Excitons in InP quantum dots

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The excitonic spectrum of InP quantum dots is investigated using an atomistic pseudopotential approach for the single-particle problem and a state-dependent screened Coulomb interaction for the many-body problem. Our calculations show a different energy distribution of single-particle states relative to the commonly used $\mathbf{k}\cdot\mathbf{p}$ theory as well as significant parity mixing in the envelope functions, forbidden in 6 3 6 $\mathbf{k}\cdot\mathbf{p}$. The calculated excitonic spectrum, including seven excitons, explains well the recent experimental measurements. @S0163-1829~98!50424-9#

Colloidally prepared semiconductor quantum dots[1–3] have such a narrow size distribution and large confining potential that an unprecedented[4,5] number of ~as many as eight to ten! distinct electron-hole excitonic transitions have been observed in, e.g., CdSe,[1] InP,[2] and InAs ~Ref. 3! dots of 20–60 Å diameters. Understanding the physical origin of these rich spectra in terms of the symmetry and envelope parity ~i.e., *s*, *p*, *d*, . . .) or the bulk parentage ~light or heavy hole; G or *L* derived! of the single-particle electron and hole wave functions, and in terms of the nature[6,7] of the *screened* many-body electron-hole Coulomb interactions is an outstanding challenge.[1–5] The traditional approach[1–3] to this problem is to use the $\mathbf{k}\cdot\mathbf{p}$ method in which the dot wave functions are expanded in terms of a small number of G-like *bulk* band-edge states, and to assume an average, state-independent Coulomb interaction with a constant bulk dielectric screening.[6] Adjustment of the $\mathbf{k}\cdot\mathbf{p}$ parameters to the spectra of the quantum dots produces[1] a good fit for the three lowest of eight excitons in CdSe, but as recently shown[2] by Bertram *et al.* fails completely for excitons in InP. This failure is not related to surface states ~which were removed via etching in the experimental procedure[8]!, it represents a significant concern because the $\mathbf{k}\cdot\mathbf{p}$

which are described using the modified Penn model[12] and the Haken formulas,[13] respectively. The excitonic transition intensity is obtained by summing over the dipole matrix elements coupling hole state (i,v) and electron state (j,c), i.e.,

$$I(E) = \sum_{i,j} \frac{4e^2}{3m^2c^2} |\langle c_{i,v}|\mathbf{P}|c_{j,c}\rangle|^2 f(E - E_{ij}). \qquad (2)$$

Here, $f(E - E_{ij})$ is a Gaussian broadening function. The single-particle pairs (i,j) contributing most to the peaks of $I(E)$ are identified. The bulk parentages of these single-particle states are then analyzed by projecting the relevant dot state c_i onto bulk states $\$ f_{n\mathbf{k}}\%$ of band n and wave vector $\mathbf{k}$ as

$$c$$

Figure 1 shows the energy distribution of the single-particle valence and conduction states of a spherical $In_{240}P_{225}$ passivated dot ~with diameter of 28 Å!, as calculated by the present direct diagonalization ~DD! and by the 6 3 6 $\mathbf{k}\cdot\mathbf{p}$ approach ~in the latter case, we use pseudopotential-derived[14] $\mathbf{k}\cdot\mathbf{p}$ parameters $g_1 5 4.94$, $g_2 5 1.79$, D

The calculated screened electron-hole Coulomb interactions J_{ij} @Eq. ~1!# between valence states i and conduction states j are shown in Fig. 3 for the InP dot of 28-Å diameter. All values are given with respect to $J_{\mathrm{VBM,CBM}}$, which for this dot is calculated to be 201 meV. In previous calculations of the excitonic spectra,[1–3] J_{ij} were taken as constant for all (ij) pairs. The latter approach gives[6] a much smaller value of 148 meV for the 28-Å dot. Interestingly, we see that the Coulomb interaction between the VBM hole and the L-like conduction states @in Fig. 3~a!# is the largest. Also, quite unexpectedly from the symmetry consideration, the dot valence states of s- and p-like symmetries @numbered 1 and 3 in Fig. 3~b!# have quite similar ~only by a 7% difference! Coulomb interactions with the s-like dot CBM.

Having obtained the single-particle energies and the Coulomb interaction energies, Fig. 4 shows the calculated ~with Coulomb interaction included! intensity $I(E)$ @Eq. ~2!# for the transitions between valence and conduction states. The main peaks are assigned the letters a to g ~in assigning the transitions we assume that it is possible to observe an *isolated* peak even if it is relatively weak!.

Before comparing our transition energies with experiments, we note that our theory corresponds to a *nonvibrating* system and neglects exchange interactions.[15] Figure 5~a! shows the experimental photoluminescence excitation ~PLE! spectrum,[2] where the phonon and exchange effects are involved. We interpret[16] the two lowest transitions in Fig. 5~a! as being phonon related: transition 1 is pure phonon band, while transition 2 originates from the process whereby the exciton is formed from a spin singlet state with simultaneous excitation of one phonon while the emission occurs from a spin triplet state. We thus remove the phonon effect by dropping from Fig. 5~a! transition 1 and by subtracting the phonon energy from transition 2. We further remove the exchange effect by subtracting the exchange splitting from both transitions 2 and 3. Higher energy transitions will not be affected significantly by phonon and exchange, and thus are kept unchanged. The ensuing experimental data with phonon and exchange effects removed are plotted in Fig. 5~b!, and are compared with the theoretical results obtained from Fig. 4. We see that our atomistic calculation explains well the excitonic transition energies without invoking adjustable parameters. Furthermore, we identify the microscopic origin of these transitions. Table I analyzes, for $D \simeq 28$ Å dot, the microscopic origins of peaks a to g in Fig. 5~b! in terms of the symmetry and bulk parentage of single-particle hole and electron states. Transition a $(s \rightarrow s)$ is the band gap. Transition b results from the excitation from s-like spin-orbit split valence state to the s-like CBM. Curve b in Fig. 5~b! has almost a constant energy separation (; 0.11 eV! from the fundamental band-gap transition ~i.e., curve a). Transitions c and d involve valence states and conduction states with different angular components or bulk origins, thus being weak. Here, the valence states numbered 12 and 13 in Fig. 2, though being sd-like in the $\mathbf{k}\cdot\mathbf{p}$ language, are found to be nearly forbidden to the s-like CBM. Transitions e, f, and g in Fig. 5~b! occur between p-like valence states and p-like conduction states, and are strong.

In summary, a fully atomistic pseudopotential approach is used to calculate the excitonic transition spectrum in InP dots in a wide energy region, and more importantly, to analyze the microscopic origin of the transitions, explaining the surprising differences relative to the standard 6×6 $\mathbf{k}\cdot\mathbf{p}$ approach.

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