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Calculation of electron-hole recombination probability using explicitly correlated Hartree-Fock method

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The electron-hole explicitly correlated Hartree-Fock method (eh-XCHF) is presented as a general strategy for investigation of electron-hole correlation and computation of electron-hole recombination probability. The eh-XCHF method is a variational method which uses explicitly correlated wavefunction that depends on the electron-hole inter-particle distances. It is shown that the explicitly correlated ansatz provides a systematic route to variationally minimize the total energy. The parabolic quantum dot is used as the benchmark system and the eh-XCHF method is used for computation of the ground state energy and electron-hole recombination probability. The results are compared to Hartree-Fock and explicitly correlated full configuration interaction (R12-FCI) calculations. The results indicate that an accurate description of the electron-hole wavefunction at short electron-hole inter-particle distances is crucial for qualitative description of the electron-hole recombination probability. The eh-XCHF method successfully addresses this issue and comparison of eh-XCHF calculations with R12-FCI shows good agreement. The quality of the mean field approximation for electron-hole system is also investigated by comparing HF and R12-FCI energies for electron-electron and electron-hole systems. It was found that performance of the mean field approximation is worse for the electron-hole system as compared to the corresponding electron-electron system. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3693765>]

I. INTRODUCTION

Electron-hole correlation plays a central role in understanding and interpretation of optical properties of a wide variety of materials.^{1–5} The role of electron-hole correlation has been investigated both experimentally and theoretically for a large number of systems including predicting excitonic ground state in quantum dots,⁶ light emission from quantum wires,^{7,8} optical response of metal clusters,⁹ excitonic effects in graphene,¹⁰ radiative lifetimes in carbon nanotubes,¹¹ excitonic states in polymers,¹² and luminescence of quantum dots.¹³ Accurate treatment of electron-hole correlation in computational studies can predict shapes of absorption spectra⁸ and biexciton formation in quantum dots.⁶ Electron-hole correlation also has a strong influence on electron-hole recombination probability in photoactive materials. Eh-recombination plays an important role in the field of photovoltaics,^{14–19} photocatalysis,^{20–23} light emitting devices,²⁴ and electroluminescence.²⁵ For light-harvesting applications, it is desirable to design materials with low probability of eh-recombination. In certain TiO₂-based photoactive materials, the eh-recombination causes reduction in the quantum yield;²¹ however, the photocatalytic activity can be enhanced by chemical modification of the material inhibiting of eh-recombination.²² In photocatalytic nanocrystals, shape of the nanocrystal was found to influence eh-recombination and synthetic modifications of the shape

of the nanocrystal can be made to suppress eh-recombination and design highly efficient photocatalysts.²³ Suppressing eh-recombination has also received attention in the field of dye-sensitized solar cells research. Chemical modifications such as addition of alkyl chains²⁶ and designing new metal centered complexes¹⁸ have been carried out to enhance light-harvesting capabilities by reducing eh-recombination. In a related application, Bose-Einstein condensation of excitons was also found to be strongly influenced by the eh-recombination probability and exciton lifetime.²⁷

In semiconductor quantum dots, eh-recombination can be reduced by introducing a core/shell heterostructure. This is generally achieved by using a core material whose valence and conduction bands are either higher or lower than those of the shell material.^{28–30} As a consequence, one of the charge carriers (electron or hole) is mostly confined to the core, while the other charge carrier is confined to the shell. The core/shell structure induces spatial separation between electrons and holes which reduces eh-recombination.^{31,32} Dissociation of electron-hole pair generates charge carriers and increases the quantum yield of the photocurrent generation processes. Consequently, it is important to have accurate theoretical and computational techniques for accurate calculation of electron-hole binding energies and recombination probabilities. Computational treatment of electron-hole interaction can be carried out using various techniques including, one and two particle Green's function method,^{33–35} effective mass approximation,³⁶ configuration-interaction (CI),^{37,38} coupled cluster,³⁹ and quantum Monte Carlo (QMC) method.^{40,41} A detailed review of various

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computational techniques has been presented by Sundholm and co-workers.⁴² The many-body pseudopotential theory for excitons in quantum dots^{43–46} has been developed by Franceschetti *et al.* that uses CI scheme to solve the electron-hole Schrodinger equation. This method has been successfully used for studying a wide range of problems including charge carrier multiplicity,⁴⁷ lifetime and recombination energies of excitons,^{48,49} and Auger scattering and recombination in quantum dots.^{50,51} Sundholm and co-workers have also used CI for calculation of lifetime and binding energies.^{52,53}

Accurate description of the two-particle cusp plays an important role both in electron-electron and electron-hole systems. In electronic systems, the importance of electron-electron cusp has been demonstrated in a large number of studies^{54–56} and is typically included in the calculation by either by using a Jastrow correlation function^{54,55,57} or by explicitly correlated R12 scheme.⁵⁶ The nature of electron-hole correlation is very different from electron-electron correlation typically encountered for the ground state calculations in many-electron systems because the particles involved are oppositely charged. As a consequence of the attractive Coulomb interaction, the quality of the electron-hole wavefunction at small inter-particle distances is very important. This has important consequence on the calculation of electron-hole (eh) recombination probability P_{eh} . The lifetime of the generated electron-hole pair is inversely proportional to the P_{eh} and serves as an important metric to assess the photovoltaic properties of quantum dots.⁵⁸ Since P_{eh} is the “on-top” probability of electrons and holes, an accurate description of the electron-hole wavefunction at small electron-hole distances is extremely important. One of the ways to achieve this is by introducing an explicit eh-inter-particle distance term in the approximation to the many-body wavefunction. This is generally done by introducing a Jastrow factor in the electron-hole wavefunction and solving the electron-hole Schrodinger equation using QMC techniques. Shumway and Ceperley have performed QMC calculations for exciton-exciton scattering.⁵⁹ Zhu and Hybertsen have also applied QMC for treating electron-hole correlation using variational Monte Carlo.⁴¹

In the present work, we present an explicitly correlated Hartree-Fock (eh-XCHF) method for treating electron-hole correlation. The eh-XCHF method is a variational method where a geminal function^{60,61} is used to incorporate explicit eh-distance in the wavefunction. The explicitly correlated method using geminal functions has been successfully used to study electron-electron,⁶² electron-proton,^{63–65} and electron-positron⁶⁶ interactions in chemical systems. The eh-XCHF formulation presented here is different from earlier methods in its requirement to correctly account for electron-hole exchange interaction. This is especially important for studying optical properties of nanomaterials where eh-exchange interaction is enhanced^{67–69} due to quantum confinement effect.^{70–74} Electron-hole exchange interaction plays an important role^{69,75,76} in understanding optical properties of nanomaterials including, dark exciton states,^{69,76–79} fine structure of excitons,^{80,81} effect on spin relaxation,^{82,83} and generation of trions in carbon nanotubes.^{84,85} In this work, the key equations of the eh-XCHF method are derived for

a general many-electron many-hole system and benchmark calculations are performed on parabolic quantum dot. The parabolic quantum dot system^{86–88} has been a test bed for investigation of electron-hole interaction in confined systems including investigation of electron-phonon coupling,⁸⁹ third harmonic generation,⁹⁰ effect of impurities on exciton binding energies,⁹¹ dipole-allowed optical transitions,⁹² biexciton formation,⁹³ exciton trapping,⁸⁶ and spin-orbit interactions in quantum dots.⁹⁴ The system consists of two charged particles in an external potential. The motion of the two charged particles is correlated and the interaction between them is described by the Coulomb potential. The 1-body external potential is described by three-dimensional harmonic oscillator term. This model system has been studied for investigation of both electron-electron and electron-hole correlation. For applications in electronic structure theory, the two charged particles have identical charges of -1 and the system is known as the harmonium or the Hook’s atom. It has been used for investigating the electron-electron correlation using wavefunction, density-matrix, and density functional based methods.^{95–97}

We use the parabolic quantum dot system to perform rigorous assessment of the eh-XCHF method for treating electron-hole correlation. In addition to eh-XCHF calculations, we have also performed Hartree-Fock (HF) and explicitly correlated full configuration interaction (R12-FCI) calculations on the model system. Comparison of ground state energy and recombination probability between all the three methods has been carried out to evaluate accuracy of the eh-XCHF method. The remainder of the article is divided as follows: the fundamental equations of the eh-XCHF method are derived in Sec. II, computational details are described in Sec. III, the results and discussion are presented in Sec. IV, and conclusions are summarized in Sec. V.

II. THEORY

The explicitly correlated ansatz for the wavefunction is defined as

$$\Psi_{\text{xc}} = (1 + \hat{G})\Phi_0^{\text{eh}}, \quad (1)$$

where Φ_0^{eh} is the reference electron-hole wavefunction. Typically, the reference wavefunction can be chosen as the product of electron and hole Slater determinants $\Phi_0^{\text{eh}} = \Phi_{\text{SD}}^{\text{e}} \Phi_{\text{SD}}^{\text{h}}$. Electron-hole exchange interaction can be included by replacing the product in the above expression by the Grassmann or wedge product^{98–101} between the electrons and holes functions $\Phi_0^{\text{eh}} = \Phi_{\text{SD}}^{\text{e}} \wedge \Phi_{\text{SD}}^{\text{h}}$. Both forms have been successfully used in computational investigation of electron-hole pairs.^{38,41,42} The selection of one form over the other is system specific and should be made on a case-by-case basis. This topic has also been discussed in a review of computational techniques by Sundholm and co-workers.⁴² The derivation of the eh-XCHF method presented below does not make any *a priori* assumption about the form of the reference wavefunction and is capable of handling both forms on the same footing.

The geminal operator \hat{G} is a two-body operator that depends on the coordinates of both the electrons and the holes

and is defined as

$$G(\mathbf{r}^e, \mathbf{r}^h) = \sum_i^{N_e} \sum_j^{N_h} g(\mathbf{r}_i^e, \mathbf{r}_j^h), \quad (2)$$

where $g(\mathbf{r}_i^e, \mathbf{r}_j^h)$ depends on the electron-hole inter-particle distance and is expressed as a linear combination of Gaussian functions

$$g(\mathbf{r}_i^e, \mathbf{r}_j^h) = \sum_k^{N_g} b_k e^{-\gamma_k |\mathbf{r}_i^e - \mathbf{r}_j^h|^2}. \quad (3)$$

The expansion coefficients b_k and the width parameter γ_k are parameters used for defining the geminal function. The geminal parameters and the constituting electron and hole orbitals are determined variationally by minimizing the expectation value of the Hamiltonian,

$$E = \frac{\langle \Psi_{xc} | H | \Psi_{xc} \rangle}{\langle \Psi_{xc} | \Psi_{xc} \rangle}. \quad (4)$$

The interaction between the electrons and the holes are described by an effective many-body Hamiltonian which can be described by the following general expression:^{38,41,102–104}

$$H = T_e + V_e^{\text{ext}} + V_{ee} + T_h + V_h^{\text{ext}} + V_{hh} + V_{eh}, \quad (5)$$

where,⁴¹

$$\begin{aligned} T_e &= \frac{-\hbar^2}{2m_e} \int d\mathbf{r}^e \hat{\psi}^\dagger(\mathbf{r}^e) \nabla^2 \hat{\psi}(\mathbf{r}^e) \\ T_h &= \frac{-\hbar^2}{2m_h} \int d\mathbf{r}^h \hat{\psi}^\dagger(\mathbf{r}^h) \nabla^2 \hat{\psi}(\mathbf{r}^h) \\ V_e^{\text{ext}} &= \int d\mathbf{r}^e \hat{\psi}^\dagger(\mathbf{r}^e) v_e^{\text{ext}} \hat{\psi}(\mathbf{r}^e) \\ V_h^{\text{ext}} &= \int d\mathbf{r}^h \hat{\psi}^\dagger(\mathbf{r}^h) v_h^{\text{ext}} \hat{\psi}(\mathbf{r}^h) \\ V_{ee} &= \int d\mathbf{r}_1^e d\mathbf{r}_2^e \hat{\psi}^\dagger(\mathbf{r}_1^e) \hat{\psi}^\dagger(\mathbf{r}_2^e) r_{ee}^{-1} \hat{\psi}(\mathbf{r}_2^e) \hat{\psi}(\mathbf{r}_1^e) \\ V_{hh} &= \int d\mathbf{r}_1^h d\mathbf{r}_2^h \hat{\psi}^\dagger(\mathbf{r}_1^h) \hat{\psi}^\dagger(\mathbf{r}_2^h) r_{hh}^{-1} \hat{\psi}(\mathbf{r}_2^h) \hat{\psi}(\mathbf{r}_1^h) \\ V_{eh} &= - \int d\mathbf{r}^e d\mathbf{r}^h \hat{\psi}^\dagger(\mathbf{r}^e) \hat{\psi}^\dagger(\mathbf{r}^h) r_{eh}^{-1} \hat{\psi}(\mathbf{r}^h) \hat{\psi}(\mathbf{r}^e). \end{aligned} \quad (6)$$

To facilitate the actual evaluation of the expectation value, it is advantageous to introduce the following conjunctive transformed operators:^{105,106}

$$\begin{aligned} \tilde{H} &= (1 + G)^\dagger H (1 + G), \\ \tilde{S} &= (1 + G)^\dagger (1 + G). \end{aligned} \quad (7)$$

Using the above equations, the energy expression can be written as

$$E = \frac{\langle \Phi_0^{\text{eh}} | \tilde{H} | \Phi_0^{\text{eh}} \rangle}{\langle \Phi_0^{\text{eh}} | \tilde{S} | \Phi_0^{\text{eh}} \rangle}. \quad (8)$$

This expression allows us to evaluate the energy in terms of matrix element of the transformed operators in Slater determinant basis. Since evaluation of matrix elements involving Slater determinants are known using Slater-Condon rules, this transformation provides a convenient route to the

computation of the matrix elements. In the present work, the transformed operators will be expressed in second quantization representation. The action of creation and annihilation operators is well known and is used to simplify the energy expression. Since the geminal operator is Hermitian, the transformed Hamiltonian is written as

$$\begin{aligned} \tilde{S} &= (1 + G)(1 + G) \\ &= 1 + 2G + GG, \end{aligned} \quad (9)$$

$$\begin{aligned} \tilde{H} &= (1 + G)H(1 + G) \\ &= H + GH + HG + GHG. \end{aligned} \quad (10)$$

The expression of the transformed operator in field operator representation is achieved in two steps. In the first step, the product of the operators are expanded as a sum of 1-particle, 2-particle, . . . , N -particle operators. The expanded versions of the transformed operators are described in Eq. (11)–(16). In the second step, the N -particle operators are written in second-quantized notation. It is important to preserve the sequence of the steps, since converting the operators first to second-quantized form and then taking the product will be identical to steps mentioned above only in the limit of infinite basis.¹⁰⁷ This topic has been discussed in a great detail with examples by Helgaker, Jorgensen, and Olsen.¹⁰⁷

The expressions for the transformed operators are given as

$$\begin{aligned} \tilde{S} &= 1 + 2G + GG \\ &= 1 + 2 \sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} g(i, i') + \left[\sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} g(i, i') \right] \\ &\quad \times \left[\sum_{j=1}^{N_e} \sum_{j'=1}^{N_h} g(j, j') \right] \\ &= 1 + \sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} O_1(i, i') + \frac{1}{2!} \sum_{i \neq j}^{N_e} \sum_{i'=1}^{N_h} O_2(i, j, i') \\ &\quad + \frac{1}{2!} \sum_{i \neq j}^{N_e} \sum_{i' \neq j'}^{N_h} O_3(i, i', j') + \frac{1}{2!2!} \sum_{i \neq j}^{N_e} \sum_{i' \neq j'}^{N_h} O_4(i, j, i', j'), \end{aligned} \quad (11)$$

$$\begin{aligned} G(T_e + V_e^{\text{ext}})G &= \left[\sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} g(i, i') \right] \left[\sum_{k=1}^{N_e} -\frac{\hbar^2}{2m_e} \nabla_k^2 + v_e^{\text{ext}}(k) \right] \left[\sum_{j=1}^{N_e} \sum_{j'=1}^{N_h} g(j, j') \right] \\ &= \sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} O_5(i, i') + \frac{1}{2!} \sum_{i=1}^{N_e} \sum_{i' \neq j}^{N_h} O_6(i, i', j') \\ &\quad + \frac{1}{2!} \sum_{i \neq j}^{N_e} \sum_{i'=1}^{N_h} O_7(i, j, i') + \frac{1}{2!2!} \sum_{i \neq j}^{N_e} \sum_{i' \neq j'}^{N_h} O_8(i, j, i', j') \\ &\quad + \frac{1}{3!} \sum_{i \neq j \neq k}^{N_e} \sum_{i'=1}^{N_h} O_9(i, i', k) + \frac{1}{3!2!} \sum_{i \neq j \neq k}^{N_e} \sum_{i' \neq j'}^{N_h} O_{10}(i, j, k, i', j'), \end{aligned} \quad (12)$$

$$\begin{aligned}
G(T_e + V_e^{\text{ext}}) + (T_e + V_e^{\text{ext}})G &= \left[\sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} g(i, i') \right] \left[\sum_{k=1}^{N_e} -\frac{\hbar^2}{2m_e} \nabla_k^2 + v_e^{\text{ext}}(k) \right] + \left[\sum_{i=1}^{N_e} -\frac{\hbar^2}{2m_e} \nabla_i^2 + v_e^{\text{ext}}(i) \right] \left[\sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} g(i, i') \right] \\
&= \sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} \sum_{k=1}^{N_e} g(i, i') \left[-\frac{\hbar^2}{2m_e} \nabla_k^2 + v_e^{\text{ext}}(k) \right] + \left[-\frac{\hbar^2}{2m_e} \nabla_k^2 + v_e^{\text{ext}}(k) \right] g(i, i') \\
&= \sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} O_{11}(i, i') + \frac{1}{2!} \sum_{i \neq j}^{N_e} \sum_{i'=1}^{N_h} O_{12}(i, j, i'), \tag{13}
\end{aligned}$$

$$\begin{aligned}
GV_{ee}G &= \left[\sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} g(i, i') \right] \left[\frac{1}{2} \sum_{k \neq l}^{N_e} r_{kl}^{-1} \right] \left[\sum_{j=1}^{N_e} \sum_{j'=1}^{N_h} g(j, j') \right] \\
&= \frac{1}{2!} \sum_{i \neq j}^{N_e} \sum_{i'=1}^{N_h} O_{13}(i, j, i') + \frac{1}{2!2!} \sum_{i \neq j}^{N_e} \sum_{i' \neq j'}^{N_h} O_{14}(i, j, i', j') \\
&\quad + \frac{1}{3!} \sum_{i \neq j \neq k}^{N_e} \sum_{i'=1}^{N_h} O_{15}(i, j, k, i') + \frac{1}{3!2!} \sum_{i \neq j \neq k}^{N_e} \sum_{i' \neq j'}^{N_h} O_{16}(i, j, k, i', j') \\
&\quad + \frac{1}{4!} \sum_{i \neq j \neq k \neq l}^{N_e} \sum_{i'=1}^{N_h} O_{17}(i, j, k, l, i') + \frac{1}{4!2!} \sum_{i \neq j \neq k}^{N_e} \sum_{i' \neq j'}^{N_h} O_{18}(i, j, k, l, i', j'), \tag{14}
\end{aligned}$$

$$\begin{aligned}
GV_{ee} + V_{ee}G &= \left[\sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} g(i, i') \right] \left[\frac{1}{2} \sum_{k \neq l}^{N_e} r_{kl}^{-1} \right] + \left[\frac{1}{2} \sum_{i \neq j}^{N_e} r_{ij}^{-1} \right] \left[\sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} g(i, i') \right] \\
&= \frac{1}{2!} \sum_{i \neq j}^{N_e} \sum_{i'=1}^{N_h} O_{19}(i, j, i') + \frac{1}{3!} \sum_{i \neq j \neq k}^{N_e} \sum_{i'=1}^{N_h} O_{20}(i, j, k, i'), \tag{15}
\end{aligned}$$

$$\begin{aligned}
GV_{eh}G &= \left[\sum_{i=1}^{N_e} \sum_{i'=1}^{N_h} g(i, i') \right] \left[\sum_{kk'}^{N_e} r_{kk'}^{-1} \right] \left[\sum_{j=1}^{N_e} \sum_{j'=1}^{N_h} g(j, j') \right] = \sum_{ijk}^{N_e} \sum_{i'j'k'}^{N_h} g(i, i') r_{kk'}^{-1} g(j, j') \\
&= \sum_i^{N_e} \sum_{i'}^{N_h} O_{21}(i, i') + \frac{1}{2!} \sum_i^{N_e} \sum_{i' \neq j}^{N_h} O_{22}(i, i', j') + \frac{1}{3!} \sum_i^{N_e} \sum_{i' \neq j \neq k}^{N_h} O_{23}(i, i', j', k') \\
&\quad + \frac{1}{2!} \sum_{i \neq j}^{N_e} \sum_{i'}^{N_h} O_{24}(i, j, i') + \frac{1}{2!2!} \sum_{i \neq j}^{N_e} \sum_{i' \neq j'}^{N_h} O_{25}(i, j, i', j') + \frac{1}{2!3!} \sum_{i \neq j}^{N_e} \sum_{i' \neq j \neq k}^{N_h} O_{26}(i, j, i', j', k') \\
&\quad + \frac{1}{3!} \sum_{i \neq j \neq k}^{N_e} \sum_{i'}^{N_h} O_{27}(i, j, k, i') + \frac{1}{3!2!} \sum_{i \neq j \neq k}^{N_e} \sum_{i' \neq j'}^{N_h} O_{28}(i, j, k, i', j') + \frac{1}{3!3!} \sum_{i \neq j \neq k}^{N_e} \sum_{i' \neq j \neq k'}^{N_h} O_{29}(i, j, k, i', j', k'). \tag{16}
\end{aligned}$$

The expression for the hole operators are obtained in a similar fashion.

It is important to note that the transformed operators $\{O_\alpha, \alpha = 1, \dots, 29\}$ must be completely symmetric when operated on by the permutation operators of the symmetric group $\{S_N\}$. For a general operator of the form $O_\alpha(1, \dots, M, 1, \dots, M')$ that couples M number of electrons with M' number of holes, the complete symmetric condition is satisfied by the following

relationship:

$$\begin{aligned}
\mathcal{P}_k \mathcal{P}_{k'} O_\alpha(1, \dots, M, 1', \dots, M') &= O_\alpha(1, \dots, M, 1', \dots, M') \\
k = 1, \dots, M!; k' = 1, \dots, M'!, \tag{17}
\end{aligned}$$

where \mathcal{P}_k and $\mathcal{P}_{k'}$ are permutation operators in the symmetric group S_M and $S_{M'}$, respectively.

The general expression for an N -particle operator in second-quantization and field operator notation is well known. The general expression of a many-body operator that couples M and M' electrons and holes, respectively, is represented in terms of electron and hole field operators as

$$\Omega_\alpha = \frac{1}{M!} \frac{1}{M'!} \sum_{i_1 \neq i_2 \neq \dots \neq i_M}^{N_e} \sum_{i'_1 \neq i'_2 \neq \dots \neq i'_{M'}}^{N_h} \times O_\alpha(i_1, i_2, \dots, i_M, i'_1, i'_2, \dots, i'_{M'}), \quad (18)$$

$$\begin{aligned} \Omega_\alpha &= \int d(1) \dots d(M) d(1') \dots d(M') \\ &\times \hat{\psi}^\dagger(1) \dots \hat{\psi}^\dagger(M) \hat{\psi}^\dagger(1') \dots \hat{\psi}^\dagger(M') \\ &\times O_\alpha(1, \dots, M, 1', \dots, M') \hat{\psi}(M') \dots \hat{\psi}(1') \\ &\times \hat{\psi}(M) \dots \hat{\psi}(1). \end{aligned} \quad (19)$$

The explicitly correlated wavefunction is obtained variationally by minimizing the total energy with respect to the electron and hole molecular orbitals and the parameters in the geminal operator. Minimizing the total energy with respect to the electron and hole molecular orbitals $\{\chi_i^e, \chi_i^h\}$ results in the following set of Fock equations:

$$\begin{aligned} f^e \chi_i^e &= \varepsilon_i^e \chi_i^e \\ f^h \chi_i^h &= \varepsilon_i^h \chi_i^h, \end{aligned} \quad (20)$$

where the electron and hole Fock operators can be defined as

$$\begin{aligned} f^e &= -\frac{\hbar^2}{2m_e} \nabla_e^2 + v_e^{\text{ext}} + v_e^{\text{eff}}[\{\chi_i^h\}], \\ f^h &= -\frac{\hbar^2}{2m_h} \nabla_h^2 + v_h^{\text{ext}} + v_h^{\text{eff}}[\{\chi_i^e\}]. \end{aligned} \quad (21)$$

The single-particle operator v_e^{eff} includes all the terms arising from the geminal expression and is equal to the HF potential v_e^{HF} in the limiting case of $G = 0$. The electronic Fock operator depends on the hole molecular orbitals, and both electron and hole Fock equations are solved self-consistently till convergence is achieved. The molecular orbitals are represented as a linear combination of atomic orbitals and the expansion coefficients are determined variationally. The integrals over atomic orbital involving the geminal function are well known and were calculated using the procedure described by Boys⁶¹ and Persson.¹⁰⁸

III. COMPUTATIONAL DETAILS

A. Details of eh-XCHF calculations

The form of the wavefunction used in the present calculation is defined to be a singlet wavefunction of the form

$$\begin{aligned} \Psi(\mathbf{x}_1, \mathbf{x}_2) &= \Psi_\alpha(\mathbf{r}_1, \mathbf{r}_2) \Psi_{\text{spin}}(\omega_1, \omega_2) \\ \alpha &= \text{HF, R12 - FCI, eh - XCHF}, \end{aligned} \quad (22)$$

where particles 1 and 2 have opposite spins and $\Psi_{\text{spin}}(\omega_1, \omega_2)$ is antisymmetric.

TABLE I. GTO basis used in HF and eh-XCHF calculations.

Exponent
2.5000×10^{-1}
2.3721×10^{-1}
3.5522×10^{-1}
5.3193×10^{-1}
7.9655×10^{-1}
1.1928
1.7862
2.6748
4.0054
1.6442×10^{-1}

The Hamiltonian for the benchmark system is defined as

$$H_\lambda = -\frac{1}{2m} \nabla_1^2 - \frac{1}{2m} \nabla_2^2 + \frac{1}{2} k r_1^2 + \frac{1}{2} k r_2^2 + \lambda \frac{1}{|\mathbf{r}^e - \mathbf{r}^h|}, \quad (23)$$

where $m_e = m_h = m = 1$ a.u., k is the force constant and all quantities are in atomic units. For the present calculations, the force constant was set to $k = 1/4$. A scaling parameter λ was introduced to scale the magnitude of the Coulomb interaction between the two particles. The Coulomb interaction between the two particles is represented by λr_{12}^{-1} , where $\lambda = +1$ if charges are identical and $\lambda = -1$ if the particles are oppositely charged. For the electron-hole system, the scaling parameter was set to $\lambda = -1$.

The explicitly correlated eh-XCHF method was used to calculate the ground state energy and electron-hole recombination probability. Gaussian-type orbitals (GTO) were used for the calculations and the coefficient used in the GTO basis are presented in Table I. All the GTOs were centered at the minimum of the parabolic potential. The FCI calculations for the two-electron Hooke's atom have been carried out earlier by Matito and co-workers⁹⁵ and the method for generating even-tempered GTO basis defined earlier⁹⁵ was used in the present work. Issues related to linear dependencies were resolved by performing canonical orthogonalization. The implementation of the computer program was checked by reproducing the FCI results obtained by Matito *et al.*⁹⁵

Since, eh-XCHF is an explicitly correlated method, a fair and accurate comparison was obtained by performing an explicitly correlated full-configuration interaction calculation using Slater-type orbitals (STOs). To emphasize this fact, the FCI method used in this work is labeled as (R12-FCI) and is described in Subsection III B. The analytical results for the two-electron Hooke's atoms with $k = 1/4$ is well known^{109,110} and was used to benchmark the R12-FCI implementation. The R12-FCI energy of 2.00074 Hartree was obtained for the Hooke's atom which was in good agreement with the exact analytical result of 2.0 Hartree.

B. Details of the R12-FCI calculation

The R12-FCI calculation was performed by transforming the 6D Hamiltonian described in Eq. (23) to a 1D radial Hamiltonian. This was done by first separating out the

center-of-mass coordinate followed by transforming into spherical polar coordinates.

Defining the relative and center-of-mass coordinates as

$$\begin{aligned}\mathbf{R} &= \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} \\ \mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2.\end{aligned}\quad (24)$$

The total Hamiltonian can be written as

$$\begin{aligned}H &= H_R + H_r \\ H_R &= -\frac{1}{2M}\nabla_R^2 + \frac{1}{2}M\omega^2 R^2 \\ H_r &= -\frac{1}{2\mu}\nabla_r^2 + \frac{1}{2}\mu\omega^2 r^2 + \lambda\frac{1}{r},\end{aligned}\quad (25)$$

where $M = m_1 + m_2$ and $\mu = m_1 m_2 M^{-1}$. The total wavefunction is defined as

$$\begin{aligned}H\Psi &= E\Psi \\ H_R\Phi_R &= E_R\Phi_R \\ H_r\Phi_r &= E_r\Phi_r \\ \Psi &= \Phi_R\Phi_r \\ E &= E_R + E_r.\end{aligned}\quad (26)$$

The center-of-mass Hamiltonian is a 3D harmonic oscillator whose eigenvalues and eigenfunctions are known analytically and is equal to $3\hbar\omega$ for the ground state.

The Hamiltonian associated with the relative coordinate was transformed into spherical polar coordinates, and the radial equation for $l = 0$ is given as

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{1}{2}\mu\omega^2 r^2 + \lambda\frac{1}{r} \right] \chi(r) = E_r \chi(r)$$

for $l = 0$. (27)

The 1D radial Schrodinger equation in Eq. (27) was solved by expanding the radial wavefunction as a linear combination of Slater-type orbitals and performing configuration interaction calculation,

$$\begin{aligned}\chi(r) &= \sum_i c_i \phi_i^{\text{STO}} \\ \phi^{\text{STO}}(r) &= r^n e^{-\alpha r}.\end{aligned}\quad (28)$$

The ground state energy was obtained by minimizing both the expansion coefficients $\{c_i\}$ and the STO exponent $\{\alpha_i\}$. The STO basis functions used for the R12-FCI calculations are listed in Table II.

The radial equation in Eq. (27) can be solved analytically for the limiting cases of $\lambda = 0$ and $\omega = 0$. The R12-FCI method can be systematically improved by addition of more basis functions and will reproduce the exact ground state energy in the limit of infinite basis functions. The R12-FCI calculation with the STO basis presented in Table II was found to reproduce the analytical energies.

TABLE II. STO basis used in the R12-FCI calculations.

n	Exponent
0	5.8600×10^{-1}
1	5.8600×10^{-1}
2	5.8600×10^{-1}
0	1.5172
1	1.5172
2	1.5172
0	3.9279
1	3.9279
2	3.9279
0	1.0169×10^1
1	1.0169×10^1
2	1.0169×10^1
0	2.6328×10^1
1	2.6328×10^1
2	2.6328×10^1

IV. RESULTS AND DISCUSSION

A. Correlation energy from HF and R12-FCI calculations

The HF theory plays an important role in electronic structure theory. The HF wavefunction is used as a zeroth order wavefunction for post-HF calculations such as perturbation theory and configuration interaction calculations. For application of the HF wavefunction as a reference wavefunction in electron-hole systems, it is very important to investigate the quality of the mean-field approximation versus highly accurate calculations. In the present work, a comparison study of the quality of the mean-field approximation for electron-hole and electron-electron system was carried out by performing a series of HF and R12-FCI calculations. The calculations were performed for H_λ and the coupling parameter λ was varied from $\lambda = -1, \dots, +1$. For each value of λ the difference between the HF and R12-FCI energies was computed using the following expression:

$$\Delta E(\lambda) = \frac{E_{\text{HF}}(\lambda) - E_{\text{R12-FCI}}(\lambda)}{E_{\text{R12-FCI}}(\lambda)} \times 100. \quad (29)$$

The difference between the HF and R12-FCI energies is used as a metric to analyze the quality of mean field approximation for electron-electron versus electron-hole system. The result of the computed ΔE as a function of λ is presented in Figure 1. It is seen that plot is not symmetric with respect to the coupling parameter. This implies that the HF approximation is worse for the electron-hole system as compared to an electron-electron system. It was found that the ΔE for electron-hole is larger than the electron-electron system by a factor of 4. This large difference in the quality of the mean field approximation for identical and oppositely charged particles can be attributed to the Coulomb interaction term in the Hamiltonian. Because of the Coulomb hole in the electron-electron system, there is a reduced probability of finding another electron in the vicinity of the first electron. For the electron-hole system, the situation is reversed and there is an enhanced probability of finding an oppositely charged particle in the vicinity of the first one. This can be seen clearly by

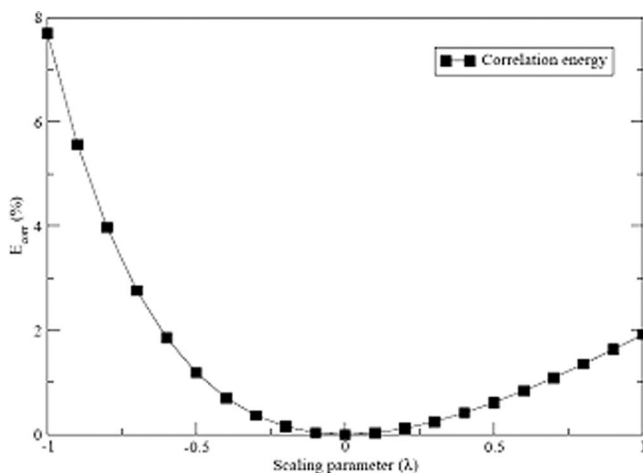


FIG. 1. Relative difference between that HF and R12-FCI energies as a function of the Coulomb scaling parameter.

deriving of the Kato cusp condition for the two-particle density. The Kato cusp condition for the ground state wavefunction for the electron-electron and electron-hole system is defined as^{111,112}

$$\Psi_{ee}(r_{12}) = \Psi_{ee}(r_{12} = 0) \left[1 + \frac{1}{2}r_{12} + O(r_{12}^2) \right], \quad (30)$$

$$\Psi_{eh}(r_{12}) = \Psi_{eh}(r_{12} = 0) \left[1 - \frac{1}{2}r_{12} + O(r_{12}^2) \right], \quad (31)$$

where we have assumed that the ground state is a S state. Using the above expression, the two-particle density can be defined as

$$\rho_{ee}(r_{12}) = \rho_{ee}(r_{12} = 0) [1 + r_{12} + O(r_{12}^2)], \quad (32)$$

$$\rho_{eh}(r_{12}) = \rho_{eh}(r_{12} = 0) [1 - r_{12} + O(r_{12}^2)]. \quad (33)$$

The above equations indicate that the probability density of finding two electrons increases with increasing r_{12} at small inter-particle separation. This is indicative of a Coulomb hole. For the electron-hole system, the probability density of finding an electron-hole pair decreases increasing r_{12} at small inter-particle separation which indicates a local enhancement of the two-particle density in the vicinity of the cusp. Since $\rho_{ee}(r_{12})/\rho_{ee}(0) > 1$ and $\rho_{eh}(r_{12})/\rho_{eh}(0) < 1$ at small inter-particle separation, the quality of the eh-wavefunction at short range, and the electronic wavefunction at intermediate range, is important for obtaining accurate results. Similar conclusion for the electronic wavefunction has been reported earlier by Prendergast *et al.*¹¹³

The Kato cusp condition is generally satisfied by incorporating Slater-type orbital (STO) functions that depend on r_{eh}

$$e^{-\zeta r_{eh}} = 1 - \zeta r_{eh} + O(r^2). \quad (34)$$

In this present work, Gaussian type geminal (GTG) functions were used to describe the form of the wavefunction at small inter-particle distances

$$e^{-\zeta r_{eh}} \simeq \sum_k^{N_g} b_k e^{-\gamma_k r_{eh}^2}, \quad (35)$$

where $\{b_k, \gamma_k\}$ are variational parameters. The GTG function was introduced by Boys⁶¹ for explicitly including R12 term in the electronic wavefunction. The necessary integrals involved in the implementation of the GTG function are well-known analytical expressions and have been derived earlier by Boys⁶¹ and Persson *et al.*¹⁰⁸ The STO is expanded as a linear combination of Gaussian function to avoid computation of integrals involving STOs. This is a general strategy to avoid computation of atomic orbital (AO) integrals using STO and has been used successfully in the field of basis set development^{114,115} and GTG calculations.^{62,116} However, we stress that the expansion in Eq. (35) is approximate and is not capable of describing the eh-cusp exactly since the Gaussian functions have zero first derivative at the cusp. The description of the electron-hole cusp can be systematically improved by performing post-SCF explicit R12 calculations. In the present work, the expansion coefficients are obtained variationally by minimizing the total energy. However, pre-computed values of the expansion coefficients and GTG functions can also be used in the above expression.⁶²

B. Energy and recombination probability from eh-XCHF calculations

The eh-XCHF calculations were performed only for the electron-hole system and Hamiltonian for the system was obtained by setting $\lambda = -1$ in Eq. (23). The total eh-XCHF wavefunction for the system is defined as

$$\Psi_{xc}(\mathbf{x}^e, \mathbf{x}^h) = [1 + G(\mathbf{r}^e, \mathbf{r}^h)] \Phi^e(\mathbf{r}^e) \Phi^h(\mathbf{r}^h) \Psi_{\text{spin}}(\omega^e, \omega^h), \quad (36)$$

where Ψ_{spin} is anti-symmetric and the electron and the hole have opposite spins. Gaussian-type orbitals (GTO) were used to describe the spatial component of the wavefunction and are defined in Table I. The number of parameters N_g in the geminal expansion were incrementally increased until convergence was achieved with respect to energy. At each value of N_g , the set of geminal parameters $\{b_k, \gamma_k\}$ were determined variationally. The energies and recombination probability from the eh-XCHF calculation are compared with HF and R12-FCI calculations and results are plotted in Figures 2 and 3, respectively,

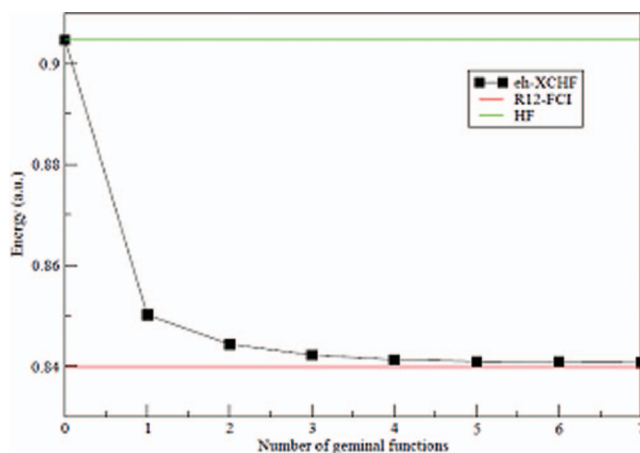


FIG. 2. Convergence of the ground state energy as a function of number of geminal parameters.

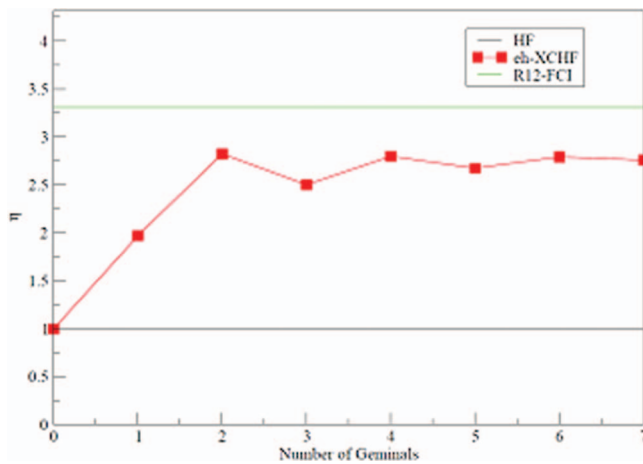


FIG. 3. Comparison of the electron-hole recombination enhancement factor from the eh-XCHF calculation with HF and R12-FCI results.

as a function of N_g . The $N_g = 0$ in the plot represents the HF solution since the eh-XCHF calculation reduces to HF in the limit of $G = 0$. The value of N_g was systematically increased and convergence with respect to the total energy was achieved at $N_g = 7$. The geminal parameters were optimized in a sequential process and parameters optimized for $N_g - 1$ step were kept fixed. As a result, for the N_g step, all parameters from the previous step $\{b_i, \gamma_i; i = 1, \dots, N_g - 1\}$ were kept fixed and only $\{b_i, \gamma_i; i = N_g\}$ was variationally optimized. The list of optimized geminal parameters are listed in Table III. The HF energy was found to be higher than the R12-FCI energy by 0.0648 Hartree (1.76 eV). The best eh-XCHF energy with $N_g = 7$ is 0.8407 Hartree and is higher than the R12-FCI energy by 0.02 eV. From Figure 2, it is seen that the eh-XCHF wavefunction can be systematically improved by addition of geminal parameters. The eh-XCHF energy for $N_g = 1$ is lower than the HF energy by 0.0545 Hartree (1.48 eV). This shows the importance of improving the short-range description of the electron-hole wavefunction that is missing in the mean-field approximation. The form of the geminal function with $N_g = 7$ is plotted as the function of inter-particle distance and is presented in Figure 4. An exponential function of the form $e^{-\zeta r_{eh}}$ is fitted to the geminal function and also shown in Figure 4. The width parameter from the exponential fit was found to be $\zeta = 0.5605$ which is close to the theoretical exact value of 0.5 from the Kato cusp condition.¹¹²

The quality of the electron-hole wavefunction can also be analyzed by computing either the electron-hole recombina-

TABLE III. Optimized geminal parameters.

k	b_k	γ_k
1	1.2100	0.3500
2	0.4640	3.9600
3	0.5800	0.0900
4	0.2270	1.9000
5	0.2800	0.1000
6	0.1028	1.6700
7	-0.1020	0.3500

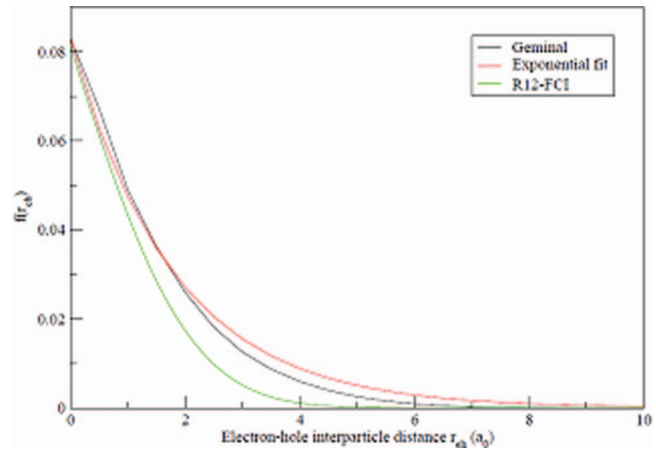


FIG. 4. Comparison of the geminal function with the fitted exponential function and R12-FCI wavefunction. The geminal function has been scaled so that the geminal and the R12-FCI curves can be plotted in the same figure.

tion rate or the associated recombination probability. Both of these quantities are computed from the electron-hole density matrix and is sensitive to accurate treatment of electron-hole correlation. The general expression for electron-hole density matrix for arbitrary number of excitons has been derived earlier by Corni and co-workers⁵² for studying transitions from $(N + 1)$ to N excitonic states.^{52,58} In a separate study, van der Horst *et al.* used electron-hole distance probability distribution function¹¹⁷ to analyze excitonic wavefunction in conjugated polymers obtained using the Bethe-Salpeter method. The electron-hole distance probability distribution function (in atomic units) is defined as¹¹⁷

$$P_{eh}^{\alpha} = \frac{\langle \Psi_{\alpha} | \delta(\mathbf{r}^e - \mathbf{r}^h) | \Psi_{\alpha} \rangle}{\langle \Psi_{\alpha} | \Psi_{\alpha} \rangle} \quad \alpha = \text{HF, R12 - FCI, XCHF}, \quad (37)$$

and was used for analyzing HF, R12-FCI, and eh-XCHF wavefunctions. Since we are interested in comparison of the correlated wavefunctions with respect to the mean-field approximation, we also defined the eh-recombination enhancement factor η which is obtained from the P_{eh} using the following expression:

$$\eta^{\alpha} = \frac{P_{eh}^{\alpha}}{P_{eh}^{\text{HF}}} \quad \alpha = \text{HF, R12 - FCI, XCHF}. \quad (38)$$

The results from eh-XCHF calculations with $N_g = 0, \dots, 7$ together with the HF and R12-FCI results are presented in Figure 3. It is seen, that the recombination probability converges as a function of geminal parameters. On comparison of results from the three methods, it is seen that HF calculation severely underestimates the recombination probability by a factor of three for both the eh-XCHF and R12-FCI methods. The recombination probability is very sensitive to form of the wavefunction at small electron-hole inter-particle distances. The ground state energies and the eh-recombination enhancement factor for HF, R12-FCI, and eh-XCHF are summarized in Table IV. The results in this table highlight the challenging aspect of computation of accurate recombination probability. The energy from the eh-XCHF wavefunction is higher than the benchmark by 0.1%. In contrast, the eh-recombination probability is lower by 16%.

TABLE IV. Comparison of calculated ground state energy and electron-hole recombination enhancement factor from HF, R12-FCI, and eh-XCHF calculations for the parabolic quantum dot. The Hamiltonian for the dot was defined by setting $k = 1/4$ in Eq. (23).

Method	Energy (Hartree)	η
HF	0.9047	1
R12-FCI	0.8399	3.29
Eh-XCHF	0.8407	2.76

It is seen in Figure 2 that the eh-XCHF energy is converged with respect to number of GTG functions. Analogous to the conventional electronic structure theory, the converged eh-XCHF method can be systematically improved using perturbation theory and configuration interaction¹¹⁸ calculation using the eh-XCHF as the reference wavefunction. This approach of successive improvement of a correlated reference wavefunction is also analogous to a typical diffusion Monte Carlo calculation where correlated wavefunction from variational Monte Carlo is used as a starting point for a more accurate calculation.

In general, it will not be possible to perform R12-FCI calculation for any system due to lack of spherically symmetric potential and numerical cost associated with using Slater-type orbitals. The eh-XCHF formulation on the other hand is a general purpose method that does not require any *a priori* assumption about the potential and utilizes GTO as opposed to STO as basis functions. The use of Gaussian type geminal function in the eh-XCHF method allow analytical evaluation of the AO integrals.^{61,108} In electronic structure theory, the resolution of identity (RI) method^{119,120} has been used successfully for integral evaluation with GTG.^{121–124} The RI method will be used in the eh-XCHF calculation for fast evaluation of many-particle integrals involving geminal functions. The eh-XCHF benchmark calculations presented here is the first in a series of calculation on various electron-hole systems. Future work using the eh-XCHF method involved investigation of effect of shell thickness on electron-hole recombination in CdSe/ZnS multilayered quantum dots¹¹⁸ and replacing HF by eh-XCHF wavefunction as the zeroth order reference wavefunction in post-SCF schemes such as MP2 and CI methods.¹²⁵

V. CONCLUSIONS

The explicitly correlated HF method for a general many-electron many-hole system is presented and was used for calculation of ground state energy and electron-hole recombination probability. The eh-XCHF method is a general technique for solving the electron-hole Schrodinger equation and can be applied to a large variety of electron-hole system by appropriate selection of the quasi-particle masses and the external potential terms in the effective electron-hole Hamiltonian. In the present work, the eh-XCHF method was applied to the parabolic quantum dot system which consists of an interacting electron-hole pair confined by the three-dimensional parabolic potential. Ground state energy and electron-hole recombination probabilities were computed and

the results were found to be in good agreement with the highly accurate explicitly correlated full configuration interaction calculations. HF calculation was also performed and the HF wavefunction was found to severely underestimate the electron-hole recombination probability. The accuracy of the HF wavefunction was compared for both electron-electron and electron-hole system and it was found that the HF approximation is worse for the electron-hole system. The results from these calculations highlight the importance of accuracy of the form of the electron-hole wavefunction at small interparticle distances for electron-hole systems and the capability of eh-XCHF method to successfully address this issue.

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- ¹M. G. Bawendi, M. L. Steigerwald, and L. E. Brus, *Annu. Rev. Phys. Chem.* **41**, 477 (1990).
- ²G. W. Bryant, *Phys. Rev. B* **37**, 8763 (1988).
- ³H. Haug and S. W. Koch, *Quantum Theory of the Optical and Electronic Properties of Semiconductors* (World Scientific, 2009), p. 470.
- ⁴S. Glutsch, *Excitons in Low-Dimensional Semiconductors* (Springer, 2004).
- ⁵K. Barnham and D. Vvedensky, *Low-Dimensional Semiconductor Structures: Fundamentals and Device Applications* (Cambridge University Press, 2001).
- ⁶L. He, G. Bester, and A. Zunger, *Phys. Rev. Lett.* **94**, 016801 (2005).
- ⁷F. Tassone and C. Piermarocchi, *Phys. Rev. Lett.* **82**, 843 (1999).
- ⁸F. Rossi and E. Molinari, *Phys. Rev. Lett.* **76**, 3642 (1996).
- ⁹G. Pal, G. Lefkidis, H. C. Schneider, and W. Hübner, *J. Chem. Phys.* **133**, 154309 (2010).
- ¹⁰D. H. Chae, T. Utikal, S. Weisenburger, H. Giessen, K. V. Klitzing, M. Lippitz, and J. Smet, *Nano Lett.* **11**, 1379 (2011).
- ¹¹V. Perebeinos, J. Tersoff, and P. Avouris, *Nano Lett.* **5**, 2495 (2005).
- ¹²P. Puschnig and C. Ambrosch-Draxl, *Phys. Rev. Lett.* **89**, 056405/1 (2002).
- ¹³N. Baer, C. Gies, J. Wiersig, and F. Jahnke, *Eur. Phys. J. B* **50**, 411 (2006).
- ¹⁴J. Krüger, R. Plass, M. Grätzel, P. J. Cameron, and L. M. Peter, *J. Phys. Chem. B* **107**, 7536 (2003).
- ¹⁵M. Achermann, M. A. Petruska, S. Kos, D. L. Smith, D. D. Koleske, and V. I. Klimov, *Nature (London)* **429**, 642 (2004).
- ¹⁶M. J. Hetzer, Y. M. Strzhemechny, M. Gao, M. A. Contreras, A. Zunger, and L. J. Brillson, *Appl. Phys. Lett.* **86**, 162105 (2005).
- ¹⁷S. Lacic and O. Inganäs, *J. Appl. Phys.* **97**, 124901 (2005).
- ¹⁸C. Chen, S. Wu, J. Li, C. Wu, J. Chen, and K. Ho, *Adv. Mater.* **19**, 3888 (2007).
- ¹⁹R. R. King, D. C. Law, K. M. Edmondson, C. M. Fetzter, G. S. Kinsey, H. Yoon, R. A. Sherif, and N. H. Karam, *Appl. Phys. Lett.* **90**, 183516 (2007).
- ²⁰C. Wang, A. Heller, and H. Gerischer, *J. Am. Chem. Soc.* **114**, 5230 (1992).
- ²¹J. Tang, J. R. Durrant, and D. R. Klug, *J. Am. Chem. Soc.* **130**, 13885 (2008).
- ²²N. O. Gopal, H. Lo, S. Sheu, and S. Ke, *J. Am. Chem. Soc.* **132**, 10982 (2010).
- ²³N. Wu, J. Wang, D. N. Tafen, H. Wang, J. Zheng, J. P. Lewis, X. Liu, S. S. Leonard, and A. Manivannan, *J. Am. Chem. Soc.* **132**, 6679 (2010).
- ²⁴C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- ²⁵C. W. Tang, S. A. Vanslyke, and C. H. Chen, *J. Appl. Phys.* **65**, 3610 (1989).
- ²⁶J. E. Kroeze, N. Hirata, S. Koops, M. K. Nazeeruddin, L. Schmidt-Mende, M. Grätzel, and J. R. Durrant, *J. Am. Chem. Soc.* **128**, 16376 (2006).
- ²⁷L. V. Butov, C. W. Lai, A. L. Ivanov, A. C. Gossard, and D. S. Chemla, *Nature (London)* **417**, 47 (2002).
- ²⁸S. Kim, B. Fisher, H.-J. Eisler, and M. Bawendi, *J. Am. Chem. Soc.* **125**, 11466 (2003).

- ²⁹S. A. Ivanov, A. Piryatinski, J. Nanda, S. Tretiak, K. R. Zavadil, W. O. Wallace, D. Werder, and V. I. Klimov, *J. Am. Chem. Soc.* **129**, 11708 (2007).
- ³⁰P. Reiss, M. Protière, and L. Li, *Small* **5**, 154 (2009).
- ³¹V. I. Klimov, *J. Phys. Chem. B* **110**, 16827 (2006).
- ³²V. I. Klimov, S. A. Ivanov, J. Nanda, M. Achermann, I. Bezel, J. A. McGuire, and A. Piryatinski, *Nature (London)* **447**, 441 (2007).
- ³³G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys.* **74**, 601 (2002).
- ³⁴M. Rohlfing and S. G. Louie, *Phys. Rev. B: Condens. Matter Mater. Phys.* **62**, 4927 (2000).
- ³⁵L. S. Cederbaum, *J. Phys. B* **8**, 290 (1975).
- ³⁶L. E. Brus, *J. Chem. Phys.* **80**, 4403 (1984).
- ³⁷M. Brskén, M. Lindberg, D. Sundholm, and J. Olsen, *Phys. Rev. B* **61**, 7652 (2000).
- ³⁸Y. Z. Hu, M. Lindberg, and S. W. Koch, *Phys. Rev. B* **42**, 1713 (1990).
- ³⁹T. Vänskä, M. Lindberg, J. Olsen, and D. Sundholm, *Phys. Status Solidi B* **243**, 4035 (2006).
- ⁴⁰J. Shumway, *Phys. E* **32**, 273 (2006).
- ⁴¹X. Zhu, M. S. Hybertsen, and P. B. Littlewood, *Phys. Rev. B* **54**, 13575 (1996).
- ⁴²O. Lehtonen, D. Sundholm, and T. Vanska, *Phys. Chem. Chem. Phys.* **10**, 4535 (2008).
- ⁴³A. Franceschetti and A. Zunger, *Phys. Rev. Lett.* **78**, 915 (1997).
- ⁴⁴A. Franceschetti, H. Fu, L. Wang, and A. Zunger, *Phys. Rev. B* **60**, 1819 (1999).
- ⁴⁵A. Franceschetti and A. Zunger, *Phys. Rev. B* **62**, 2614 (2000).
- ⁴⁶L. W. Wang, M. Califano, A. Zunger, and A. Franceschetti, *Phys. Rev. Lett.* **91**, 056404 (2003).
- ⁴⁷J. W. Luo, A. Franceschetti, and A. Zunger, *Nano Lett.* **8**, 3174 (2008).
- ⁴⁸M. Califano, A. Franceschetti, and A. Zunger, *Phys. Rev. B* **75**, 115401 (2007).
- ⁴⁹G. Narvaez, G. Bester, and A. Zunger, *Phys. Rev. B* **72**, 245318 (2005).
- ⁵⁰M. Califano, A. Zunger, and A. Franceschetti, *Nano Lett.* **4**, 525 (2004).
- ⁵¹M. Califano, A. Zunger, and A. Franceschetti, *Appl. Phys. Lett.* **84**, 2409 (2004).
- ⁵²S. Corni, M. Brasken, M. Lindberg, J. Olsen, and D. Sundholm, *Phys. Rev. B* **67**, 085314 (2003).
- ⁵³S. Corni, M. Brasken, M. Lindberg, J. Olsen, and D. Sundholm, *Phys. E* **18**, 436 (2003).
- ⁵⁴W. Lester and B. Hammond, *Annu. Rev. Phys. Chem.* **41**, 283 (1990).
- ⁵⁵W. Foulkes, L. Mitás, R. Needs, and G. Rajagopal, *Rev. Mod. Phys.* **73**, 33 (2001).
- ⁵⁶W. Klopper, F. R. Manby, S. Ten-No, and E. F. Valeev, *Int. Rev. Phys. Chem.* **25**, 427 (2006).
- ⁵⁷W. von der Linden, *Phys. Rep.*, *Phys. Lett.* **220**, 53 (1992).
- ⁵⁸S. Corni, M. Brasken, M. Lindberg, J. Olsen, and D. Sundholm, *Phys. Rev. B* **67**, 045313 (2003).
- ⁵⁹J. Shumway and D. M. Ceperley, *Phys. Rev. B* **63**, 165209 (2001).
- ⁶⁰B. J. Persson and P. R. Taylor, *J. Chem. Phys.* **105**, 5915 (1996).
- ⁶¹S. F. Boys, *Proc. R. Soc. London, Ser. A* **258**, 402 (1960).
- ⁶²S. A. Varganov and T. J. Martínez, *J. Chem. Phys.* **132** (2010).
- ⁶³C. Swalina, M. V. Pak, A. Chakraborty, and S. Hammes-Schiffer, *J. Phys. Chem. A* **110**, 9983 (2006).
- ⁶⁴A. Chakraborty, M. V. Pak, and S. Hammes-Schiffer, *J. Chem. Phys.* **129**, 014101 (2008).
- ⁶⁵A. Chakraborty and S. Hammes-Schiffer, *J. Chem. Phys.* **129**, 204101 (2008).
- ⁶⁶M. V. Pak, A. Chakraborty, and S. Hammes-Schiffer, *J. Phys. Chem. A* **113**, 4004 (2009).
- ⁶⁷M. Chamarro, C. Gourdon, P. Lavallard, O. Lublinskaya, and A. Ekimov, *Phys. Rev. B* **53**, 1336 (1996).
- ⁶⁸A. L. Efros and M. Rosen, *Annu. Rev. Mater. Sci.* **30**, 475 (2000).
- ⁶⁹T. Takagahara, *Phys. Rev. B* **47**, 4569 (1993).
- ⁷⁰G. W. Bryant, *Phys. Rev. B* **37**, 8763 (1988).
- ⁷¹T. Takagahara and K. Takeda, *Phys. Rev. B* **46**, 15578 (1992).
- ⁷²B. Delley and E. F. Steigmeier, *Phys. Rev. B* **47**, 1397 (1993).
- ⁷³S. H. Tolbert, A. B. Herhold, C. S. Johnson, and A. P. Alivisatos, *Phys. Rev. Lett.* **73**, 3266 (1994).
- ⁷⁴G. Ledoux, J. Gong, F. Huiskens, O. Guillois, and C. Reynaud, *Appl. Phys. Lett.* **80**, 4834 (2002).
- ⁷⁵A. Franceschetti, L. Wang, H. Fu, and A. Zunger, *Phys. Rev. B* **58**, 13367 (1998).
- ⁷⁶J. Luo, A. Franceschetti, and A. Zunger, *Nano Lett.* **9**, 2648 (2009).
- ⁷⁷F. Reboredo, A. Franceschetti, and A. Zunger, *Phys. Rev. B* **61**, 13073 (2000).
- ⁷⁸A. Efros and M. Rosen, *Annu. Rev. Mater. Sci.* **30**, 475 (2000).
- ⁷⁹S. Brovelli, R. D. Schaller, S. A. Crooker, F. Garcia-Santamaria, Y. Chen, R. Viswanatha, J. A. Hollingsworth, H. Htoon, and V. I. Klimov, *Nat. Commun.* **2**, 280 (2011).
- ⁸⁰G. Bester, S. Nair, and A. Zunger, *Phys. Rev. B* **67**, 161306 (2003).
- ⁸¹I. A. Akimov, K. V. Kavokin, A. Hundt, and F. Henneberger, *Phys. Rev. B: Condens. Matter Mater. Phys.* **71**, 1 (2005).
- ⁸²G. V. Astakhov, A. V. Koudinov, K. V. Kavokin, I. S. Gaggis, Y. G. Kusrayev, W. Ossau, and L. W. Molenkamp, *Phys. Rev. Lett.* **99**, 016601 (2007).
- ⁸³J. He, H. Zhong, and G. D. Scholes, *Phys. Rev. Lett.* **105**, 046601 (2010).
- ⁸⁴S. M. Santos, B. Yuma, S. Berciaud, J. Shaver, M. Gallart, P. Gilliot, L. Cagnet, and B. Lounis, *Phys. Rev. Lett.* **107**, 187401 (2011).
- ⁸⁵R. Matsunaga, K. Matsuda, and Y. Kanemitsu, *Phys. Rev. Lett.* **106**, 037404 (2011).
- ⁸⁶W. F. Xie, *Physica B* **358**, 109 (2005).
- ⁸⁷G. Lamouche and G. Fishman, *J. Phys.: Condens. Matter* **10**, 7857 (1998).
- ⁸⁸M. Elsaid, *Semicond. Sci. Technol.* **9**, 272 (1994).
- ⁸⁹S. Chen, *Physica B* **406**, 2033 (2011).
- ⁹⁰C. M. Duque, M. E. Mora-Ramos, and C. A. Duque, *J. Nanopart. Res.* **13**, 6103 (2011).
- ⁹¹E. Sadeghi and A. Avazpour, *Physica B* **406**, 241 (2011).
- ⁹²W. Xie, *Opt. Commun.* **282**, 2604 (2009).
- ⁹³M. Ikezawa, S. V. Nair, H. W. Ren, Y. Masumoto, and H. Ruda, *Phys. Rev. B* **73**, 125321 (2006).
- ⁹⁴T. Chakraborty and P. Pietiläinen, *Phys. Rev. Lett.* **95**, 136603 (2005).
- ⁹⁵E. Matito, J. Cioslowski, and S. F. Vyboishchikov, *Phys. Chem. Chem. Phys.* **12**, 6712 (2010).
- ⁹⁶J. P. Coe, A. Sudbery, and I. D'Amico, *Phys. Rev. B* **77** (2008).
- ⁹⁷N. H. March and A. Rubio, *Chem. Phys. Lett.* **398**, 445 (2004).
- ⁹⁸D. Hestenes, *Am. J. Phys.* **39**, 1013 (1971).
- ⁹⁹P. Cassam-Chenai, *J. Math. Chem.* **15**, 303 (1994).
- ¹⁰⁰K. C. Mundim, M. Giambiagi, and M. S. De Giambiagi, *J. Phys. Chem.* **98**, 6118 (1994).
- ¹⁰¹P. Cassam-Chenai and F. Patras, *J. Math. Phys.* **44**, 4884 (2003).
- ¹⁰²U. Woggon, *Optical Properties of Semiconductor Quantum Dots* (Springer, 1996), p. 252.
- ¹⁰³E. Burovski, A. Mishchenko, N. Prokof'ev, and B. Svistunov, *Phys. Rev. Lett.* **87**, 186402 (2001).
- ¹⁰⁴M. Wimmer, S. V. Nair, and J. Shumway, *Phys. Rev. B* **73**, 165305 (2006).
- ¹⁰⁵M. C. Pease III, *Methods of Matrix Algebra* (Academic, New York, 1965), p. 406.
- ¹⁰⁶R. C. James, *Mathematics Dictionary* (Springer, 1992), p. 548.
- ¹⁰⁷T. Helgaker, P. Jorgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, 2000), p. 938.
- ¹⁰⁸B. J. Persson and P. R. Taylor, *Theor. Chem. Acc.* **97**, 240 (1997).
- ¹⁰⁹J. Karwowski and L. Cyrnek, *Collect. Czech. Chem. Commun.* **70**, 864 (2005).
- ¹¹⁰J. Karwowski, *Int. J. Quantum Chem.* **109**, 2456 (2009).
- ¹¹¹R. T. Pack and W. Byers Brown, *J. Chem. Phys.* **45**, 625 (1966).
- ¹¹²C. R. Myers, C. J. Umrigar, J. P. Sethna, and J. D. Morgan III, *Phys. Rev. A* **44**, 5537 (1991).
- ¹¹³D. Prendergast, M. Nolan, C. Filippi, S. Fahy, and J. C. Greer, *J. Chem. Phys.* **115**, 1626 (2001).
- ¹¹⁴W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).
- ¹¹⁵R. F. Stewart, *J. Chem. Phys.* **52**, 425 (1970).
- ¹¹⁶S. Ten-no, *Chem. Phys. Lett.* **398**, 56 (2004).
- ¹¹⁷J.-. Van Der Horst, P. A. Bobbert, M. A. J. Michels, and H. Bässler, *J. Chem. Phys.* **114**, 6950 (2001).
- ¹¹⁸J. Elward, J. Hoffman, and A. Chakraborty, "Investigation of electron-hole correlation using explicitly correlated configuration interaction method," *Chem. Phys. Lett.* (in press).
- ¹¹⁹R. A. Kendall and H. A. Früchtl, *Theor. Chem. Acc.* **97**, 158 (1997).
- ¹²⁰F. Neese, *J. Comput. Chem.* **24**, 1740 (2003).
- ¹²¹E. F. Valeev, *Chem. Phys. Lett.* **395**, 190 (2004).
- ¹²²D. P. Tew, W. Klopper, and F. R. Manby, *J. Chem. Phys.* **127**, 174105 (2007).
- ¹²³H.-J. Werner, T. B. Adler, and F. R. Manby, *J. Chem. Phys.* **126**, 164102 (2007).
- ¹²⁴E. F. Valeev, *J. Chem. Phys.* **125**, 244106 (2006).
- ¹²⁵J. Elward, J. Hoja, and A. Chakraborty, "Application of XCCI method for many-electron systems" (unpublished).