Coulomb Effects in the Optical Spectra of Semiconductor Quantum Dots

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Abstract

We theoretically study the optical emission spectra of multi-exciton states using a configuration interaction approach for a few excitons and a density functional calculation for several excitons in a single quantum dot. Considering InP quantum dots as an example, we show that the biexciton binding energy is determined by a delicate balance of contributions from several configurations. We discuss how Coulomb correlations and spin fine structure of multi-excitonic states clearly manifest in the emission spectrum of highly excited quantum dots. We also predict a new kind of configuration crossing transitions that lead to weak emission lines several tens of meV below the exciton ground state.

1 Introduction

The physics of quantum dots (QDs) is often compared to that of atoms and molecules because of the discrete nature of their energy levels. Although this analogy helps understanding, one difference worth emphasising is the possibility of creating multiple electron hole pair excitations in a QD. Such multi-particle complexes quickly relax into a quasi-equilibrium state in which they would exhibit features of a spatially confined many particle system such as an atom, with an added advantage that the eventual radiative decay of this state offers a convenient way to probe the intricacies of multi-particle correlations.

Experimentally, excitation of multiple electron hole pairs in a single QD is relatively easy, especially in self-assembled QDs that offer an efficient channel for pumping through the barrier material. Together with developments in single QD spectroscopy, controlled optical studies of many electron-hole pairs in a QD has become a reality[1,2]. Motivated by these considerations we present a theoretical study of multi-exciton states in semiconductor QDs.

For small number of electron-hole pairs (up to three electrons and holes) we use a configuration-interaction (CI) approach and study the details of the spin structure and Coulomb correlation that would appear in the optical emission spectrum. For larger number of particles, we use the density functional theory within the local density approximation (LDA).

2 Single particle states

As typical self-assembled QDs have shapes of low symmetry, a many-body calculation of the excitonic states is numerically forbidding. We, therefore, make a cylindrically symmetric approximation and first obtain the strain distribution by minimising the elastic energy using a finite element approach. With the external potential (confining potential) determined by the strain distribution and the band offsets, we calculate the single particle energies and eigen functions of the electron and the hole. To this end we discretise the Schrödinger equation within a cylindrical domain that enclose the QD and use an efficient sparse-matrix algorithm to obtain a few lowest energy eigen values.

All the results presented here are for an InP QD embedded in an InGaP matrix. The QD shape is taken to be a truncated pyramid with height 7 nm, and base and top faces 30 nm and 16 nm in diameter, respectively. For the strain calculation we consider a large cylindrical region of diameter 120 nm and height 100 nm while the energy level calculation is done in a smaller region of diameter 60 nm and height 21 nm.

The hole states are assumed to be derived from the heavy-hole band. Then the electron and hole single particle states may be written as

$$\Psi^{\pm 1/2}_{nm}(\mathrm{r}) = \Psi^{e}_{nm}(r,z)\exp(-im\varphi)\,\chi_c^{\pm 1/2} \quad (1)$$

$$\Psi^{\pm 3/2}_{nm}(\mathrm{r}) = \Psi^{h}_{nm}(r,z)\exp(-im\varphi)\,\chi_v^{\pm 3/2} \quad (2)$$

where the envelope functions $\Psi(r,z)$'s are labelled by the radial (n) and angular (m) quantum numbers, $\chi_c^{1/2} = \mathrm{S}\uparrow$, $\chi_c^{-1/2} = \mathrm{S}\downarrow$ are the conduction band Bloch

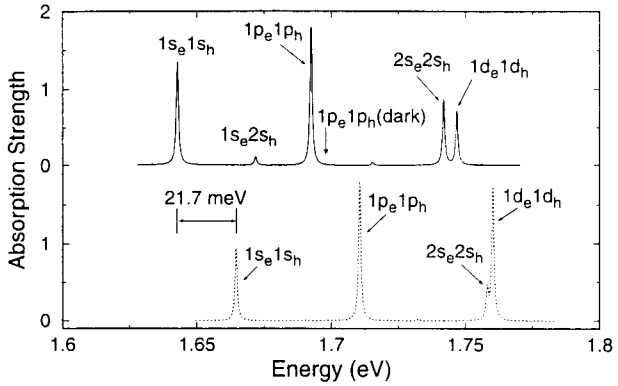

Figure 1: Excitonic absorption by an InP quantum dot calculated with (solid line) and without (dashed line) including the electron-hole Coulomb interaction.

functions with axial angular momenta (spin) $\pm 1/2$ and $\chi_v^{3/2} = -\frac{(X+iY)}{\sqrt{2}}\uparrow$, $\chi_v^{-3/2} = \frac{(X+iY)}{\sqrt{2}}\downarrow$ are the valence band(heavy-hole) Bloch functions of axial angular momenta (spin-orbit coupled) $\pm 3/2$.

3 Few excitons: Configuration interaction approach

Owing to the assumed cylindrical symmetry each multi-particle state may be characterised by the total axial angular momentum (M) of the envelope wave function and the total Bloch function angular momentum of the electrons (J_e) and the holes (J_h). For interband optical transitions we restrict to light polarised in the x-y plane so that the following selection rules hold:

$$\Delta J = \pm 1 \text{ and } \Delta M = 0\,, \qquad (3)$$

where $J = J_e + J_h$.

Multi-particle basis states for N_e electrons and N_h holes are constructed as a product of an N_e electron Slater-determinant and N_h hole Slater-determinant, within a restricted subspace spanned by 12 lowest single particle states of electrons and holes. The calculated exciton (X) absorption spectrum is shown in Fig. 1. The dominant single particle configurations for some representative excitonic states are indicated in the figure. Here s and p denote the lowest m = 0 and m = 1 eigen states, the subscripts e and h refer to electron and hole states and the superscript is the occupancy (omitted when the occupancy is 1). Two features are immediately apparent. The electron-hole Coulomb interaction shifts the lowest transition energy by 21.7 meV (excitonic binding) and also causes a noticeable transfer of oscillator strengths between allowed transitions.

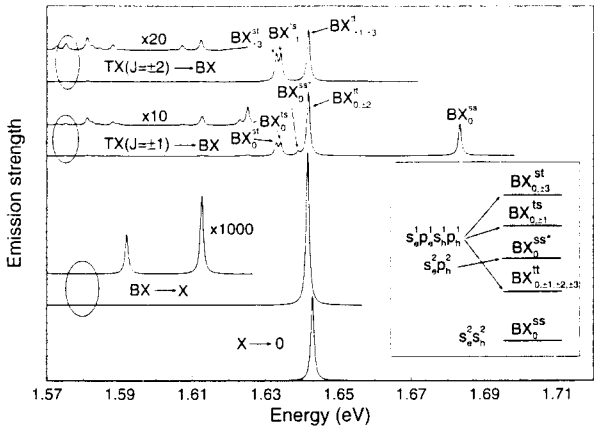

Figure 2: Emission spectra of single exciton(X), biexciton(BX) and triexciton(TX) ground states in an InP quantum dot as calculated by a configuration interaction approach. The triexciton emission lines are labelled by the final biexciton state involved in the transition. A schematic of the relevant biexciton level structure is shown in the inset (shaded box). See the text for details.

A similar behaviour has been recently reported in the PLE spectrum of InAs QDs[4]. The exciton binding energy is rather accurately given by the first order perturbation theory (20.5 meV) which is equivalent to considering a single configuration consisting of the lowest electron and hole single particle states. Inclusion of all other excited configurations contributes only 1.2 meV.

It is interesting that the Coulomb interaction also splits the four-fold degenerate (excluding spin) $m_e = \pm 1$, $m_h = \pm 1$ state in to an optically active M = 0 state separated by about 5 meV from a "dark" M = 0 state, and two $M = \pm 2$ states. While the original 4-fold degeneracy is due to the assumed cylindrical symmetry, it is important to note that the Coulomb interaction induced splitting is comparable to that expected due the low symmetry of realistic structures[6]. In the absence of electron-hole exchange interaction, all the optically active exciton states considered are four-fold degenerate, only two of which ($J = \pm 1$) are excited by light polarised in the x-y plane as it follows from the selection rules stated above. In Fig.2 we show the emission spectrum from single exciton (X), biexciton(BX) and triexciton(TX) ground states. The main biexciton emission(from the BX ground state with J = 0) corresponds to the the transition that leaves behind an exciton in the ground state, and is red-shifted from the exciton emission line by 1.4 meV. Unlike the case of the exciton, the biexciton binding energy is determined by a delicate balance of

contributions from several excited configurations. In fact the first order perturbation theory (single configuration) gives a negative binding energy of 0.75 meV. This negative contribution arises due to the relatively strong repulsion between the two holes occupying the same single particle orbitals, because the hole eigen functions in this structure tend to concentrate closer to the wider base of the pyramid, compared to the electrons which are more uniformly spread out. Inclusion of multi-particle correlations through excited configurations eventually leads to the binding energy of 1.4 meV. Experiments on QDs similar to that considered here show a rather wide scatter in the biexciton binding energy in the range 1-3 meV[5].

It must be noted that the energetics of biexciton binding discussed above is not universal. In structures where the electron and hole eigen functions differ considerably from each other, the repulsive energy of the like particles may dominate over the electron-hole attraction leading to a negative biexciton binding energy.

A very interesting feature in the biexciton spectrum is the low energy emission lines, though very weak, that appear several tens of meV below the main biexciton emission line. These transitions correspond to the biexciton decay leaving behind excited excitonic states. Similar to the corresponding phenomenon in bulk semiconductors, known as the inverse exciton series[7], these transitions reveal the mixing of excited configurations in the biexciton ground state. Considering the the virtual inter-configuration switching associated with these transitions, we refer to them as *configuration crossing* transitions. Fig. 3 illustrates this process in more detail.

The triexciton emission spectrum (Fig. 2) shows two dominant sets of transitions. To understand the TX to BX emission process, we refer to the schematic energy level structure shown in the inset of Fig. 2. A few relevant low energy BX states with $M = 0$ are shown with the dominant single particle configuration indicated against each. BX states with two electrons (holes) in the singlet combination ($J_e = 0$) are labelled by a superscript s and those with the triplet combination ($J_e = \pm 1$) by t. A second superscript s or t denotes the singlet ($J_h = 0$) and triplet ($J_h = \pm 2$) spin states of the holes. The numeral subscript is the total J value.

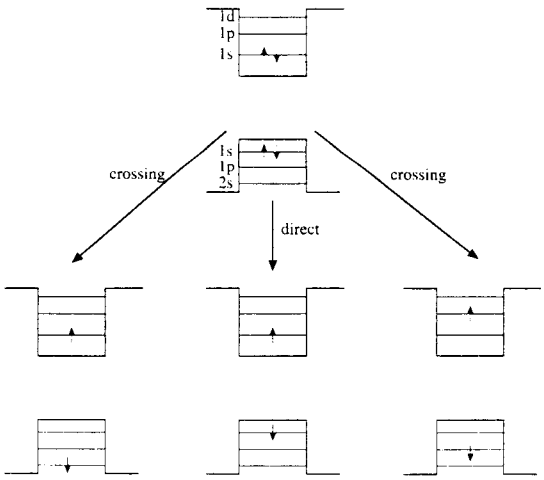

Figure 3: A schematic showing the dominant configuration in the biexciton ground state and its optical decay to the exciton ground state (marked direct) where the final confguration is strongly present in the intial state, and to excited excitonic states (marked crossed) whose configurations are only weakly present in the initial state. The latter are referred to as configuration crossing transitions in the text. Similar processes exist in the triexciton and other multi-exciton emissions as well.

The main configuration in the triexciton ground state ($M = 0$) involves two electrons (holes) in the lowest single particle state and one electron (hole) in the first excited state. This is a 4-fold degenerate ($J = \pm 1$ and $J = \pm 2$) state out of which the $J = \pm 1$ states emit to the BX ground state ($J = 0$) producing the high energy emission line labelled TX $\rightarrow$ BX_0^{ss}. The set of emission lines appearing close to and below the BX and X emission lines correspond to the transition that involves annihilation of an electron-hole pair in the ground state, leaving behind in an excited BX state with various spin combinations as indicated in Fig. 2. Thus, the singlet-triplet splitting of about 10 meV of this excited BX state leads to a fine structure in the TX emission line at the band edge. These processes are further illustrated in Fig. 4. As in the case of the biexciton, the triexciton emission spectrum also shows some lines much below the band edge which are configuration crossing transitions due to the high energy configurations weakly mixed in the TX ground state.

4 Many excitons: LDA approach

Now we discuss the results of an LDA calculation of many electron-hole pair states. The approach used is a generalisation of our earlier calculation for spherical QDs[3]. We use the Vashishta-Kaliya[8] exchange

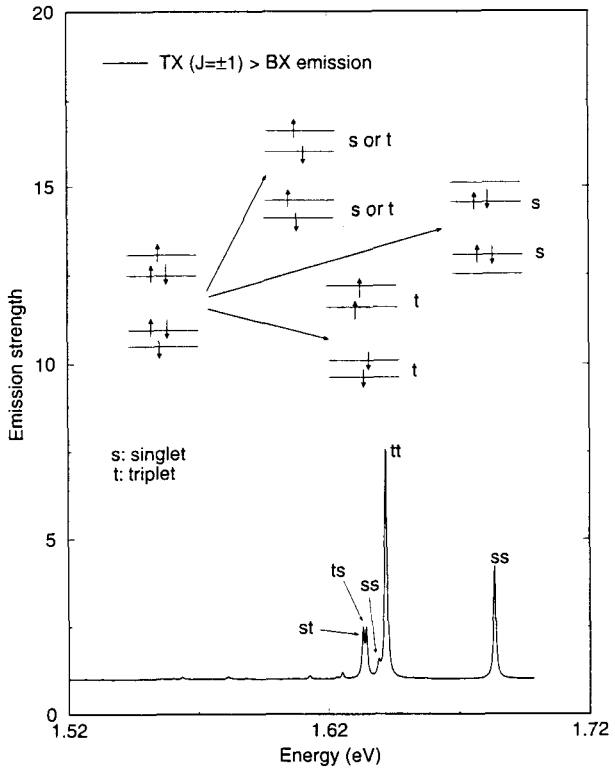

Figure 4: The emission spectrum of the J = 1 triexciton state shown in Fig. 2, along with a schematic illustration of the processes involved.

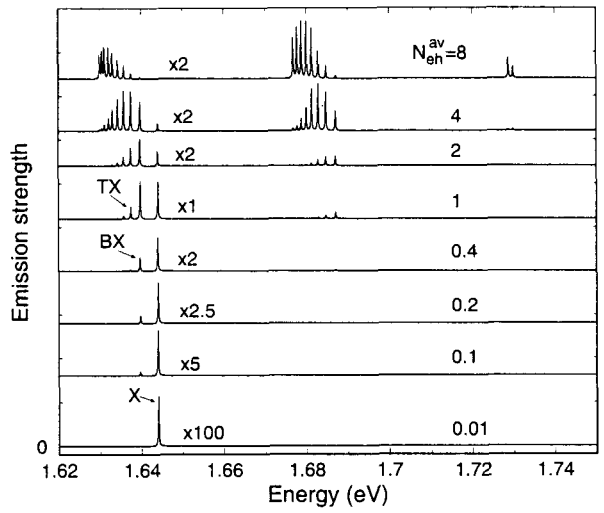

Figure 5: Emission spectra of multi-excitons in an InP quantum dot as calculated by a density functional approach. Each spectrum corresponds to a definite optical pump intensity and are labelled by the average number of electron hole pairs N_{eh}^{av} excited.

correlation potential for the electron-hole gas, and solve the Kohn-Sham equations for the electron and the hole by a finite difference discretisation within a cylindrical domain enclosing the QD. Self-consistency is achieved by iteration.

The emission spectra calculated for various pumping powers, assuming asteady state generation of carriers are shown in Fig. 5. The average number of electron hole pairs in the QD is indicated against each spectrum. As the number of electron-hole pairs in the QD is increased, the energy of the lowest optical transition gradually shifts to the lower energy side, similar to the band-gap renormalisation of bulk semiconductors. Although LDA without self-interaction correction is not expected to be accurate when the number of particles is small, it is interesting to note that the exciton binding energy is found to be 17 meV, only 20% lower than that given by the CI calculation. The biexciton binding energy is found to be 4.3 meV, considerably larger than the CI value. The most probable reason for this discrepancy is the use of Vashishta-Kaliya potential that is appropriate only for a locally neutral electron-hole gas while the calculated electron and hole densities show considerable mismatch (deviation from local charge neutrality). To check this point further, and to test the validity of LDA as applied to the biexciton, we performed an accurate calculation of the biexciton binding energy in a spherical QD using a correlated Gaussian basis[9]. For an 8 nm radius InAs spherical QD for which the local charge neutrality condition is better satisfied, the biexciton binding energy is found to be 3.9 meV which compares well with the LDA result of 4.5 meV for the same system[3].

Further, the triexciton state is predicted to emit 6.5 meV below the exciton state. As this calculation uses spin averaged electron hole densities, this triexciton emission line should be understood as an average of the spin fine-structure predicted by the CI calculation.

The real strength of the LDA approach is the relative ease with which large number of electron-hole pairs can be handled and it is exactly in this many particle regime that the accuracy of LDA is at its best. The spectra in Fig. 5 show the appearance of gradually red-shifted multi-exciton emission lines below the exciton ground state, as well as emission from excited excitonic states that get occupied and renormalised as the pump power is increased. These features are clearly observed in single QD spectra of InP QDs[5]. Theoretically, very similar results were earlier reported by us for spherical QDs[3].

5 Conclusions

In conclusion, we have studied multiple electron hole pairs in a quantum dot and shown that Coulomb correlation between carriers shows up in the optical spectra in a variety of interesting ways such as the biexciton binding energy, a spin fine structure in the triexciton emission spectrum, and configuration crossing transitions. The last two features are not yet experimentally observed. We find that the LDA approach is rather reliable and computationally convenient for studying the electronic structure of QDs containing a few to several tens of electron-hole pairs. However, for effective application of this method an improved exchange correlation potential applicable to a non-neutral, spin-polarised electron-hole gas is highly desirable.

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