Full configuration interaction calculations of electron-hole correlation effects in strain-induced quantum dots

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(Received 26 October 1999)

A full configuration interaction (FCI) approach for solving the Schrödinger equation for electrons and holes in a strain-induced quantum dot, within the effective-mass approximation, has been developed. The FCI calculations have been performed on a weakly confined quantum dot system containing up to four electron-hole pairs. The results show the importance of correlation effects in reproducing the different features of the experimental quantum dot spectra. It is also shown that the all singles and doubles configuration interaction model, which can be used to study larger systems, is a relatively good approximation to FCI by considering more than 90% of the correlation energy.

The effects of the correlations between the electrons and holes in semiconductor quantum dots (QD) has been an area of active research over the last ten years.[1–3] Depending on the size of the quantum dot, two different theoretical approaches have been developed for calculating the energy structure. Calculations on small (~10–50 Å) quantum dots, where the effective-mass approximation is expected to give incorrect results, has been studied as atomic clusters using many-body pseudopotential theory.[4] For larger quantum dots (~10–100 nm), the cluster approach leads to a numerically intractable problem. However, the effective-mass approximation is expected to be valid for these weakly confining quantum dots.[5] The full configuration interaction (FCI) model,[6] represents the exact solution of the effective-mass Schrödinger equation, and allows a systematic, numerical study of the correlations in the few-body quantum dot system. The FCI calculations are therefore the only convincing way of treating the correlations and testing the accuracy of various approximation methods, such as Hartree-Fock (HF),[7] subspace diagonalization techniques,[8] and truncated CI expansions.[3]

In this article we present the results of a FCI calculation performed on a strain-induced QD.[9] The number of CI coefficients of our largest FCI calculation (four electrons and four holes) is approximately 9 million (i.e., 9 million Slater determinants). The FCI results show the importance of the correlations in predicting the biexcitonic binding energy and in reproducing the different features of the measured QD photoluminescence (PL) spectra, such as the observed rigidity of the QD PL lines as a function of excitation intensity and the shell structure of the pair addition/subtraction spectra.[9–11]

The QD sample modeled in our calculations is shown in Fig. 1(a). It is a strain-induced QD formed by the self-organizing growth of an InP island ($D \sim 80$ nm) on top of a GaAs/InGaAs quantum well (QW).[9] As the QD is formed in the dislocation free region inside the QW, the QD PL spectra will be of a very high quality (Fig. 2). A further advantage of these QD's, is that the confinement potential [Fig. 1(b)] can be calculated using only the material parameters and the sample structure as input,[12] thus allowing no adjustable parameters in our model. To keep our model simple, we have neglected the heavy-hole/light-hole (HH-LH) mixing in the many-particle effective-mass Hamiltonian.[13] This approximation, made by most authors, could in our case be justified by the fact that the QW strain will split the HH and LH states by ~40 meV. Free particle calculations done on the same QD sample[14] show that the splitting results in the HH component dominating for the lowest hole states, and that the HH-LH coupling will shift the single-particle energies by only a few meV's.

Since the confinement potential has a cylindrical symmetry, the eigenstates can be labeled by the total angular momentum $L_z = L_z^e + L_z^h$, where the states $|L_z| = 0,1,2,\ldots$ will be denoted $\Sigma, \Pi, \Delta, \ldots$, and by the total spin $S = S^e + S^h$. The superscripts e and h denote electrons and holes, respectively. As the QD sample is optically excited in our experiments, and the concentration of spin-flipping impurities are very low, we will focus on charge neutral, closed shell, spin singlet ($S=0$) states. To solve the many-particle Schrödinger equation, the single-particle wave functions for electrons and holes are expanded in a Gaussian basis set of the form $x^{l_x} y^{l_y} z^{l_z} e^{-\alpha(x^2+y^2)} e^{-\beta z^2}$, where we denote the functions with $l_x + l_y + l_z = 0,1,2,\ldots$ by the letters $s,p,d,\ldots$. The chosen ranges of values for the α's and β's are centered around the ones giving a spatial extent of the Gaussian function approximately equal to the extent of the confinement potential. The use of the same coefficient α for the x and y functions is due to the cylindrical symmetry of the QD potential. The strong QW confinement allows us to reduce the size of our basis set, and to describe the z dependence by

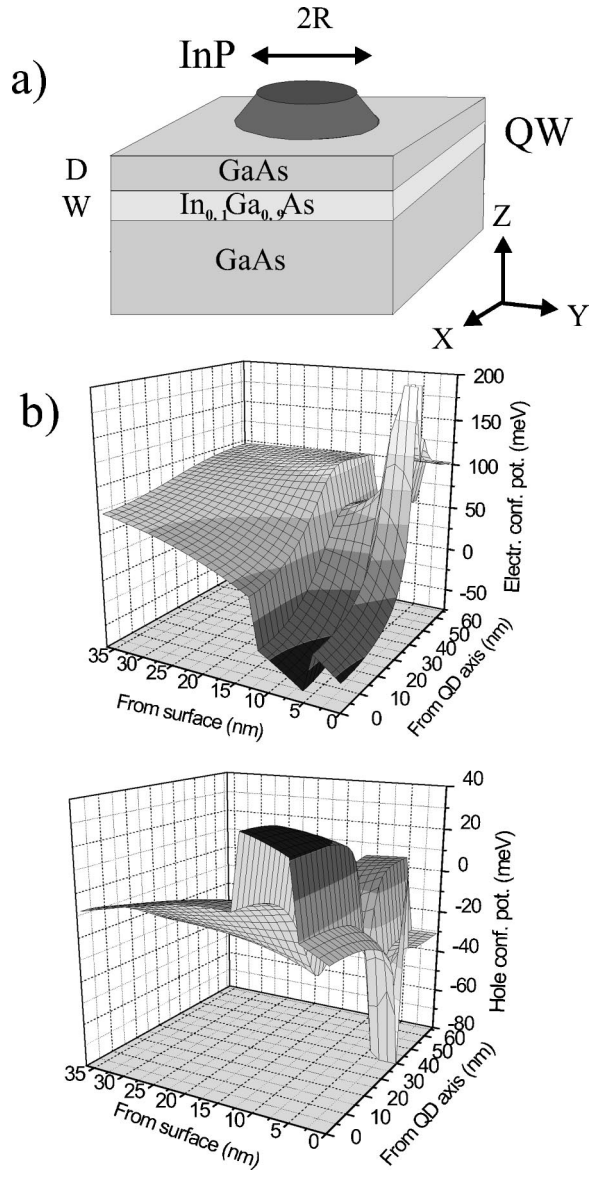

FIG. 1. The figure shows the QD sample (a), and the calculated confinement potential (b). The dimensions of the QD sample are $D=5$ nm, $2R=80$ nm, and $W=7$ nm.

using only a few Gaussians with $l_z=0$. In the calculations two different basis sets have been used. The smaller basis set consisted of $3s3p2d$, yielding 13 basis functions in D_{2h} symmetry. The larger basis set consisted of $4s4p3d$ (18 basis functions). The main advantage of using a Gaussian-type basis set, is that it allows us to evaluate the overlap, kinetic energy, and two-body Coulomb integrals analytically, while the interaction integrals originating from the general confinement potential can easily be calculated numerically. As a first step in our computational approach, the one- and two-body interaction integrals are evaluated. These are then used to solve the restricted HF equation. The solution of the HF equation gives a set of optimized, occupied single particle orbitals, and a complementary set of unoccupied ones. The correlation effects, which are neglected in the one-determinant HF approximation, are incorporated automatically when the original N-particle Hamiltonian is diagonalized in the configuration state function (CSF) basis. The FCI

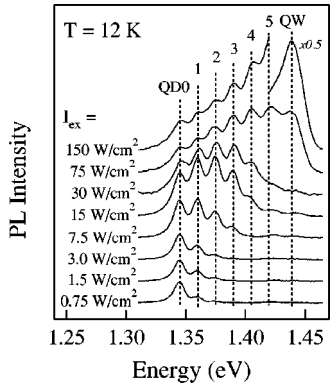

FIG. 2. The experimentally measured QD luminescence spectra at different excitation intensities. The QD transitions are labeled QD0-QD5.

CSF basis consists of the Slater determinants obtained by exciting all possible combinations of electrons and holes from the HF reference to the unoccupied orbitals. In truncated CI models, such as all singles and doubles CI (SDCI), the wave function is obtained by diagonalizing the Hamiltonian in the CSF basis obtained by exciting at most two electrons and holes from the HF determinant.

The main problem with the FCI method is the factorial growth of the number of expansion parameters (Slater determinants) with the size of the single-particle basis set and the number of electrons and holes. The two-pair problem, using a modest basis set of 15 basis functions, would result in the explicit diagonalization of a Hamiltonian matrix of dimension of about 7000. For a system containing more than two pairs, the explicit diagonalization would be impossible on any present-day computer. However, by using the direct CI approach,[6] as implemented in the computer program LUCIA,[15,16] it is possible to do a FCI calculation on a QD system containing up to four pairs, using only a modest workstation. LUCIA is a CI program originally developed for atomic and molecular systems. It uses a generalization of the restricted active space (RAS) (Ref. 17) concept, called general active space (GAS),[15] for dividing the orbital space into subspaces. The flexibility of the GAS method makes it possible to designate some subspaces to the electrons and others to the holes. The only modification introduced into the original CI program, was in restricting the spin quantum numbers of the configurations describing the electrons and the holes, in order to prevent a situation where a spin-flip of an electron is followed by a counter spin-flip of a hole. This restriction makes our electron-hole problem formally similar to atomic and molecular electronic structure problems, and allows us to make use of efficient algorithms developed in the field of *ab initio* computational chemistry.[6]

To compare our numerical results with the measured QD PL spectra of Fig. 2, we assume that the electron-hole system is in its ground state when an electron and a hole recombine. The energy for adding/removing an electron-hole pair, $\mu(N)=E_g(N)-E_g(N-1)$, will be equal to the energy of the absorbed/emitted photon. Not all the QD PL originates from the ground-state transitions, but for reasons elaborated further below we assume that they are the dominating ones. The pair addition/subtraction spectra, calculated using FCI, SDCI, and HF, are shown in Fig. 3. The energy for adding

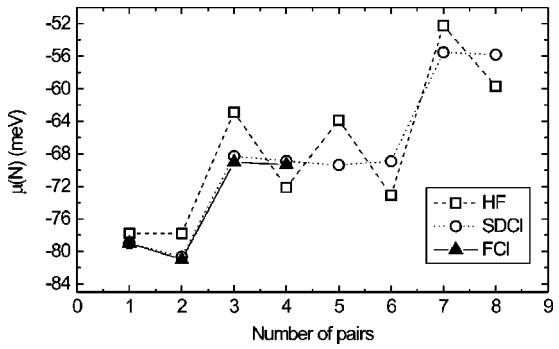

FIG. 3. A comparison between the calculated addition/subtraction spectra, defined as $\mu(N)=E_g(N)-E_g(N-1)$, obtained at FCI, SDCI, and HF levels.

the first and second electron-hole pairs to the QD differs slightly, and should be observable as a 2-meV splitting of the ground-state PL. However, the QD line broadening, due to the simultaneous excitation of many QD's in the experiment, prevents us from resolving this splitting. The energy gained by adding a third pair to the QD is 10.5 meV less than that of one–two pairs. This reflects the fact that the first shell is already filled and the pair must be added to the next higher shell. The calculated shell energy separation of 10.5 meV agrees quite well with the measured 13 meV QD0-QD1 peak separation. The use of the free particle model for determining the sample parameters contributes to the small discrepancy. At the FCI and SDCI levels, the energy of adding the fourth pair is very close to that of adding the third pair. This is consistent with the observed rigidity of the QD PL lines in Fig. 2 as a function of excitation intensity. In the two–four pair case the SDCI model is a good approximation to the FCI and accounts for more than 90% of the correlation energy, defined as $E_{corr}=E_{FCI}-E_{HF}$ (for one pair SDCI ≡ FCI). Figure 3 shows that for a larger number of electron-hole pairs, the SDCI results continue to reproduce the experimentally observed rigidity, simple shell structure, and equal spacing of the QD PL peaks. Our SDCI results are also in qualitative agreement with those reported by Jacak *et al.*,[13] using a combination of exact diagonalization and HF. The present CI results do not, however, show any of their reported even-odd pair oscillations. The even-odd oscillation is present at the HF level, but disappears at the correlated level.

A major advantage of the FCI method is that low-lying excited states can easily be obtained. In Fig. 4 the FCI calculations of the lowest part of the one–four pair energy spectra are shown. For comparison, the HF and free particle (FP) ground state energies have also been included. For the two–four pair cases, the energy levels shown in Fig. 4 are given relative to the *s*- and *p*-exciton energies E_X^s and E_X^p ($E_X^p-E_X^s=15.2$ meV). The two-pair, three-pair, and four-pair energies are obtained as $E'(2)=E(2)-2E_X^s$, $E'(3)=E(3)-2E_X^s-E_X^p$, and $E'(4)=E(4)-2E_X^s-2E_X^p$, respectively. Although the calculated HF and FCI energies differ only by 5 meV in the two-pair case, we see that the HF theory gives no bound bi-excitons, while the FCI calculation gives a positive binding energy of $\Delta_{XX}=2.0$ meV. The results show also that the higher exciton complexes form bound states in our QD. One would perhaps expect that as more carriers are added to the QD, the screening effects

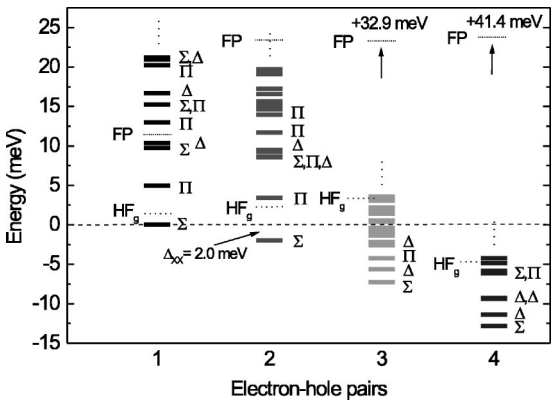

FIG. 4. The calculated spin singlet energy spectrum for one, two, three, and four electron-hole pairs. The calculated HF and FP ground-state energies are also shown. The energy of one pair has been taken as the zero level. The energy scales used in the two–four pair cases are explained in the text.

would become more important, and the system would approach a weakly interacting electron-hole gas. The CI results, however, show no indication of this. Thus, at least for a QD containing a relatively few (two–ten) electron-hole pairs, the free particle picture should not be very accurate. Surprisingly though, a free particle calculation of the QD spectra is also in good agreement with the measured spectra.[12]

The size of the energy separation of the levels in Fig. 4 have a direct effect on the carrier relaxation in the QD. The noninteracting electron-hole model, with an electron level spacing of >10 meV and a hole level spacing of 3 meV, would predict the existence of a phonon bottleneck[18] in our QD system. The mixing of the electron and hole states by the Coulomb interaction gives, however, a maximum level separation of 5 meV. It is known from calculations on single excitons in a parabolic QD,[19] that the LA-phonon rate exceeds the radiative recombination rate for a level spacing of this order. We therefore expect that the QD is in its ground state when an electron and a hole recombine. This reasoning does not rule out the possibility of ground state → excited Σ-state radiative transitions. However, their role in the measured QD PL spectra is still unclear.

Figure 4 shows that the energy splitting between ground and first excited state is significantly reduced when going

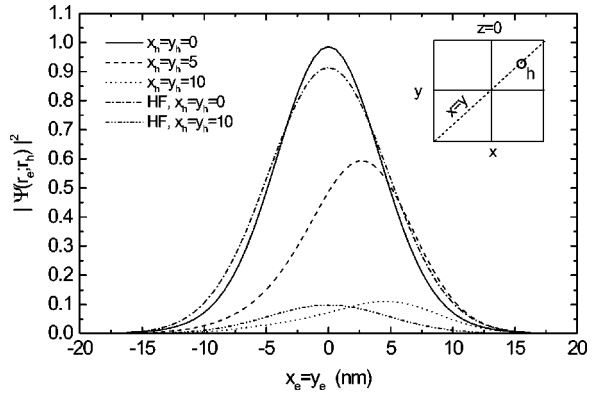

FIG. 5. The $\mathbf{r}_e$ dependence of the electron-hole correlation function, taken in the middle of the QW ($z_e=z_h=0$), for the one-pair case as calculated by FCI. The graph has been constructed by fixing the hole coordinates to $x_h=y_h=0$, 5, and 10 nm, respectively.

from one and two pairs, to three and four pairs in the QD. The first excited state possesses a Π symmetry for one and two pairs, and a Δ symmetry for three and four pairs. This implies that in order to treat the excitation spectra correctly for a QD with more than four pairs, higher angular momentum functions than *d* functions should be included in the one-particle basis set.

The energy shifts in the many-particle states, as compared to the HF energies, illustrate the importance of the correlation effects in the QD system. Another way to detect the importance of the correlation is to compare the largest CSF coefficients of the FCI calculation with the HF value. At the HF level, the ground-state configuration for one to four pairs are $[1s^1]_e[1s^1]_h$, $[1s^2]_e[1s^2]_h$, $[1s^21p^1]_e[1s^21p^1]_h$, and $[1s^21p^2]_e[1s^21p^2]_h$, respectively. The HF configuration accounts for 94, 87, 84, and 53% of the total wave function, respectively. Thus the more electron-hole pairs, the more important are the correlation effects. Correlation effects are considered by including excited configurations. The FCI calculations show that in order to account for 99% of the many-particle wave function, it is necessary to include at least 2, 150, 228, and 6870 excited Slater determinants in the CI expansion for one to four pairs, respectively. These numbers should be compared to the <10 configurations used by Hawrylak,[3] in order to describe the correlations in a self-assembled InAs quantum dot.

The electron-hole correlation is displayed explicitly by the square of the single electron-hole pair wave function, $|\Psi(\mathbf{r}_e;\mathbf{r}_h)|^2$. In the free particle and HF approximations the electrons and holes are distributed independently of each other in the QD. The correlation between the electron and the hole shows in that the electron (hole) distribution varies with varying hole (electron) coordinates. The $\mathbf{r}_e$ dependence of $|\Psi(\mathbf{r}_e;\mathbf{r}_h)|^2$, taken in the middle of the QW ($z_e=z_h=0$), for a few fixed hole positions is plotted in Fig. 5. When the hole is moved along the $x_h=y_h$ line, the hole drags the electron along with it, which does not happen in the free particle or HF descriptions. The effect again indicates a strong excitonic correlation between the electron and the hole.

The authors would like to thank J. Tulkki for countless, illuminating discussions, and H. Lipsanen, M. Sopanen, and J. Ahopelto for generously providing us with the experimental data. The financial support of the Academy of Finland under Contract No. 37789 is gratefully acknowledged.

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