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 *Nth exciton charging energy* W_N is the minimum energy needed to add to a dot having $N-1$ electron-hole pairs (excitons) in their ground state one additional exciton,

$$W_N = E_{N,N} - E_{N-1,N-1}. \tag{4}$$

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 $N-1$ excitons. The difference between successive multiexciton charging energies is the *Nth exciton addition energy* $\Delta^{(X)}_{N,N-1}$,

$$\Delta^{(X)}_{N,N-1} = W_N - W_{N-1} = E_{N-1,N} - E_{N,N}$$

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,

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, $R_i, R_{i+1}, \ldots$, 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 $R = 0$ 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 radiuscorrelation6(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* [33

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 $\Delta^{(X)}_{N,N\,1\,1}$ [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

change interaction splits the lowest energy excitonic state (h_0^1, e_0^1) into two doublets, having total angular momentum $F = 2$ and $F = 1$, respectively (see Fig. 8). The lower energy doublet $(F = 2)$ is optically forbidden, while the higher energy doublet $(F = 1)$ 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-

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 multiband 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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