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Theory of multiexciton complexes bound to donors in multivalley semiconductors

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We report a theory for bound multiexciton complexes (BMEC) associated with donors in multivalley semiconductors. The energy separations between the low-lying electronic states and the ground state are calculated in the Hartree-Fock approximation. By incorporating the effect of the anisotropic, multivalley band structures with interparticle interactions, we obtain energy separations in good agreement with the available experimental data. This agreement between theory and experiment suggests that the assignment of electrons and holes to single-particle states is a good description of the BMEC in multivalley semiconductors.

I. INTRODUCTION

Recent experimental studies have revealed the existence of an interesting excited state in semiconductor systems, in which a number of electron-hole pairs (EHP) are bound to a neutral impurity.[1] This finite many-body system is called a bound "exciton" (BE) when one EHP is bound and a bound "multiexciton" complex (BMEC) when more than one EHP are bound to a single neutral impurity. Photoluminescence resulting from the recombination of an EHP in BMEC typically yields a series of sharp lines lying at the long-wavelength side of the associated BE luminescence line. These spectra were first reported by Kaminskii *et al.*[2] and later by several authors.[3] Some theoretical speculations have been put forward to explain these experimental spectra.[4,5] The shell model (SM) proposed by Kirczenow[5] has successfully interpreted many features of the spectroscopy associated with BMEC in Si.

In a previous paper,[6] we have reported a theoretical calculation for the excitation spectra of bound excitons associated with donors in Si. Our results for the energy separations between the low-lying one-electron excited states and the ground state are in good agreement with the experimental data interpreted using the SM, hence lend support to the assignment of single particles into the shell-like structure.

In this paper, we present theoretical calculations for the excitation spectra of BMEC associated with donors in Si and Ge. We find that the excitation energy for one Γ_1 symmetry electron being excited into a state of Γ_3 or Γ_5 symmetry[7] in BMEC is approximately independent of the number of EHP. This condition holds for most donors in Si and Ge. This independence of the number of EHP on the energy separations between the low-lying excited states and the ground state for BMEC in Si was pointed out by Elliott and McGill,[8] based on a systematic study of the experimental data. Our theoretical results for these excitation energies of BMEC associated with donors in Si are in good agreement with the experimental data.[8-10] This indicates that the assignment of electrons to one-electron donor states is a good description of the BMEC. For donors in Ge, only optical transitions from the ground state of the $m=2$ BMEC (two EHP bound to a neutral donor) to the excited states of the bound exciton are available.[11] Hence, our theoretical calculation for the excited states of BMEC associated with donors in Ge cannot be compared with the experimental data but may serve as a guidance for later experimental work. A preliminary report of this work was presented in Ref. 12.

In Sec. II, we present a general theory for BMEC in semiconductors. In Sec. III, we discuss our calculation method for BMEC associated with donors in Si and Ge. In Sec. IV, we discuss our theoretical results and compare them with the available experimental data. Finally, a summary is presented in Sec. V.

II. GENERAL THEORY

In this section, we discuss the general theory for BMEC in semiconductors. For definiteness, we will treat the BMEC associated with donors. This discussion may be applied to BMEC associated with acceptors as well. BMEC's associated with donors are denoted by D^0X_m (where m is the number of EHP), whose effective-mass Hamiltonian can be written as[13]

$$H_{D^0X_m}=\sum_{i=1}^{m+1}h_e(\vec{r}_i)+\sum_{j=1}^{m}h_h(\vec{s}_j)+\sum_{i<i'}^{m+1}v_{ee}(\vec{r}_i-\vec{r}_{i'})+\sum_{j<j'}^{m}v_{hh}(\vec{s}_j-\vec{s}_{j'})+\sum_{i=1}^{m+1}\sum_{j=1}^{m}v_{eh}(\vec{r}_i-\vec{s}_j)\;. \tag{1}$$

h_e and h_h represent the single-particle Hamiltonian for an electron and hole, respectively, interacting with the donor; v_{ee}, v_{hh}, and v_{eh} represent the electron-electron, hole-hole, and electron-hole mutual interactions, respectively. We have used the indices i (or i') to label the $(m+1)$ electrons with spatial coordinates $\vec{r}_i$ and j (or j') to label the m holes with spatial coordinates $\vec{s}_j$. This Hamiltonian is invariant under the point group T_d. Therefore, the eigenfunctions of $H_{D^0X_m}$ should transform according to the irreducible representations (labeled by Γ) of T_d, i.e.,

$$H_{D^0X_m}\Psi^{\Gamma\mu}(\{\vec{r}_i\}\chi_i,\{\vec{s}_j\}\chi_j)=E^{\Gamma}\Psi^{\Gamma\mu}(\{\vec{r}_i\}\chi_i,\{\vec{s}_j\}\chi_j)\;, \tag{2}$$

where $\Psi^{\Gamma\mu}$ is the eigenfunction of $H_{D^0X_m}$ which transforms like a basis vector (labeled by μ) of the representation Γ^m. E^{Γ} is the associated eigenvalue. χ_i and χ_j are the spinors associated with the ith electron and the jth hole, respectively. To solve Eq. (2), one can expand $\Psi^{\Gamma\mu}$ on a complete set of basis wave functions with symmetry $(\Gamma\mu)$.

$$\Psi^{\Gamma\mu}(\{\vec{r}_i\}\chi_i,\{\vec{s}_j\}\chi_j)=\sum_{\alpha n}D^{\Gamma\mu}_{\alpha n}\beta^{\Gamma\mu}_{\alpha n}(\{\vec{r}_i\}\chi_i,\{\vec{s}_j\}\chi_j)\;. \tag{3}$$

It is customary to choose $\beta^{\Gamma\mu}_{\alpha n}$ as the linear combination of the Hartree-Fock (HF) solutions associated with the configuration αn, where α labels the crystalline symmetries for the associated single-particle states and n labels their remaining quantum numbers. Each single-particle state in a given HF solution is chosen to transform according to an irreducible representation of T_d. We will use Γ_i and Γ_j to denote the crystalline symmetries of the single-particle envelope functions associated with the ith electron and the jth hole in the HF solutions, respectively. For each electron of symmetry Γ_i and hole of symmetry Γ_j, there can be infinite number of states labeled by n_i and n_j, respectively, corresponding to infinite number of HF excited states. In analogy to atomic physics, n_i (or n_j) denotes the orbital symmetry ($s,p,d,\ldots$) and the principal quantum number (1,2,3,...) of the single-particle envelope functions. However, since the single-particle effective-mass Hamiltonians h_e and h_h are not rotationally invariant, the states of different orbital symmetries are usually mixed together.[14] We can denote each configuration αn as the product of a "crystalline configuration" labeled by $\alpha\equiv\{\Gamma_i,k=1,\ldots,m+1;\;\Gamma_j,\,j=1,\ldots,m\}$ and an "atomic configuration" labeled by $n\equiv\{n_i,\,i=1,\ldots,m+1;\;n_j,j=1,\ldots,m\}$. Then, we can write

$$\beta^{\Gamma\mu}_{\alpha n}(\{r_i\}\chi_i,\{s_j\}\chi_j)=\sum_{\substack{\{\mu_i\chi_i,i=1,\ldots,m+1\}\\ \{\mu_j,j=1,\ldots,m\}}}C(\Gamma\mu\,|\,\{\Gamma_i\mu_i\chi_i,\Gamma_j\mu_j\})A\left[\prod_{i=1}^{m+1}\phi_{n_i}^{\Gamma_i\mu_i}(\vec{r}_i)\chi_i\right]A\left[\prod_{j=1}^{m}\phi_{n_j}^{\Gamma_j\mu_j}(\vec{s}_j)\right]\;, \tag{4}$$

where $\phi_{n_i}^{\Gamma_i\mu_i}(\vec{r}_i)$ and $\phi_{n_j}^{\Gamma_j\mu_j}(\vec{s}_j)$ are the Hartree-Fock single-particle solutions with symmetry $(\Gamma_i\mu_i)$ and $(\Gamma_j\mu_j)$ for the electron and hole, respectively; n_i and n_j label the remaining quantum numbers. $C(\Gamma\mu\,|\,\{\Gamma_i\mu_i\chi_i,\Gamma_j\mu_j\})$ are the coupling coefficients (including spinors) which can be determined by the group theory. The symbol A is the antisymmetrization operator producing a Slater determinant. The hole spinors χ_j have been absorbed into the double-group representations Γ_j. We have treated the electrons and holes as nonidentical particles, since the electron-hole exchange is usually negligible. Substituting Eq. (3) into Eq. (2), we readily obtain

$$\sum_{\alpha'n'}\langle\beta^{\Gamma\mu}_{\alpha n}\,|\,H_{D^0X_m}\,|\,\beta^{\Gamma\mu}_{\alpha'n'}\rangle D^{\Gamma\mu}_{\alpha'n'}=E^{\Gamma}D^{\Gamma\mu}_{\alpha n}\;. \tag{5}$$

In Eq. (5), the matrix $\langle\beta^{\Gamma\mu}_{\alpha}\,|\,H_{D^0X_m}\,|\,\beta^{\Gamma\mu}_{\alpha'n'}\rangle$ is usually referred to as the "configuration interaction" (CI) matrix. The standard procedure of solving

Eq. (2) is first to solve the Hartree-Fock equations for $\phi_{n_i}^{\Gamma_i \mu_i}$ and $\phi_{n_j}^{\Gamma_j \mu_j}$, and then diagonalize the CI matrix to find $D_\alpha^{\Gamma\mu}$ and the eigenvalues E^Γ. In practice, the CI calculation is unmanageable when the number of particles becomes large. Equation (5) will be greatly simplified if the coupling of states belonging to different crystalline configurations (labeled by α) can be neglected, i.e.,

$$\langle \beta_{\alpha n}^{\Gamma\mu} | H_{D^0 X_m} | \beta_{\alpha' n'}^{\Gamma\mu} \rangle = \delta_{\alpha\alpha'} \langle \beta_{\alpha n}^{\Gamma\mu} | H_{D^0 X_m} | \beta_{\alpha' n'}^{\Gamma\mu} \rangle \ . \quad (6)$$

We assume Eq. (6) is valid provided

$$| \langle \beta_{\alpha n}^{\Gamma\mu} | H_{D^0 X_m} | \beta_{\alpha' n'}^{\Gamma\mu} \rangle | << | E_{\alpha n}^{\Gamma} - E_{\alpha n'}^{\Gamma} | \quad \text{for } \alpha \neq \alpha' \ , \quad (7)$$

where $E_{\alpha n}^{\Gamma}$ and $E_{\alpha n'}^{\Gamma}$ are the energy expectation values of $H_{D^0 X_m}$ in the states of interest. In this paper, we are interested in the ground state and the low-lying excited states in which one Γ_1-symmetry electron is excited into a state of Γ_3 or Γ_5 symmetry, i.e., the states containing mainly the lowest-lying HF states $\beta_{\alpha 0}^{\Gamma\mu}$ of low-lying crystalline configurations (α). It is conceivable that

$$| \langle \beta_{\alpha n}^{\Gamma\mu} | H_{D^0 X_m} | \beta_{\alpha' n'}^{\Gamma\mu} \rangle | << | \langle \beta_{\alpha 0}^{\Gamma\mu} | H_{D^0 X_m} | \beta_{\alpha' 0}^{\Gamma\mu} \rangle | \quad \text{for } n > 0 \text{ or } n' > 0 \ , \quad (8)$$

since these coupling are determined by the interparticle interactions, which are larger for states of the lowest atomic configuration and more localized in space. The criterion for Eq. (6) to be valid reduces from Eq. (7) to

$$| \langle \beta_{\alpha 0}^{\Gamma\mu} | H_{D^0 X_m} | \beta_{\alpha' 0}^{\Gamma\mu} \rangle | << | E_{\alpha 0}^{\Gamma} - E_{\alpha' 0}^{\Gamma} | \ . \quad (9)$$

The matrix element $\langle \beta_{\alpha 0}^{\Gamma\mu} | H_{D^0 X_m} | \beta_{\alpha' 0}^{\Gamma\mu} \rangle$ ($\alpha \neq \alpha$) includes the matrix elements for the electron-electron interactions, electron-hole interactions and hole-hole interactions. As discussed in our previous paper,[6] both the electron-electron and electron-hole couplings between the lowest-lying states associated with different crystalline configurations are of the same order of magnitude as the "fine-structure" splittings (splittings between states associated with the same configuration caused by the interparticle interactions) which are about 0.5 meV for Si and 0.1 meV for Ge. It will be shown in Sec. III that this argument also holds for the hole-hole coupling. The fine-structure splittings due to the hole-hole interactions are similar to the splittings for the low-lying states of an exciton bound to an acceptor through the "*j-j* coupling" scheme.[15] But the $D^0 X_m$ system, all the holes are loosely bound, and these fine-structure splittings will be much smaller than that for the acceptor-bound exciton.

When these coupling terms are neglected, Eq. (5) can be rewritten for each crystalline configuration α and overall symmetry $\Gamma\mu$ as

$$\sum_{n'} \langle \beta_{\alpha n}^{\Gamma\mu} | H_{D^0 X_m} | \beta_{\alpha n'}^{\Gamma\mu} \rangle D_{\alpha n'}^{\Gamma\mu} = E_{\alpha}^{\Gamma} D_{\alpha n}^{\Gamma\mu} \ . \quad (10)$$

From Eq. (10), it is observed that the energy spectra of the BMEC (labeled by E_α^Γ) can be described approximately by assigning electrons and holes to various crystalline configurations (labeled by α). This approximation has been used in the shell model[5] to interpret the experimental data for the BMEC observed in Si and Ge. In the shell model,[5] it is further assumed that the ordering of the energy levels associated with various crystalline configurations is determined by single-particle states contained in these crystalline configurations. It is not clear whether or not this assumption could hold unless Eq. (10) for various crystalline configurations is solved. It is conceivable that the correlation energy obtained by solving Eq. (10) will be approximately independent of the labeling α for the states close to each other in energy. Therefore the ordering of the states containing mainly lowest-lying HF states (labeled by $n = 0$) is approximately determined by the energy expectation values for the associated Hartree-Fock solutions, i.e., $\langle \beta_{\alpha 0}^{\Gamma\mu} | H_{D^0 X_m} | \beta_{\alpha 0}^{\Gamma\mu} \rangle$. For our purposes here (finding the energy differences between these states and the ground state), we only solve the Hartree-Fock equations for the energies $\langle \beta_{\alpha 0}^{\Gamma\mu} | H_{D^0 X_m} | \beta_{\alpha 0}^{\Gamma\mu} \rangle$. For BMEC whose number of EHP (m) is less than five, all the electrons and holes can be assigned to states of different spin or crystalline symmetries. For the states of interest, all the four holes should occupy the Γ_8 representation. In this case, if we neglect the exchange interaction between electrons of the same spin but different crystalline symmetries and that between holes (which again yields the fine-structure splittings of the same size as that produced by the other coupling schemes), then the problem of solving the Hartree-Fock equations reduces to that of solving the Hartree self-consistent equations. In Sec. III, we describe the calculation method which we used to solve the self-consistent Hartree equations for BMEC associated with donors in Si and Ge.

III. CALCULATION METHOD

To obtain the self-consistent Hartree-Fock solutions, we expand each of the single-particle wave functions $[\phi^{\Gamma_i\mu_i}(\vec{r}_i)$ or $\phi^{\Gamma_8\mu_j}(\vec{s}_j)]$ on a set of basis functions, denoted by $\beta_{b_i}^{\mu_i}(\vec{r}_i)$ and $\beta_{b_j}^{\mu_j}(\vec{s}_j)$ for the electron and hole, respectively, viz.,

$$\phi_0^{\Gamma_i\mu_i}(\vec{r}_i)=\sum_{b_i} C_{\Gamma_i}(b_i)\beta_{b_i}^{\mu_i}(\vec{r}_i) ,$$

and

$$\phi_0^{\Gamma_8\mu_j}(\vec{s}_j)=\sum_{b_j} C_{\Gamma_8}(b_j)\beta_{b_j}^{\mu_j}(\vec{s}_j) . \tag{11}$$

For electrons, the basis functions are selected to be linear combinations of seven ellipsoidal Slater-type orbitals (ESTO) of the form

$$\beta_{b_n}^{\mu}(\vec{r})=\sum_{j}^{N}\alpha_j(\mu)e^{i\vec{k}_j\cdot\vec{r}}e^{-b_n(x^2+y^2+z^2/\zeta^2)^{1/2}} , \tag{12}$$

where $\alpha_j(\nu)$ are proper coefficients which are chosen to make this basis function transform as a basis vector (labeled by μ) associated with an irreducible representation of the group T_d.[7] The $\vec{k}_j$ denotes the positions of the N equivalent conduction-band minima. ζ is the eccentricity factor determined by minimizing the energy expectation value of the donor Hamiltonian on $\beta_b^{\mu}(\vec{r})$, in which the exponent b is also allowed to vary. We find that the value of ζ are 0.57 and 0.355 for Si and Ge, respectively, and they are approximately the same for Γ_1, Γ_3, and Γ_5 states. The exponents are chosen to be

$$b_n=b_0/Z_n,\quad n=1,\ldots,7$$

with

$$\begin{gathered} b_0=2\ \text{bohr}^{-1}\ \text{for Si, } 4\ \text{bohr}^{-1}\ \text{for Ge,} \\ Z_n=(1,2,4,8,16,\tfrac{1}{2},\tfrac{1}{4})\ \text{for Si and Ge .} \end{gathered} \tag{13}$$

For the holes, seven s-like and seven d-like Slater-type orbitals (STO) are used to account for the warping of the conduction band. The products of these STO and the $j=\frac{3}{2}$ spinors, which transform as basis vectors associated with the Γ_8 representation of T_d, are constructed to form the basis-hole wave functions,[16] viz.,

$$\beta_{b_n}^{\mu}=\begin{cases} e^{-b_n r}\,|\,l=0,j=\frac{3}{2};F=\frac{3}{2},F_z=\mu\rangle & \text{for } l=0\ , \\ re^{-b_n r}\,|\,l=2,j=\frac{3}{2};F=\frac{3}{2},F_z=\mu\rangle & \text{for } l=2\ , \end{cases} \tag{14}$$

where $\vec{F}\equiv\vec{l}+\vec{j}$; $b_n=C_0/Z_n$, $n=1,\ldots,7$ with $C_0=0.5$ bohr^{-1} and Z_n's given by Eq. (13). States with $F\neq\frac{3}{2}$ are not included, because they are not directly coupled to the s-like orbitals.[16] The single-particle Hamiltonian seen by a given electron (say, $i=1$) due to the average charge distribution of other particles is

$$H_e(\vec{r}_1)\equiv h_e(\vec{r}_1)+\sum_{i=2}^{m+1}\int|\phi_0^{\Gamma_i\mu_i}(\vec{r}_i)|^2 v_{ee}(1,i)d^3r_i+\sum_{j=1}^{m}\int|\phi_0^{\Gamma_8\mu_j}(\vec{s}_j)|^2 v_{eh}(1,j)d^3s_j , \tag{15}$$

where h_e is the donor Hamiltonian and v is the mutual Coulomb interaction. Similarly, the Hamiltonian seen by a given hole (say, $j=1$) is

$$H_h(\vec{s}_1)\equiv h_h(\vec{s}_1)+\sum_{i=1}^{m+1}\int|\phi_0^{\Gamma_i\mu_i}(\vec{r}_i)|^2 v_{eh}(1,i)d^3r_i+\sum_{j=2}^{m}\int|\phi_0^{\Gamma_8\mu_j}(\vec{s}_j)|^2 v_{hh}(1,j)d^3s_j . \tag{16}$$

To obtain the Hartree-Fock solution for each configuration, we first set up the Hamiltonian matrix for one particle, H_e or H_h, with the remaining single-particle wave functions fixed by the initial guess. This matrix is then diagonalized to obtain an improved solution for the coefficients $C_{\Gamma_i}(b_i)$ and $C_{\Gamma_8}(b_j)$. This process is repeated for each particle and the whole procedure is then iterated until a self-consistent solution is obtained. The matrix elements for H_e are the sum of the matrix elements for a donor Hamiltonian h_e, electron-electron interaction, and electron-hole interaction. The matrix elements for H_h are the sum of the matrix elements for a hole Hamiltonian h_h, electron-hole interaction, and hole-hole interaction. All these matrix elements except the hole-hole interaction term have been discussed in our previous papers,[6,17] and are briefly reviewed here.

For the donor Hamiltonian, h_e, we include the intravalley and intervalley terms for both the kinetic and potential energies as well as the effect of the short-range core potential. The short-range core potential is approximated by a contact potential[14] [i.e., $J_\lambda \delta(\vec{r})$] with the strength parameters J_λ (where $\lambda = 1,2,3$ for intravalley, intertransverse, and interlogitudinal scattering terms, respectively) determined semiempirically. Since we only include the s-like ESTOs, the energy eigenvalues obtained by diagonalizing h_e on this basis set are slightly higher (about 1%) than the exact eigenvalues of h_e. For our purpose here, we adjust the parameters J_λ to fit the eigenvalues of h_e (in the present basis set) to the experimental results. The values of the adjusted parameters J_λ were reported in Ref. 17. For the hole Hamiltonian h_h, we neglect the mixing with the split-off band. This is a valid approximation, since the orbital energy of the hole (i.e., the lowest eigenvalue of H_h) is small compared to the separation between the top of the valence band and the split-off band. For the electron-electron interaction, the matrix elements can be written as[17]

$$\langle \mu_1\mu_2 \,|\, v_{ee}(1,2) \,|\, \mu_1'\mu_2' \rangle = U_0 \delta_{\mu_1\mu_1'} \delta_{\mu_2\mu_2'} + \sum_{\lambda=1}^{4} U_\lambda G_\lambda(\mu_1\mu_2, \mu_1'\mu_2') \,, \tag{17}$$

where $\mu_1(\mu_1')$ and $\mu_2(\mu_2')$ denote the single-particle symmetries of the two electrons (labeled by 1 and 2), respectively. U_0 represents the intravalley mutual interaction between two electrons with major axes of their ellipsoidal charge distributions along the same axis. $U_\lambda (\lambda = 1,2,3,4)$ are terms which lead to splittings within a given crystalline configuration and couple states of different configurations but the same overall symmetry. G_λ $(\lambda = 1,\ldots,4)$ are the electron-electron coupling matrices defined in Ref. 17. In the present calculation, the terms U_λ, $\lambda = 1,2,3,4$ are neglected. For the electron-hole interaction, the matrix elements can be written as

$$\langle \mu_e\mu_h \,|\, v_{eh} \,|\, \mu_e'\mu_h' \rangle = (V_{ss} + V_{dd}) \delta_{\mu_e\mu_e'} \delta_{\mu_h\mu_h'} + V_{sd}\, j(\mu_e\mu_e', \mu_h\mu_h') \,, \tag{18}$$

where $\mu_e(\mu_e')$ and $\mu_h(\mu_h')$ denote the single-particle symmetries of the electron and hole, respectively. V_{ss}, V_{dd}, and V_{sd} represent the mutual interactions between the ellipsoidal charge distribution of the electron and the charge distribution of the hole. V_{ss} and V_{dd} represent the coupling between two s-like and two d-like hole states, respectively; V_{sd} represents the coupling between one s-like and one d-like hole state. $j(\mu_e\mu_e', \mu_h\mu_h')$ is the electron-hole coupling matrix defined in Ref. 6. In the present calculation, the electron-hole coupling term (involving V_{sd}) is neglected.

The hole-hole interaction has not been treated previously and is discussed here in more detail. In Appendix A, we derive the hole-hole interaction matrix elements between the two-hole states denoted by $|\mu_1\mu_2\rangle$ and $|\mu_1'\mu_2'\rangle$, with $\mu_1(\mu_1')$ and $\mu_2(\mu_2')$ labeling the basis vectors of the Γ_8 representation for the two holes. It is shown in this appendix that the off-diagonal terms (with $\mu_1' \neq \mu_1$, or $\mu_2 \neq \mu_2'$) are 2 orders of magnitude smaller than the diagonal term (with $\mu_1' = \mu_1$ and $\mu_2 = \mu_2'$). Therefore, the mixing of hole states through the off-diagonal term (hole-hole coupling) can be neglected. Neglecting these off-diagonal terms, we can write the matrix elements for the hole-hole interaction as (see Appendix A for derivation)

$$\langle \mu_1\mu_2 \,|\, v_{hh} \,|\, \mu_1\mu_2 \rangle = \begin{cases} 2\int f_{b_1}(r_1) f_{b_1'}(r_1) \dfrac{1}{r_>} f_{b_2}(r_2) f_{b_2'}(r_2) r_1^2 r_2^2 \, dr_1 \, dr_2 & \text{for } l_1 = l_1' \text{ and } l_2 = l_2' \\ \frac{2}{25} \int f_{b_1}(r_1) f_{b_1'}(r_1) \dfrac{r_<^2}{r_>^3} f_{b_2}(r_2) f_{b_2'}(r_2) r_1^2 r_2^2 \, dr_1 \, dr_2 & \text{for } l_1 \neq l_1' \text{ and } l_2 \neq l_2' \\ 0 \text{ otherwise} \,, \end{cases} \tag{19}$$

where f_{b_1} (f_{b_1}') and f_{b_2} (f_{b_2}') are the radial parts of the basis functions ($\beta_{b_j}^{\mu_j}$'s) given by Eq. (14); l_1 (l_1') and l_2 (l_2') denote the angular momenta associated with the states $\beta_{b_1}^{\mu_1}$ $(\beta_{b_1'}^{\mu_1})$ and $\beta_{b_2}^{\mu_2}$ $(\beta_{b_2'}^{\mu_2})$, respectively. We have introduced the normalized units in which distance and energy are measured in units of $\epsilon_0\hbar^2/m_t e^2$ and $e^4 m_t/2\epsilon_0^2\hbar^2$, respectively. ϵ_0 and m_t are the static dielectric constant and the transverse effective mass, respectively.

In Sec. IV, we discuss our theoretical results for the energies of the lowest-lying HF states associated with various configurations for several donors in Si and Ge.

IV. RESULTS AND DISCUSSION

A. Si

The total energies of the low-lying states for D^0X_m in Si:P, Si:As, and Si:Sb are listed in Table I. For complexes with $m \geq 2$, some states with configurations of the type $\{\Gamma_1,\Gamma_3,\Gamma_5;2\Gamma_8\}$, in which three electrons are assigned to different symmetry states, are not listed. These states can be inserted between states with configurations of the types

$$\{\Gamma_1,2\Gamma_3;2\Gamma_8\} \text{ and } \{\Gamma_1,2\Gamma_5;2\Gamma_8\} \,.$$

It should be noted that the separations between these states are of the same order of magnitude as the splitting caused by interparticle interactions; therefore, all these states are strongly mixed together and the assignment of electrons and holes into single-particle states is no longer a good description for these states in BMEC. However, a shell model[5] in which states associated with the Γ_3 and Γ_5 single-particle symmetries are considered as belonging to a single-crystalline configuration is still a good description of the BMEC.

In the photoluminescence spectrum from the BMEC two series of lines (α_m and β_m) are observed.[9] In the shell model,[5] the α-series and β-series luminescence are interpreted as the ground-to-excited-state and ground-to-ground-state transitions, respectively,[5,9] i.e.,

$$\alpha_m \text{ transition: } \{2\Gamma_1,(m-1)\Gamma_{3,5};m\Gamma_8\} \rightarrow \{\Gamma_1,(m-1)\Gamma_{3,5};(m-1)\Gamma_8\} \,,$$

$$\beta_{m-1} \text{ transition: } \{2\Gamma_1,(m-1)\Gamma_{3,5};m\Gamma_8\} \rightarrow \{2\Gamma_1,(m-2)\Gamma_{3,5};(m-1)\Gamma_8\} \,.$$

The excitation energies of these excited states can therefore be deduced from the separations between the positions of the α_m and β_{m-1} lines. A systematic study of these energy separations for various donors in Si has been given by Elliott *et al.*[8] In Fig. 1 we plot our theoretical predictions of these separations obtained in the present approximation and the experimental data.[8-10] The results presented here are slightly different (within 5%) from those presented previously.[12] In Ref. 12 we did not adjust the parameters J_λ to fit the eigenvalues of h_e (in the present basis set) to the experimental results. We have relabeled the β_2 and β_3 lines in Ref. 8 as β_3 and β_4 and assumed that the

TABLE I. Total energies of the low-lying states for D^0X_m in Si:P, Si:As, and Si:Sb obtained in Hartree-Fock approximation. All energies are in meV.

Complex	Configuration	Si:P	Si:As	Si:Sb
D^0X	$\{2\Gamma_1;\Gamma_8\}$	-57.36	-66.65	-54.25
	$\{\Gamma_1,\Gamma_5;\Gamma_8\}$	-53.22	-60.82	-50.54
	$\{\Gamma_1,\Gamma_3;\Gamma_8\}$	-53.00	-60.69	-50.11
D^0X_2	$\{2\Gamma_1,\Gamma_5;2\Gamma_8\}$	-64.29	-73.70	-61.11
	$\{2\Gamma_1,\Gamma_3;2\Gamma_8\}$	-64.25	-73.69	-61.02
	$\{\Gamma_1,2\Gamma_5;2\Gamma_8\}$	-60.04	-67.44	-57.36
	$\{\Gamma_1,2\Gamma_3;2\Gamma_8\}$	-59.73	-67.23	-56.76
D^0X_3	$\{2\Gamma_1,2\Gamma_5;3\Gamma_8\}$	-70.75	-80.10	-67.55
	$\{2\Gamma_1,2\Gamma_3;3\Gamma_8\}$	-70.65	-80.04	-67.35
	$\{\Gamma_1,3\Gamma_5;3\Gamma_8\}$	-66.59	-73.80	-63.88
	$\{\Gamma_1,3\Gamma_3;3\Gamma_8\}$	-66.21	-73.52	-63.14
D^0X_4	$\{2\Gamma_1,3\Gamma_5;4\Gamma_8\}$	-76.96	-86.26	-73.70
	$\{2\Gamma_1,3\Gamma_3;4\Gamma_8\}$	-76.84	-86.16	-73.44
	$\{\Gamma_1,4\Gamma_5;4\Gamma_8\}$	-72.76	-79.79	-70.01
	$\{\Gamma_1,4\Gamma_3;4\Gamma_8\}$	-72.32	-79.43	-69.17

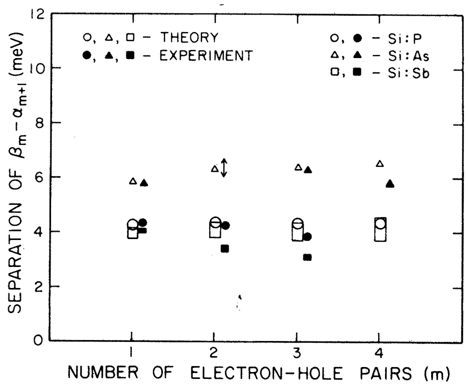

FIG. 1. Theoretical and experimental energy separations between the α_{m+1} and β_m lines plotted against the number of electron-hole pairs bound to a donor. The experimental data are taken from Ref. 9 for Si:P and Ref. 8 for Si:Sb and Si:As (see text for reinterpretation). The arrow indicates the range of the values of the $\beta_2-\alpha_3$ separation for Si:As.

β_2 line is hidden under the TO phonon-assisted α_1 line. Hence, we cannot precisely locate the β_2 line as indicated by a range in the figure. This relabeling of lines in Si:As results in the $\alpha_{m+1}-\beta_m$ separations being almost independent of the index m as in Si:P and Si:Sb. Good agreement between theory and experiment is found for all complexes.

We can make systematic studies of the correlation energies of D^0X_m in Si. We define the dissociation energies δE_m by

$$\delta E_m \equiv (E_{m-1}+E_x)-E_m \;, \tag{20}$$

where E_m and E_x are the ground-state energies for D^0X_m and a free exciton, respectively. Expanding the free-exciton wave function on our basis set, we obtain a value -14.2 meV for E_x, which is slightly higher than the experimental value -14.7 meV (Ref. 18) and the theoretical value obtained with a larger basis set.[19] Taking the difference between the experimental values for the dissociation energies, δE_m (SM) (Refs. 8–10) (from the luminescence data interpreted using the shell model[5]) and the HF values δE_m (HF), we can obtain the correlation energies δE_m^{corr} for binding one EHP to the $(m-1)$ complex. In Fig. 2 the correlation energies per EHP so obtained (δE_m^{corr}) are plotted against the number of EHP in D^0X_m for various donors in Si. As shown in this figure, δE_m^{corr} increases monotonically, reaching a limiting value $\delta E_{\text{EHD}}^{\text{corr}}$, the correlation energy per EHP in the electron-hole droplet (EHD). The value 17 meV for $\delta E_{\text{EHD}}^{\text{corr}}$ is obtained by taking the difference between the experimental binding energy[20] and the binding energy calculated in the Hartree-Fock approximation.[21] For Si:As, we have relabeled the β_2, β_3, and β_4 lines as before. The values of δE_3^{corr} are indicated by a range in the figure, because we cannot precisely locate the β_2 line.

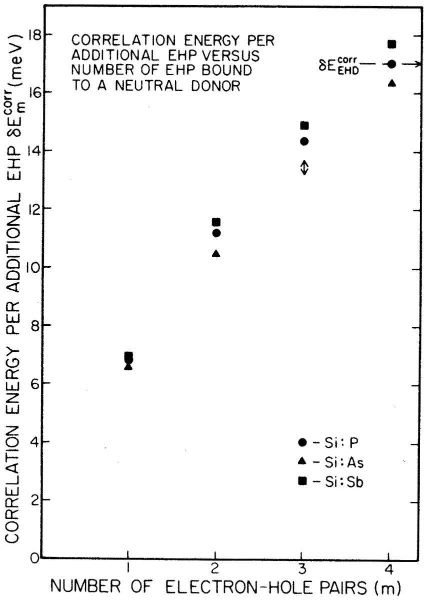

FIG. 2. Correlation energies per electron-hole pair (EHP) plotted against the number of EHP bound to a neutral donor for Si:P, Si:As, and Si:Sb. The arrow indicates the range of the values of δE_3^{corr} for Si:As. The experimental data used for obtaining these correlation energies are taken from Ref. 9 for Si:P and Ref. 8 for Si:Sb and Si:As (see text for reinterpretation).

B. Ge

In Table II, we list the total energies of the ground states $[\{2\Gamma_1,(m-1)\Gamma_5;m\Gamma_8\}]$ and the one-electron excited states $(\{\Gamma_1,m\Gamma_5;m\Gamma_8\})$ for complexes D^0X_m obtained in the present approximation for Ge:P, Ge:As, and Ge:Sb. For illustrative purposes, we plot in Fig. 3 the energy separations between these one-electron excited states and the ground states ($\beta_m-\alpha_{m+1}$ separations) for complexes associated with various donors. As shown in this figure, the energy separations for all donors are approximately independent of the index m (the

TABLE II. Total energies of the low-lying states for D^0X_m in Ge:P, Ge:As, and Ge:Sb, obtained in Hartree-Fock approximation. All energies are in meV.

Complex	Configuration	Ge:P	Ge:As	Ge:Sb
D^0X	$\{2\Gamma_1;\Gamma_8\}$	-16.12	-17.73	-13.35
	$\{\Gamma_1,\Gamma_5;\Gamma_8\}$	-15.10	-16.43	-13.20
D^0X_2	$\{2\Gamma_1,\Gamma_5;2\Gamma_8\}$	-18.11	-19.56	-15.09
	$\{\Gamma_1,2\Gamma_5;2\Gamma_8\}$	-17.02	-18.15	-14.98
D^0X_3	$\{2\Gamma_1,2\Gamma_5;3\Gamma_8\}$	-19.81	-21.26	-16.82
	$\{\Gamma_1,3\Gamma_5;3\Gamma_8\}$	-18.71	-19.81	-16.69
D^0X_4	$\{2\Gamma_1,3\Gamma_5;4\Gamma_8\}$	-21.36	-22.81	-18.49
	$\{\Gamma_1,4\Gamma_5;4\Gamma_8\}$	-20.25	-21.34	-18.27

number of EHP in D^0X_m). For Ge:Sb, these separations are of the same order of magnitude as the electron-electron coupling (about 0.1 meV).[6] Hence we expect a substantial mixing between the one-electron excited states and the ground states for $m \geq 2$ complexes. Therefore the shell model is not a good description for BMEC in Ge:Sb. The energy separations for the first one-electron excited states for bound excitons (D^0X) in Ge:P and Ge:As are in good agreement (to within 0.05 meV) with the experimental data [the separations between the α_1 ($1s\Gamma_5$) and γ_1^2 lines] observed by Mayer and Lightowlers.[11] The experimental data for the other $\beta_m - \alpha_{m+1}$ separations are not available for a comparison with our theoretical results. The observation of the luminescence from higher complexes in Ge is difficult because these lines are mixed with the luminescence associated with electron-hole droplets and are difficult to resolve.[22]

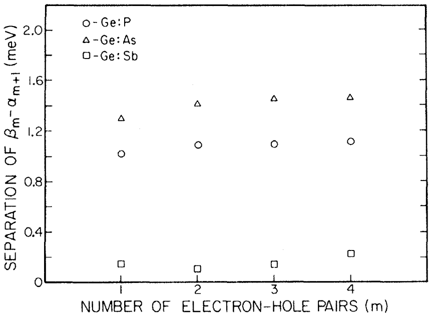

FIG. 3. Energy separations between the one-electron excited states and the ground state for D^0X_m in Ge:P, Ge:As, and Ge:Sb, plotted against the number of EHP.

V. CONCLUSION

We have calculated the electronic excitation spectra of the BE and BMEC's for donors in Si and Ge. Good agreement between our calculation and the experimental data interpreted using the shell model strongly suggests that the BE and BMEC can be understood in terms of a shell-like model. Throughout this calculation we have neglected correlation effects which are essential in obtaining the correct binding energies. These correlation energies are estimated to be approximately 10 meV for each EHP in the D^0X_m in Si. The correlation effect could be included by expanding the total wave function in terms of the HF solutions. However, we expect the splittings evaluated on the "correlated" states to be still of the same order of magnitude as above. Hence, we conclude that the correlation effect, although substantial in magnitude, does not affect the splittings substantially. Our calculation provides a better understanding of the BMEC's in multivalley semiconductors.

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APPENDIX A: MATRIX ELEMENTS FOR HOLE-HOLE INTERACTION

In this appendix, we derive the expression for the hole-hole interaction matrix elements of the type

$$\langle \mu_1\mu_2 | v_{hh} | \mu_1'\mu_2' \rangle \equiv \langle \beta_{b_1}^{\mu_1}\beta_{b_2}^{\mu_2} | v_{hh}(1,2) | \beta_{b_1'}^{\mu_1'}\beta_{b_2'}^{\mu_2'} \rangle , \tag{A1}$$

where β_b^μ's are given by Eq. (14) with b and μ denoting the exponent and symmetry (index for the Γ_8 representation), respectively. More specifically, we can write

$$\beta_b^\mu(\vec{r}) = f_b(r) \sum_m C_l(\mu,m) Y_{lm}(\Omega) \chi_{\mu-m} , \tag{A2}$$

where

$$f_b(r) = \begin{cases} e^{-br} & \text{for } l=0 \\ re^{-br} & \text{for } l=2 . \end{cases} \tag{A3}$$

The coefficients $C_{l=0}(\mu,m=0)=1$ for all μ. The coefficients $\sqrt{5}C_{l=2}(\mu,m)$ are listed in Table III. Substituting Eq. (A2) into Eq. (A1) and using the relation

$$v_{hh}(1,2) = \frac{2}{|\vec{r}_1-\vec{r}_2|} = \sum_{LM} \frac{8\pi}{(2L+1)} \frac{r_<^L}{r_>^{L+1}} Y_{LM}^*(\Omega_1) Y_{LM}(\Omega_2) , \tag{A4}$$

We obtain

$$\begin{aligned} \langle \mu_1\mu_2 | v_{hh} | \mu_1'\mu_2' \rangle = 4\pi \sum_{m_1 m_2} & C_{l_1}(\mu_1,m_1) C_{l_1'}(\mu_1',\mu_1'-\mu_1+m_1) C_{l_2}(\mu_2,m_2) C_{l_2'}(\mu_2',\mu_2'-\mu_2+m_2) \\ & \times \sum_{LM} J_L(b_1,b_2,b_1',b_2') \int Y_{l_1 m_1}^*(\Omega_1) Y_{l_1',\mu_1'-\mu_1+m_1}(\Omega_1) Y_{LM}^*(\Omega_1)\, d\Omega_1 \\ & \times \int Y_{l_2 m_2}^*(\Omega_2) Y_{l_2',\mu_2'-\mu_2+m_2}(\Omega_2) Y_{LM}^*(\Omega_2)\, d\Omega_2 , \end{aligned} \tag{A5}$$

where

$$J_L(b_1,b_2,b_1',b_2') \equiv \frac{2}{2L+1} \int f_{b_1}(r_1) f_{b_1'}(r_1) \frac{r_<^L}{r_>^{L+1}} f_{b_2}(r_2) f_{b_2'}(r_2) r_1^2 r_2^2 dr_1 dr_2 . \tag{A6}$$

In Eq. (A5), the integrals over $d\Omega_1$ and $d\Omega_2$ yield coefficients proportional to $\delta_{\mu_1'-\mu_1,M}$ and $\delta_{\mu_2-\mu_2',M}$, respectively. Therefore $\langle \mu_1\mu_2 | v_{hh} | \mu_1'\mu_2' \rangle$ vanishes unless

$$\mu_1'-\mu_1 = \mu_2-\mu_2' . \tag{A7}$$

TABLE III. Expansion coefficients $\sqrt{5}C_l(\mu,m)$ for the $l=2$ hole basis functions on the products of spherical harmonics and $j=\frac{3}{2}$ spinors.

		μ			
$\sqrt{5}C_{l=2}(\mu,m)$		$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
	-2	$\sqrt{2}$	$\sqrt{2}$	0	0
	-1	$-\sqrt{2}$	0	$\sqrt{2}$	0
m	0	1	-1	-1	1
	1	0	$\sqrt{2}$	0	$-\sqrt{2}$
	2	0	0	$\sqrt{2}$	$\sqrt{2}$

We discuss the diagonal terms ($\mu_1=\mu_1'$ and $\mu_2=\mu_2'$) and off-diagonal terms ($\mu_1\neq\mu_1'$ and $\mu_2\neq\mu_2'$) separately

(1) Diagonal term ($\mu_1=\mu_1'$ and $\mu_2=\mu_2'$).

(a) $l_1=l_1'$ and $l_2=l_2'$:

$$\begin{aligned}\langle\mu_1\mu_2\,|\,v_{hh}\,|\,\mu_1\mu_2\rangle&=4\pi\sum_L J_L(b_1,b_2,b_1',b_2')\int\sum_{m_1}|\,C_{l_1}(\mu_1,m_1)Y_{l_1m_1}(\Omega_1)\,|^2\times Y^*_{L0}(\Omega_1)\,d\Omega_1\\&\quad\times\int\sum_{m_2}|\,C_{l_2}(\mu_2,m_2)Y_{l_2m_2}(\Omega_2)\,|^2\,Y_{L0}(\Omega_2)\,d\Omega_2\\&=J_0(b_1,b_2,b_1',b_2')\,,\end{aligned}\tag{A8}$$

where we have used the relation (see Table III)

$$\sum_m|\,C_l(\mu,m)Y_{lm}(\Omega)\,|^2=\frac{1}{(2l+1)}\sum_m|\,Y_{lm}(\Omega)\,|^2=\frac{1}{4\pi}\,.\tag{A9}$$

(b) $l_1\neq l_1'$ and $l_2\neq l_2'$:

$$\begin{aligned}\langle\mu_1\mu_2\,|\,v_{hh}\,|\,\mu_1\mu_2\rangle&=\tfrac{1}{5}\sum_L J_L(b_1,b_2,b_1',b_2')\int Y_{20}(\Omega_1)Y_{L0}(\Omega_1)\,d\Omega_1\int Y_{20}(\Omega_2)Y_{L0}(\Omega_2)\,d\Omega_2\\&=\tfrac{1}{5}J_2(b_1,b_2,b_1',b_2')\,.\end{aligned}\tag{A10}$$

(c) For the other cases ($l_1=l_1'$ and $l_2\neq l_2'$) and ($l_1\neq l_1'$ and $l_2=l_2'$),

$$\langle\mu_1\mu_2\,|\,v_{hh}\,|\,\mu_1\mu_2\rangle=0\,.$$

Substituting Eq. (A3) into Eqs. (A8) and (A10), we obtain

$$\langle\beta^{\mu_1}_{b_1}\beta^{\mu_2}_{b_2}\,|\,v_{hh}\,|\,\beta^{\mu_1}_{b_1'}\beta^{\mu_2}_{b_2'}\rangle=\begin{cases}64(b_1b_1'b_2b_2')^{3/2}\left[\dfrac{1}{\alpha_1^2\alpha_2^2(\alpha_1+\alpha_2)}+\dfrac{1}{\alpha_1\alpha_2(\alpha_1+\alpha_2)^3}\right]\ \text{for } l_1=l_1'=l_2=l_2'=0 & \text{(A11a)}\\[2ex] \dfrac{256(b_1b_1'b_2b_2')^{5/2}}{\alpha_1^4\alpha_2^4x^7}[2(\alpha_1^4+\alpha_2^4)x^2+10\alpha_1\alpha_2x^4-25\alpha_1^3\alpha_2^3]\ \text{for } l_1=l_1'=l_2=l_2'=2 & \text{(A11b)}\\[2ex] \dfrac{128(b_1b_1')^{3/2}(b_2b_2')^{5/2}}{\alpha_2^4\alpha_1^2x^5}(x^4+\alpha_2x^3+\alpha_1\alpha_2^2x+2\alpha_1\alpha_2^3)\ \text{for } l_1=l_1'=0\,,\ \ l_2=l_2'=2 & \text{(A11c)}\\[2ex] \dfrac{256(b_1b_2)^{3/2}(b_1'b_2')^{5/2}}{\alpha_1\alpha_2x^5}\ \ \text{for } l_1=l_2=0,\ l_1'=l_2'=2 & \text{(A11d)}\end{cases}$$

where

$$\alpha_1\equiv b_1+b_1',\ \ \alpha_2\equiv b_2+b_2',\ \ x\equiv\alpha_1+\alpha_2\,.$$

The other cases can be obtained from Eq. (A11) by symmetry.

(2) Off-diagonal terms ($\mu_1\neq\mu_1'$ and $\mu_2\neq\mu_2'$). Let $M\equiv\mu_1'-\mu_1\neq0$, then $\mu_2-\mu_2'=M$ [from Eq. (A7)]. Equation (A5) can be written as

$$\begin{aligned}\langle \mu_1\mu_2 | v_{hh} | \mu_1'\mu_2' \rangle = {} & (2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1)]^{1/2} \\ & \times \sum_{m_1 m_2} C_{l_1}(\mu_1,m_1)C_{l_1'}(\mu_1',M+m_1)C_{l_2}(\mu_2,m_2)C_{l_2'}(\mu_2',m_2-M)(-1)^{m_1}(-1)^{m_2}(-1)^M \\ & \times \sum_{L\geq |M|} (2L+1)J_L(b_1,b_2,b_1',b_2') \\ & \times \begin{bmatrix} l_1 & l_1' & L \\ -m_1 & m_1-M & -M \end{bmatrix} \begin{bmatrix} l_1 & l_1' & L \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_2 & l_2 & L \\ -m_2 & m_2-M & M \end{bmatrix} \begin{bmatrix} l_2 & l_2 & L \\ 0 & 0 & 0 \end{bmatrix} ,\end{aligned} \tag{A12}$$

where we have used the relation

$$\int Y_{lm}Y_{l'm'}Y_{LM}d\Omega = \left[\frac{(2l+1)(2l'+1)(2L+1)}{4\pi} \right]^{1/2} \begin{bmatrix} l & l' & L \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l & l' & L \\ m & m' & M \end{bmatrix} . \tag{A13}$$

The right-hand side of Eq. (A12) vanishes for $l_1 = l_1' = 0$ or $l_2 = l_2' = 0$, since the coefficient

$$\begin{bmatrix} 0 & 0 & L \\ m & m' & M \end{bmatrix} = 0 \text{ unless } L = M = 0 .$$

Therefore, the most important contribution to $\langle \mu_1\mu_2 | v_{hh} | \mu_1'\mu_2' \rangle$ [Eq. (A12)] comes from $l_1 = l_2 = 0$ and $l_1' = l_2' = 2$ (or equivalent cases, e.g., $l_1 = l_2' = 0$ and $l_1' = l_2 = 2$, etc.). For this case, we obtain

$$\langle \mu_1\mu_2 | v_{hh} | \mu_1'\mu_2' \rangle = C_2(\mu_1',M)C_2(\mu_2',-M)J_2(b_1,b_2,b_1',b_2') \leq \tfrac{2}{5}J_2(b_1,b_2,b_1',b_2') . \tag{A14}$$

We can compare the size of the contribution for Eq. (A14) to that from Eq. (A11). If we assume that in the ground state, the hole wave function ϕ_h is described by

$$\phi_h = a_s\phi_s + a_d\phi_d , \tag{A15}$$

with ϕ_s and ϕ_d being the s-like and d-like components of ϕ_h, respectively, then Eq. (A14) will yield a contribution to the total energy of magnitude

$$\tfrac{4}{5}a_s a_d J_2(b_s,b_s,b_d,b_d) , \tag{A16}$$

with b_s and b_d being the exponent associated with the wave functions ϕ_s and ϕ_d, respectively. Taking $b_s = b_d$ and $\frac{4}{5}a_s a_d \simeq 0.3$, we obtain a contribution from (A16) about 2% of that from the hole-hole interaction given by Eq. (A11a).

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