

Correlation versus mean-field contributions to excitons, multiexcitons, and charging energies in semiconductor quantum dots

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Single-dot spectroscopy is now able to resolve the energies of excitons, multiexcitons, and charging of semiconductor quantum dots with ≈ 1 meV resolution. We discuss the physical content of these energies and show how they can be calculated via quantum Monte Carlo (QMC) and configuration interaction (CI) methods. The spectroscopic energies have three pieces: i) a “perturbative part” reflecting carrier-carrier direct and exchange Coulomb energies obtained from *fixed* single-particle orbitals, ii) a “self-consistency correction” when the single particle orbitals are allowed to adjust to the presence of carrier-carrier interaction, and iii) a

c) *Multiexciton energies.* The *N*th exciton charging energy W_N is the minimum energy needed to add to a dot having $N \geq 1$ electron-hole pairs (excitons) in their ground state one additional exciton,

$$W_N \leq E_{N,N} - E_{N-1,N-1}. \quad (4)$$

Physically, W_N is the highest possible energy for a photon emitted in the transition from the lowest energy state of N excitons to a state with $N \geq 1$ excitons. The difference between successive multiexciton charging energies is the *N*th exciton addition energy $\Delta_{N,N-1}^{(X)}$,

$$\Delta_{N,N-1}^{(X)} \leq W_N - W_{N-1} \leq E_{N-1,N} - E_{N-1,N-1}$$

TABLE II. Measurable quantities for our single-band spherical model dot, with effective masses $m_e \lesssim 0.1$ and $m_h \lesssim 0.5$, dielectric constant $\epsilon \lesssim 12$, dot material band gap $E_{\text{gap}} \lesssim 1$ eV, and band offsets $\Delta E_v \lesssim 200$ eV and $\Delta E_c \lesssim 400$ meV. For each quantity we give the magnitude (as calculated by QMC), the mean-field value, the correlation correction, and the percent of the energy recovered by CI expansion using all bound states. All energies are given in meV, and electron charging and total energies are measured relative to the dot material CBM.

Quantity	Magnitude	Mean field	Correlation	% CI
Exciton <i>total</i> energy $E_{1,1}(e_0^1, h_0^1)$	1136.3	1138.3	2.0	100.1
Biexciton <i>total</i> energy $E_{2,2}(e_0^2, h_0^2)$	2266.5	2277.3	10.9	100.2
<i>Total</i> energy of two electrons $E_{0,2}(e_0^2)$	335.0	335.8	0.8	100.1
Exciton <i>transition</i> energy E_X [Eq. 1]	1136.3	1138.3	2.0	100.1
Exciton <i>binding</i> energy Δ_X [Eq. 2]	46.2	44.1	2.0	97.8
Biexciton <i>binding</i> energy Δ_{XX} [Eq. 3]	6.2	-0.6	6.8	64.5
1st exciton <i>charging</i> energy W_1 [Eq. 4]	1136.3	1138.3	2.0	100.1
2nd exciton <i>charging</i> energy W_2 [Eq. 4]	1130.1	1139.0	8.9	100.2
1st exciton <i>addition</i> energy $\Delta_{1,2}^{(X)}$ [Eq. 5]	-6.2	0.6	6.8	64.5
1st electron <i>charging</i> energy $\mu_1^{(e)}$ [Eq. 6]	147.5	147.5	0.0	100.0
2nd electron <i>charging</i> energy $\mu_2^{(e)}$ [Eq. 6]	187.5	188.3	0.8	100.1
1st electron <i>addition</i> energy $\Delta_{1,2}^{(e)}$ [Eq. 7]	40.0	40.8	0.8	101.4

minimum CBM), while addition energies are $\Delta_{1,2}^{(e)} \approx 40$ meV. Of this, correlation energy is very small (~ 1 meV), so mean-field or even perturbation theory describes dot charging and addition energies very well.

For our realistic CdSe dot we find that CI can be effectively combined with an accurate pseudopotential description of the single-particle problem, thus incorporating surface effects, hybridization, and multiband coupling. Furthermore, CI can calculate excited states easily, thus obtaining the many transitions seen experimentally, rather than only the ground-state-to-ground-state decay calculated by conventional QMC (note, however, that extensions of QMC to several excited states are possible^{51,52}).

II. METHODS OF CALCULATION

A. Uncorrelated methods: perturbation theory and mean-field methods

The first-order perturbation energy $E_{M,N}^{PT}$ [Eq. 8]) can be written analytically as

$$E_{M,N}^{PT} \approx E_{0,0} + \left(\sum_c \sum_{c'} J_{c,c'} - \sum_v \sum_{v'} K_{v,v'} \right) + \left(\sum_{c,c'} J_{c,c'} - \sum_{v,c} K_{v,c} \right), \quad (9)$$

where ϵ_i are the single-particle energies, $J_{i,j}$ are the direct Coulomb energies, and $K_{i,j}$ are the exchange energies. The single-particle energies ϵ_i are often obtained from the solution of an effective single-particle Schrödinger equation,

$$\left\{ \frac{1}{2} \nabla^2 + V_{\text{eff}} \right\} \psi_i = \epsilon_i \psi_i, \quad (10)$$

where V_{eff} is an effective potential. The Coulomb and exchange energies are given in terms of the single-particle wave functions ψ_i by

$$J_{i,j} \approx \int \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{\epsilon(\mathbf{r}, \mathbf{r}') |\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}',$$

$$K_{i,j} \approx \int \frac{\psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}) \psi_i(\mathbf{r}') \psi_j(\mathbf{r}')}{\epsilon(\mathbf{r}, \mathbf{r}') |\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (11)$$

where ϵ is the dielectric constant of the quantum dot.

The self-consistent contribution $E_{M,N}^{\text{SC}}$, given by the first two terms on the right hand side of Eq. 8), arises from the self-consistent rearrangement of the single-particle wave function in response to the electrostatic field, Eq. 11), generated by the excitation of electrons and holes.

B. The correlated, many-particle methods

1. Quantum Monte Carlo method

The original QMC method⁵³ was based on the variational technique, a simple yet powerful theoretical tool. In a variational calculation, one proposes a parametrized trial wave function $\Psi_T^{\{\lambda\}}(R)$, where λ represents a set of variational parameters and R represents the coordinates of all the particles. The energy expectation value

$$E_T^{\{\lambda\}} \approx \frac{\int dR \Psi_T^{\{\lambda\}*}(R) H \Psi_T^{\{\lambda\}}(R)}{\int dR \Psi_T^{\{\lambda\}*}(R) \Psi_T^{\{\lambda\}}(R)} \quad (12)$$

may be minimized with respect to the variational parameters λ to give an estimate for the ground state energy and ground state wave function. This integral may be evaluated analyti-

cally, or Monte Carlo integration may be used. In this simplest formulation, QMC is formally equivalent to the variational techniques commonly applied to excitons in nanostructures.⁵⁴ Because the integral is over all electron and hole coordinates R , variational QMC calculations resemble classical simulations: a configuration of particle positions R undergoes a random walk through configuration space, using the rules of Metropolis Monte Carlo integration. The sequence of configurations, R_i, R_{i+1}, \dots , samples the density $|\Psi_T(R)|^2$.

The real power of QMC is that it can go beyond the variational formalism and actually project the true ground state energy from an input variational trial function Ψ_T .⁵⁵

By weighting the configuration as it samples configuration

h0 4 02.562 j 6[6.8(foe1]TJ -1n(foe1]TJ -1(foe1]TJ 9.6(goe1]TJ]TJ 0 -eqm1]TJ)18.2(eqm1]TJ-418.2(2 -1.10 1865TD [(space),.3

and h_0 as a function of dot radius R are shown in Fig. 2 a).
When the radius R of the dot goes to infinity we have a
three-dimensional 3D

creases the total energy by about another 0.8 meV. Our CI expansion again captures about half this correlation energy, leading to a negligibly small overestimation of the total energy (, 0.1%).

ies; thus the calculated biexciton binding energy can actually *decrease* when the CI basis is improved. We also show the results of SDCI in Fig. 4 b).

1. Dependence on dot size

We have varied the dot radius from $R=50$ to $R=80$ Å, all in the strongly confined regime, $R \ll a_0 = 76.2$ Å. Figure 2 b) shows the exciton and biexciton binding energies as calculated by QMC. Figures 2 c) and 2 d) decompose the contributions to the exciton and biexciton binding into 1) first-order perturbation theory, 2) self-consistency corrections, and 3) correlation corrections, as in Eq. 8).

The small R limit is the energy of a bulk-II material, and all excitonic binding energy is from correlation. As the radius

correlation6(d /F10 .-tei3/F10 1 u8ei3/9(asrelation6(d /F13)-322.1(ma /F13)-277(bindingng)-431t As)-3 [e335.8293.7(aqA)-3Aei T* [3

C. Multiexciton energies

Figure 6 shows mean-field and exact QMC) results for the multiexciton charging energies W_N [Eq. 4], and the multiexciton addition energies $\Delta_{N,N+1}^{(X)}$ [Eq. 5]. The most prominent feature is the jump in the charging energy for W_3

The small value of correlation and the good agreement of our CI calculations for dot charging are summarized in the last three lines of Table II.

IV. APPLICATION OF CI TO A MULTIBAND DOT DESCRIBED VIA PLANE-WAVE PSEUDOPOTENTIALS

QMC calculations are currently limited to either small systems containing up to a few hundreds of electrons,^{42,63,64} or highly simplified model Hamiltonians such as the EMA). A more accurate description of the electronic structure (Fig. 1) of semiconductor quantum dots can be obtained using the pseudopotential approach.⁴⁸ Unfortunately, QMC methods are presently unable to deal with the large number of electrons of a typical quantum dot, and CI is the only viable approach to treat correlation effects in large quantum dots described by atomistic pseudopotentials. In addition, the diagonalization of the CI Hamiltonian gives access to the excited states (unavailable in ground state QMC calculations) as well as the ground state of the electronic system, thus enabling the calculation of the optical spectrum of quantum dots.

In order to illustrate the capabilities of the CI approach combined with a pseudopotential description of the electronic structure, we consider a nearly spherical CdSe quantum dot having the wurtzite lattice structure and a diameter of 38.5 Å. The surface dangling bonds are fully passivated using ligandlike atoms.⁴⁷ This quantum dot is representative of CdSe nanocrystals grown by colloidal chemistry methods.

We consider here only low energy excitations of the electronic system, which are obtained by promoting electrons

from states near the top of the valence band to states near the bottom of the conduction band. The band-edge solutions of Eq. 10) can be efficiently obtained using the folded spectrum method,^{43–45} which allows one to calculate *selected* eigenstates of the Schrödinger equation with a computational cost that scales only linearly with the size of the system. In this approach, Eq. 10) is replaced by the folded-spectrum equation

$$[2^{-1} V_{ps}(\mathbf{r}) + \hat{V}_{NL} - \epsilon_{ref}]^2 \psi_i(\mathbf{r}, \epsilon) = (\epsilon - \epsilon_{ref})^2 \psi_i(\mathbf{r}, \epsilon), \quad (15)$$

where ϵ_{ref} is an *arbitrary* reference energy. The lowest energy eigenstate of Eq. 15) coincides with the solution of the Schrödinger equation [Eq. 10)] whose energy is closest to the reference energy ϵ_{ref} . Therefore, by choosing the reference energy in the band-gap, the band edge states can be obtained by minimizing the functional $A[\psi] = \langle \psi | (\hat{H} - \epsilon_{ref})^2 | \psi \rangle$.

The solution of Eq. 15) is performed by expanding the wave functions $\psi_i(\mathbf{r}, \epsilon)$ in a plane-wave basis set. For this purpose, the total pseudopotential $V_{ps}(\mathbf{r})$ is defined in a periodically repeated supercell Ω containing the quantum dot and a portion of the surrounding material. The supercell Ω is sufficiently large to ensure that the solutions of Eq. 15) are converged within 1 meV. The single-particle wave functions can then be expanded as $\psi_i(\mathbf{r}, \epsilon) = \sum_{\mathbf{G}} c_i(\mathbf{G}, \epsilon) \exp(i\mathbf{G} \cdot \mathbf{r})$, where the sum runs over the reciprocal lattice vectors \mathbf{G} of the supercell Ω . The energy cutoff of the plane-wave expansion is the same used to fit the bulk electronic structure, to ensure that the band structure consistently approaches the bulk limit. The minimization of the functional $A[\psi]$ is carried out in the plane-wave basis set using a preconditioned conjugate-gradient algorithm.

In the next step we construct a set of Slater determinants $|\Phi_{h_1, \dots, h_N, e_1}$

change interaction splits the lowest energy excitonic state (h_0^1, e_0^1) into two doublets, having total angular momentum $F\bar{5}2$ and $F\bar{5}1$, respectively see Fig. 8). The lower energy doublet ($F\bar{5}2$) is optically forbidden, while the higher energy doublet ($F\bar{5}1$) is optically allowed. We find an energy separation of ~ 5 meV between the two doublets. The emission peak A_1 observed in Fig. 9 comes from the recombination of the higher energy doublet, which is thermally popu-

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Note that a calculation considering only ground state to ground state transitions would miss most of the peaks observed in Fig. 9. The capability of the CI expansion to access excited states, coupled with the possibility of using a multi-band pseudopotential Hamiltonian for the calculation of the single-particle energies and wave functions, makes it the method of choice for calculating excited states of semiconductor quantum dots.

V. CONCLUSION

We have studied the effects of correlation on a simplified, single-band model dot using both QMC and CI, and have studied correlation in the multiexciton PL spectra of a realistically modeled CdSe dot using CI. Our results for the simplified, single-band model are summarized in Table II. We find the following results for our model: 1) total energies for an exciton, a biexciton, and two electrons are dominated by mean-field effects, so that correlation energies and CI convergence errors are less than 1% [see Fig. 3]; 2) typical exciton transition energies, which are ~ 1 eV, can be calcu-

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