Effect of dot size on exciton binding energy and electron-hole recombination probability in CdSe quantum dots

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I. Introduction

Semiconductor quantum dots and rods have been the focus of intense theoretical and experimental research because of inherent size-dependent optical and electronic properties. Generation of bound electron-hole pairs (excitons) and dissociation of excitons into free charge carriers are the two important factors that directly impact the light-harvesting efficiency of the semiconductor quantum dots. The dissociation of excitons is a complex process that is influenced by various factors such as shape and size of the quantum dots, presence of surface defects, and coupling with phonon modes. The energetics of the electron-hole interaction in quantum dots is quantified by the exciton dissociation process. Exciton binding energy decreases with increasing dot size. The size of the quantum dots have significant impact on the Auger recombination, multiple exciton generation, and blinking effect in quantum dots. Electron and hole densities have been widely used to investigate quasi-particle distribution in quantum dots. For example in core/shell quantum dots, presence of the heterojunction induces asymmetric spatial distribution of electrons and holes which, in turn, facilitates the exciton dissociation. Asymmetric electron probability density in the shell region of the core/shell quantum dots has been attributed to fast electron transfer from the quantum dots.

The central challenge in the theoretical investigation of quantum dots is efficient computational treatment of large number of electrons in the system. For small clusters where all-electron treatment is feasible, ground state and excited-state calculations have been performed using GW Bethe-Salpeter, density functional theory (DFT), time-dependent DFT (TDDFT), and MP2. For bigger quantum dots where all-electron treatment is computationally prohibitive, atomistic semiemperical pseudopotential methods have been used extensively. In this approach, the
one-electron Schrödinger equation incorporating the pseudopotential $v_{ps}$

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{ps} \right] \phi_i = \lambda_i \phi_i, \quad (1)$$
is solved and the eigenfunctions are used in construction of the quasiparticle states.$^{32,37}$ The quasiparticle states serve as a basis for both configuration interaction (CI) and perturbation theory calculations. Solution of Eq. (1) is generally obtained by introducing a set of basis functions (typically plane-waves), constructing the Hamiltonian matrix in that basis, and diagonalizing it. The computational efficiency of CI has been greatly improved by using only states near the band gap for construction of the CI space.$^{57,72}$ This technique alleviates the need to compute the entire eigenspectrum of the Hamiltonian matrix, however successful implementation of this approach requires computation of selected eigenvalues and eigenfunctions of the Hamiltonian matrix. Computation of the specific eigenvalues of large matrices is challenging and various methods such as the folded-spectrum method,$^{53,74}$ the filter-diagonalization method,$^{69,75}$ and generalized Davidson method$^{68,77}$ have been specifically developed to address this problem.

The main goal of this article is to compare the effect of dot size on exciton binding energy and electron-hole recombination probability. The central quantity of interest for the present work is the electron-hole pair density $\rho(r_e, r_h)$. The electron-hole pair density is defined as the probability density of finding an electron and a hole in the neighborhood of $r_e$ and $r_h$, respectively. The pair density is a mathematically complicated quantity and is generally obtained from an underlying wavefunction. Direct construction of the pair-density is also possible as long as $N –$ representability can be enforced.$^{78}$ For an interacting electron-hole system, the pair density is not equal to the product of electron and hole densities

$$\rho_{ch}(r_e, r_h) \neq \rho_e(r_e) \rho_h(r_h). \quad (2)$$

Furthermore, the electron-hole pair density contains information about the correlated spatial distribution of the electrons and hole that cannot be obtained from the product of individual electron and hole densities. Both electron-hole recombination probability and exciton binding energy can be computed directly from the pair density. The relationship between the exciton binding energy $E_{BE}$ and electron-hole pair density is given by the following expression,

$$E_{BE} = \int d^3r_e d^3r_h \rho_{ch}(r_e, r_h) \epsilon_{ch}^{-1}(r_e, r_h), \quad (3)$$

where, $\epsilon^{-1}(r_e, r_h)$ is the inverse dielectric function. The electron-hole recombination probability, $P_{ch}$ is related to the pair density as

$$P_{ch} = \frac{1}{N_e N_h} \int d^3r_e \int_{-\frac{\Delta}{2}}^{\epsilon_e + \frac{\Delta}{2}} d^3r_h \rho_{ch}(r_e, r_h), \quad (4)$$

where $N_e$ and $N_h$ are number of electron and holes, respectively. In the above equation, we define electron-hole recombination probability as the probability of finding a hole in a cube of volume $\Delta^3$ centered at the electron position. The computation of the recombination probability is especially demanding because it requires evaluation of the pair density at small interparticle distances. As a consequence, the form of the electron-hole wavefunction near the electron-hole coalescence point is very important.$^{79–84}$ In the present work, we address this challenge by using the electron-hole explicitly correlated Hartree-Fock (eh-XCHF) method.$^{79,80}$ The eh-XCHF method is a variational method where the wavefunction depends explicitly on the electron-hole interparticle distance and has been used successfully for investigating electron-hole interaction$^{30,79,80}$.

The remainder of the article is organized as follows. The theoretical details of the eh-XCHF and its computational implementation for CdSe quantum dots are presented in section II and section III, respectively. The results from the calculations are presented in section IV, and the conclusions from the study are discussed in section V.

II. Theory

In the eh-XCHF method,$^{79,80}$ the electron-hole wavefunction is represented by multiplying the mean-field wavefunction with an explicitly correlated function as shown in the following equation

$$\Psi_{eh-XCHF} = \Phi^e \Phi^h, \quad (5)$$

where $\Phi^e$ and $\Phi^h$ are electron and hole Slater determinants and $G$ is a Gaussian-type geminal (GTG) function$^{85}$ which is defined as,

$$G(r_e, r_h) = \sum_{i=1}^{N_e} \sum_{j=1}^{N_h} \sum_{k=1}^{N_e} b_{ik} \exp[-\gamma_{ik} r_{ij}^2]. \quad (6)$$

The GTG function depends on the $r_{ch}$ term and is responsible for introduction of the electron-hole inter-particle distance dependence in the eh-XCHF wavefunction. The coefficients $b_{ik}$ and $\gamma_{ik}$ are expansion coefficients which are obtained variationally. The use of Gaussian-type geminal functions offers three principle advantages. First, the variational determination of the geminal parameters $\{b_{ik}, \gamma_{ik}\}$ results in accurate description of the wavefunction near the electron-hole coalescence point. This feature is crucial for accurate computation of electron-hole recombination probability. Second, the integrals of GTG functions with Gaussian-type orbitals (GTO) can be performed analytically and have been derived earlier by Boys$^{85}$ and Persson et al.$^{86}$ This alleviates the need to approximate the integrals using numerical methods. The third advantage of the GTG function is that it allows construction of a compact representation of an infinite-order configuration interaction expansion. This can be seen explicitly by introduction of the closure relationship,

$$G_{|\Phi_{rel}} = \sum_{i=1}^{\infty} \Phi^e_i \Phi^h_i \Phi^e_i \Phi^h_i | G_{|\Phi_{rel}}. \quad (7)$$

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The electron-hole interaction was described using the effective electron-hole Hamiltonian\textsuperscript{84,87–97} which is defined in the following equation:

\[
H = \sum_{ij}(\frac{-\hbar^2}{2m_e} + v_{ext}(r_j))e_i^a e_j^a + \sum_{ij}(\frac{-\hbar^2}{2m_h} + v_h(r_j))h_i^a h_j^a + \sum_{ijl}v_{el}(r_j)\Phi_i^e(r_l)\Phi_j^h(r_l) + \sum_{ijkl}w_{ijkl}^e(r_j)e_i^a h_j^a e_k^h h_l^h.
\]  

(8)

The effective electron-hole Hamiltonian provides a computationally efficient route for investigating large systems and in the present work was used for investigating CdSe clusters in the range of Cd\textsubscript{2}Se\textsubscript{19} to Cd\textsubscript{74}Se\textsubscript{483}. We have also developed eh-XCHF method using a pseudopotential,\textsuperscript{98} but the current implementation is restricted to cluster sizes of 200 atoms and cannot be applied to large dot sizes.

The effective Hamiltonian in Eq. (8) was used in combination with parabolic potential which has been used extensively\textsuperscript{99–108} for approximating the confining potential in quantum dots and wires. The electron and hole external potentials \(v_{ext}^\alpha\) were expressed as

\[
v_{ext}^\alpha = \frac{1}{2}k_\alpha |r_\alpha|^2 \quad \alpha = e, h.
\]  

(9)

The form of the external potential directly impacts the electron-hole pair density and is important for accurate computation of the binding energy and recombination probability. In this work, we have developed a particle number based search procedure for the external potential. The central idea of this method is to find an external potential such that the computed 1-particle electron and hole densities are spatially confined within the volume of the quantum dot. Mathematically, this is implemented by obtaining the force constant \(k\) by the following minimization process

\[
\min_{k_{min}} \left(N_\alpha - \int_0^{\frac{D_{dot}}{4}} d\Omega \int d\mathbf{r} \rho_\alpha(\mathbf{r}) \left|v_{ext}^\alpha(\mathbf{r})\right|^2\right)^2,
\]  

(10)

where \(\alpha = e, h\), \(D_{dot}\) is the dot diameter, and \(k_{min}\) is the smallest force constant that satisfies the above minimization conditions. The single-particle density is a functional of the external potential and is denoted explicitly in the above equation.

The eh-XCHF wavefunction is obtained variationally by minimizing the eh-XCHF energy

\[
E_{\text{eh-XCHF}} = \min_{G,\Phi^e,\Phi^h} \frac{\langle \Psi_{\text{eh-XCHF}} | H | \Psi_{\text{eh-XCHF}} \rangle}{\langle \Psi_{\text{eh-XCHF}} | \Psi_{\text{eh-XCHF}} \rangle}.
\]  

(11)

Instead of evaluating the above equation directly, it is more efficient to first transform the operators and then perform the integration over the coordinates. The transformed operators are obtained by performing congruent transformation\textsuperscript{109,110} which is defined as follows

\[
\tilde{H} = G^\dagger HG \quad \tilde{I} = G^\dagger I G.
\]  

(12)

The eh-XCHF energy is obtained from the transformed operators using the following expression

\[
E_{\text{eh-XCHF}} = \frac{\langle \phi^e, \phi^h | \tilde{H} | \phi^e, \phi^h \rangle}{\langle \phi^e, \phi^h | \phi^e, \phi^h \rangle}.
\]  

(14)

This is identical to the Roothaan-Hall equation where \(G_G^\dagger\) and \(G_G^\dagger\) are Fock matrices for electron and holes, respectively. The subscript \(G\) in the above expression denotes that the Fock operators were obtained from the congruent transformed Hamiltonian and contains contribution from the geminal operator. The functional form of the congruent transformed operators and the Fock operators have been derived earlier and can be found in Ref. 80. The single-particle basis for electrons and holes are constructed from the eigenfunctions of zeroth order single-particle Hamiltonian

\[
H_0^\alpha \phi^\alpha_i = \varepsilon_i^\alpha \phi^\alpha_i \quad \alpha = e, h.
\]  

(17)

where the zeroth-order Hamiltonian is obtained from \(H\) using the following limiting condition

\[
H_0^e + H_0^h = \lim_{r_{eh} \rightarrow \infty} H.
\]  

(18)

Equations (8) to (18) summarize the key steps of the eh-XCHF method.

### III. Computational Details

The material parameters for the CdSe quantum dots used in the electron-hole Hamiltonian in Eq. (8) were obtained from Ref. 89 and are presented in Table I. The single-particle basis was constructed using a set of ten s,p,d GTOs and the details of the basis functions and the external potential parameters used in the calculations are presented in Table II. A set of three geminal functions were used for each dot size, where the geminal
IV RESULTS AND DISCUSSION

TABLE II. Parameters for the external potential and the GTOs used in the eh-XCHF calculation. All values are given in atomic units.

| D_{dot}(nm) | b_2 | b_3 | b_1 | \gamma_1 | \gamma_2 |
|-------------|-----|-----|-----|----------|----------|
| 1.19        | 3.35 \times 10^{-2} | 1.20 \times 10^{-2} | 1.08 \times 10^{-1} | 4.59 \times 10^{-2} |
| 1.69        | 6.21 \times 10^{-2} | -1.22 \times 10^{-2} | 3.21 \times 10^{-1} | 1.23 \times 10^{-1} |
| 2.71        | 3.10 \times 10^{-2} | 1.07 \times 10^{-2} | 3.22 \times 10^{-2} | 1.48 \times 10^{-2} |
| 2.96        | 2.88 \times 10^{-2} | 1.07 \times 10^{-2} | 3.19 \times 10^{-2} | 1.47 \times 10^{-2} |
| 3.23        | 2.34 \times 10^{-2} | 4.31 \times 10^{-3} | 1.96 \times 10^{-2} | 1.22 \times 10^{-2} |
| 3.76        | 2.87 \times 10^{-2} | 1.06 \times 10^{-2} | 2.09 \times 10^{-2} | 1.37 \times 10^{-2} |
| 4.79        | 2.03 \times 10^{-2} | 7.41 \times 10^{-3} | 1.74 \times 10^{-2} | 1.24 \times 10^{-2} |
| 6.58        | 2.55 \times 10^{-2} | 1.06 \times 10^{-2} | 1.86 \times 10^{-2} | 1.37 \times 10^{-2} |
| 9.98        | 4.96 \times 10^{-2} | 1.38 \times 10^{-2} | 1.89 \times 10^{-2} | 1.49 \times 10^{-2} |
| 15.0        | 4.85 \times 10^{-2} | 9.42 \times 10^{-3} | 1.79 \times 10^{-2} | 1.36 \times 10^{-2} |
| 19.9        | 1.69 \times 10^{-2} | 7.41 \times 10^{-3} | 1.60 \times 10^{-2} | 1.24 \times 10^{-2} |

TABLE III. Optimized geminal parameters obtained by minimizing the eh-XCHF energy. The first set of geminal parameters were set to b_1 = 1 and g_1 = 0 and the details are presented in the text. All values are given in atomic units.

| D_{dot}(nm) | b_2 | b_3 | \alpha_c | \alpha_b |
|-------------|-----|-----|----------|----------|
| 1.19        | 2.66 \times 10^{-2} | 9.10 \times 10^{-3} | 2.94 \times 10^{-2} | 2.94 \times 10^{-2} |
| 1.69        | 6.22 \times 10^{-2} | 2.13 \times 10^{-3} | 1.42 \times 10^{-2} | 1.42 \times 10^{-2} |
| 2.71        | 1.10 \times 10^{-2} | 3.76 \times 10^{-4} | 5.98 \times 10^{-3} | 5.98 \times 10^{-3} |
| 2.96        | 8.10 \times 10^{-2} | 2.77 \times 10^{-4} | 5.13 \times 10^{-3} | 5.13 \times 10^{-3} |
| 3.23        | 5.52 \times 10^{-4} | 1.89 \times 10^{-4} | 4.24 \times 10^{-3} | 4.24 \times 10^{-3} |
| 3.76        | 3.09 \times 10^{-4} | 1.06 \times 10^{-4} | 3.17 \times 10^{-3} | 3.17 \times 10^{-3} |
| 4.79        | 1.20 \times 10^{-4} | 4.12 \times 10^{-4} | 1.98 \times 10^{-3} | 1.98 \times 10^{-3} |
| 6.58        | 3.38 \times 10^{-5} | 1.16 \times 10^{-5} | 1.05 \times 10^{-3} | 1.05 \times 10^{-3} |
| 9.98        | 6.41 \times 10^{-6} | 2.19 \times 10^{-6} | 4.57 \times 10^{-4} | 4.57 \times 10^{-4} |
| 15.0        | 1.26 \times 10^{-6} | 4.33 \times 10^{-7} | 2.03 \times 10^{-4} | 2.03 \times 10^{-4} |
| 19.9        | 4.01 \times 10^{-7} | 1.37 \times 10^{-7} | 1.14 \times 10^{-4} | 1.14 \times 10^{-4} |

parameters were optimized variationally. The optimized parameters for all the dot sizes are presented in Table III. The first set of geminal parameters were always set to b_1 = 1 and g_1 = 0 to ensure that the eh-XCHF energy is always bounded from above by the mean-field energy during the geminal optimization.\(^{79,80}\)

IV. Results and discussion

A. Exciton binding energy

The exciton binding energy was computed for a series of CdSe clusters ranging from Cd_{20}Se_{19} to Cd_{74608}Se_{74837}. The approximate diameters of these quantum dots are in the range of 1 to 20nm, respectively and the results are presented in Table IV. It is seen that binding energy decreases as the size of the quantum dot increases. This trend is in agreement with earlier results.\(^{32-34}\) In Figure 1, the computed binding energies are compared with previously reported experimental and theoretical results.\(^{32-34,57-40}\) For D_{dot} equal to 1.8, 3.32 and 4.82nm, Franceschetti and Zunger have computed binding energies using atomistic pseudopotential based configuration interaction method\(^{32}\) and the exciton binding energies shown in Figure 1 were obtained from the tabulated values in Ref. 32. In a recent combined experimental and theoretical investigation, Jasieniak et al.\(^{34}\) have reported size-dependent valence and conduction band energies of CdSe quantum dots. The values from the Jasieniak et al. studies in Figure 1 were obtained from the least-square fit equation provided in Ref. 34. The remaining data points were obtained from the plot in Ref. 34. The log-log plot in Figure 1 shows that the computed binding energy is described very well by a linear-fit and the exciton binding energy scales as D^{-n} with respect to the dot size. This observation is consistent with trend observed in earlier studies.\(^{32-34}\) We find that the exciton binding energy from
the atomistic pseudopotential calculations by Wang et al.\textsuperscript{37} the eh-XCHF calculations are in very good agreement with present results from earlier studies by Wang et al.\textsuperscript{37, 38}, Franceschetti et al.\textsuperscript{39}, Meulenberg et al.\textsuperscript{40}, Jasieniak et al.\textsuperscript{41}, Inamdar et al.\textsuperscript{42}, and Querner et al.\textsuperscript{43} The details of the comparison are presented in the text.

FIG. 1. Log of binding energy ($E_{BE}$) versus log of diameter for CdSe quantum dots. The values from the eh-XCHF calculations are compared with results from earlier studies by Wang et al.\textsuperscript{37, 38}, Franceschetti et al.\textsuperscript{39}, Meulenberg et al.\textsuperscript{40}, Jasieniak et al.\textsuperscript{41}, Kucur et al.\textsuperscript{42}, Inamdar et al.\textsuperscript{42}, and Querner et al.\textsuperscript{43} The details of the comparison are presented in the text.

the eh-XCHF calculations are in very good agreement with the atomistic pseudopotential calculations by Wang et al.\textsuperscript{37} and Franceschetti et al.\textsuperscript{39} Comparing between eh-XCHF and Jasieniak et al.\textsuperscript{41} results show that the eh-XCHF values are lower than the Jasieniak et al. values for small dot sizes, but the difference becomes smaller with increasing dot size. One possible explanations for this observation is that the smaller quantum dots have high surface to volume ratios and their optical properties are dominated by surface effects\textsuperscript{112, 113} that are not currently included in the eh-XCHF calculations. The plot in Figure 1 highlights the ability of the eh-XCHF method to predict exciton binding energies for large quantum dots.

B. Electron-hole Coulomb energy

Another important quantity that is directly related to the electron-hole interaction is the electron-hole Coulomb energy. We have used the definition given by Franceschetti and Zunger\textsuperscript{32} and calculated the electron-hole Coulomb energy using the following expression

$$A = \int d\mathbf{r}_e d\mathbf{r}_h \rho_{eh}(\mathbf{r}_e, \mathbf{r}_h)^{-1}.$$  \hspace{1cm} (19)

In Figure 2, we have compared the electron-hole Coulomb energy with the pseudopotential+CI calculations by Franceschetti and Zunger and the results were found to be in good agreement with each other. If the dielectric function is approximated by a constant, then the exciton binding energy is related to Coulomb energy by the expression

$$E_{BE} = \epsilon^{-1}A \quad \text{for} \quad \epsilon(\mathbf{r}^e, \mathbf{r}^h) = \epsilon.$$ \hspace{1cm} (20)

The Coulomb energy is a very important quantity because it allows us to directly compare the quality of electron-hole pair density without introducing any additional approximation due to the choice of the dielectric function used for computation of the binding energy. The good agreement between the two methods provides important verification of the implementation of the eh-XCHF method.

C. Recombination probability

In addition to exciton binding energies, electron-hole recombination probabilities were also calculated. Using the expression in Eq. (4), the electron-hole pair density from the eh-XCHF method was used in the computation of electron-hole recombination probabilities and the results are presented in Figure 3. A log-log plot of $P_{eh}$ versus $D_{dot}^{-n}$ indicates that the recombination probability also follows $D_{dot}^{-n}$ dependence with dot diameter. One of the key results from this study is that the electron-hole recombination probability decreases at a much faster rate that the exciton-binding energy with increasing dot size. This is illustrated in Figure 4, where comparison of the relative binding energy and recombination probability is presented with respect to dot size. It was found that for a factor of 16.1 change in the dot diameter, the exciton binding energy and the recombination probability decrease by a factor of 14.4 and $5.5 \times 10^6$, respectively. The linear regression equations of the Coulomb energy, exciton binding energy and electron-hole recombination probability as function of dot diameter are summarized in Table V. It is seen that the slope
for the recombination is substantially higher than the binding energy.

V. Conclusions

In conclusion, we have presented a multifaceted study of effect of dot size on electron-hole interaction in CdSe quantum dots. The electron-hole explicitly correlated Hartree-Fock method was used for computation of exciton binding energy and electron-hole recombination probability. It was found that both exciton binding energy and electron-hole recombination probability decreases with increasing dot size and both quantities scale as $D^{-n}$ with respect to the diameter of the quantum dot. The computed exciton binding energies were found to be in good agreement with previously reported results. One of significant results from these calculations is that the electron-hole recombination probability decreases at a substantially higher rate than the binding energy with increasing dot size. Changing the dot size by a factor of 14 resulted in a decrease in the electron-hole recombination probability by a factor of $10^6$. We believe this to be a significant result that can enhance our understanding of the electron-hole interaction in quantum dots.

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