is derived from both the bulk spin-orbit, heavy- and light-hole states. This initial state has a total angular momentum that ranges from 3.03 to 3.75. The final conduction state is the same as in peak ~a!. In the approximate $k \cdot p$ language this transition is closest to the $S_{7/2}$ to $S_{1/2}$ transition.

~f! ''peak f'' corresponds to a transition with very weak intensity that is only observed in the two smaller dots. It has the same initial state as ''peak a,'' but the final state is the next highest conduction state. This conduction state is a triply degenerate state, with a *p*-like envelope function and a total angular momentum that ranges from 2.15 to 2.19. In the approximate $k \cdot p$ language, this transition is closest to the $S_{3/2}$ to $P_{3/2}$ transition.

~g! ‘‘peak g'' corresponds to a transition from thee the56 .6(a 0 y)-43a 0 y

$$P\text{~}R\text{!} = \frac{1}{\sqrt{2\,p\,s_R}} e^{-(R-R_0)^2/2s_R^2}. \qquad \text{~32!}$$

In Fig. 11~a! we plot ensemble absorption spectra calculated from Eq. ~24! for quantum dots with a mean diameter of 23.9 Å and standard deviations, s_R, of 0, 5 and 10% of the mean size. The function $I(E,R)$ in Eq. ~24! was obtained by fitting the size dependence of each of the peaks, *i*, in Fig. 9 to $E_i(R) = E_i^0 + aR^N$ and then summing the contributions from all the peaks so that

$$I\text{~}E,R\text{!} = \sum_{peaks,i} a \quad + \quad => \quad > \quad > \quad + \quad > \quad =- + \quad > -+ + \quad >\times \quad + \quad +$$

close to the experimental E_5 peak. For the two smaller dots, the peak splits into two peaks ~g! and ~h! with different size scaling behavior.

~5! Peak ~j! is only resolvable from peaks ~g! and ~h! in the two smaller dots, where it could correspond to either the experimental E_6 or E_7 peaks.

~6! The weaker peaks ~b!, ~e!, and ~k! are not individually resolvable for any size of dot in the ensemble spectra.

IV. CONCLUSIONS

We have performed pseudopotential calculations of the electronic structure of both the ground and excited states of free standing InAs quantum dots for a range of experimentally realistic sizes. Using calculated electron-hole Coulomb energies and dipole matrix transition probabilities we have constructed single-dot absorption spectra for 4 different sizes of quantum dot. These spectra exhibit a series of clearly resolvable exciton peaks. The size dependence of the spacing

[34] More details can be found in the ''downloadable data'' section of http://www.sst.nrel.gov
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