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Theory of D^- states in Ge and Si

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We present a theory for the D^- states in Ge and Si, including the effects of realistic band structures. We obtain binding energies of these states, which are about twice as large as those obtained from using a spherical model. This enhancement in binding is due to the anisotropic, multivalley character of the conduction bands. We predict many bound excited D^- states for Ge:Sb and Si:Li. Our binding energies are in substantial disagreement with those obtained in recent submillimeter photoconductivity measurements. This disagreement is attributed to the presence of compensating (A^-) centers in the sample which interact with the D^- center through Coulomb interaction.

I. INTRODUCTION

It is well known that an electron can bind to a hydrogen atom to form a H^- system.[1] The binding energy for this sytem is about 0.0555 times that for the hydrogen atom.[1] From a simple analogy to H^-, Lampert[2] predicted that an electron in a semiconductor can bind to a neutral donor to form a D^- system with binding energy being 0.0555 times that for the neutral donor. In the past, some experiments[3-6] suggested that a trapping center such as the D^- state exists in Si and Ge. However, it was found that the electron affinities of the center for Ge are about three times as large as those predicted for the D^- state by Lampert.[2] Narita and Taniguchi[6] suggested that this increase in binding is due to the multivalley character of the conduction band of this system. However, more recent experimental studies[7-9] indicated that D^- states in Ge:Sb and Ge:As are bound by about 0.625 and 0.75 meV, respectively. These values are much closer to the binding energy for the D^- predicted by Lampert.[2] By studying the concentration and temperature dependence of the photoconductivity spectrum of Ge:Sb, Taniguchi *et al.*[8] concluded that the higher energy threshold observed previously[3-6] is due to the formation of D^- complexes (one electron bound to two or more neutral donors) and isolated D^- states can only be observed at very low temperature ($\lesssim 0.5$ K) and very low concentrations ($\lesssim 10^{14}$ cm^{-3}). Similar results have also been observed in n-type Si.[6,9,10]

Theoretically, Natori and Kamimua[11] have studied D^- states in multivalley semiconductors. They include the multivalley effect by assigning the two electrons in the D^- valleys along different axes, thus obtaining an enhancement in binding by about 0.26 and 0.27 meV for Ge and Si, respectively. However, they neglected the effects of the central-cell correction and the intervalley exchange interaction, which are important for treating D^- states in the stress-free case. Moreover, they find that their trial wave function yields only half of the total binding energy of the H^- system.

In this paper, we develop a theory for D^- states in two multivalley semiconductors, Si and Ge. The anisotropy and the multivalley character of the conduction-band structures as well as the short-range core potential for the impurity are taken into account properly. We use the standard configuration-interaction (CI) method to compute the energies of the lowest-lying states associated with various "crystalline configurations," in which each electron is assigned to a single-particle state transforming according to a certain irreducible representation of the T_d point group. For the H^- case, our method is able to produce 98% of the total binding energy. For D^- states in Ge and Si, we obtain the binding energies, which are about twice as large as those for the corresponding D^- states obtained by Lampert.[2] These values are about 50% larger than those obtained experimentally by Taniguchi and Narita.[8,10] Our theoretical results for the total energy should be an upper bound to the exact values. We attribute this difference in binding to the existence of compensating (A^-) centers in Ge and Si. One reasonable explanation for the difference between the observed values and the theoretical ones for the binding energy is due to the presence of compensating centers in the samples investigated so far. We find that a concentration as low as 10^{12} cm^{-3} yields substantial reductions in the binding energy of the D^-.

In Sec. II, we present the general theory for D^- systems in multivalley semiconductors. We briefly review the valley-orbit interaction of an electron interacting with the donor, which has been discussed in detail in Ref. 12. Various scattering mechanisms for the mutual interaction between the two electrons in the D^- system are discussed. This discussion of the mutual interaction between electrons can also be applied to the calculation of the electronic spectra of donor bound excitons which we will carry out in a future publication. In Sec. III we discuss the method of calculation and derive the matrix elements for the total Hamiltonian. In Sec. IV we discuss our theoretical results and compare them with the available experimental data. In Sec. V a summary is presented.

II. GENERAL THEORY

A. Basis problems

The D^- system consists of two electrons and a positively charged impurity center. The total Hamiltonian of this two-electron system can be written as

$$H_{D^-}=h_e(1)+h_e(2)+v(1,2)\ , \tag{1}$$

where $h_e(1)$ and $h_e(2)$ are the single-particle Hamiltonians for the two electrons (labeled by 1 and 2) interacting with the donor. $v(1,2)$ represents the mutual interaction whose Fourier transform (in SI units) is

$$\tilde{v}(\vec{q})=\frac{e^2}{\epsilon(\vec{q})q^2}\ , \tag{2}$$

where $\epsilon(\vec{q})$ is the $\vec{q}$-dependent dielectric function.[13] The exact eigenstate of H_{D^-} can be expanded in terms of products of two pseudo-Bloch-functions [denoted $\phi^c_{\vec{k}_1}(\vec{r}_1)$ and $\phi^c_{\vec{k}_2}(\vec{r}_2)$] as

$$\psi(\vec{r}_1,\vec{r}_2)=\sum_{\vec{k}_1\vec{k}_2} D(\vec{k}_1,\vec{k}_2)\phi^c_{\vec{k}_1}(\vec{r}_1)\phi^c_{\vec{k}_2}(\vec{r}_2)\ . \tag{3}$$

The expansion coefficients $D(\vec{k}_1,\vec{k}_2)$ (which are antisymmetric with respect to the interchange of particles 1 and 2) satisfy the Schrödinger equation

$$H_{D^-}D(\vec{k}_1,\vec{k}_2)=ED(\vec{k}_1,\vec{k}_2)\ , \tag{4}$$

where H_{D^-} is the integral operator defined as

$$\begin{aligned} H_{D^-}D(\vec{k}_1,\vec{k}_2)\equiv{}& [E_c(\vec{k}_1)+E_c(\vec{k}_2)]D(\vec{k}_1,\vec{k}_2)+\sum_{\vec{k}'_1}\langle\vec{k}_1\,|\,V_\phi\,|\,\vec{k}'_1\rangle D(\vec{k}'_1,\vec{k}_2)\\ &+\sum_{\vec{k}'_2}\langle\vec{k}_2\,|\,V_\phi\,|\,\vec{k}'_2\rangle D(\vec{k}_1,\vec{k}'_2)+\sum_{\vec{k}'_1\vec{k}'_2}\langle\vec{k}_1\vec{k}_2\,|\,v\,|\,\vec{k}'_1\vec{k}'_2\rangle D(\vec{k}'_1,\vec{k}'_2)\ . \end{aligned} \tag{5}$$

In Eq. (5), $E_c(\vec{k})$ represents the dispersion relation for the conduction bands in the extended-zone scheme, V_ϕ is the impurity pseudopotential,[12] and $|\,\vec{k}\rangle$ represents the pseudo-Bloch-function $\phi^c_{\vec{k}}(\vec{r})$ associated with the conduction band. Comparing Eqs. (1) and (5) one can see that the integral operator defined by

$$h_e\phi(\vec{k})\equiv E_c(\vec{k})\phi(\vec{k})+\sum_{\vec{k}'}\langle\vec{k}\,|\,V_\phi\,|\,\vec{k}'\rangle\phi(\vec{k}') \tag{6}$$

describes the interaction of an electron with the donor, and the kernel $\langle\vec{k}_1\vec{k}_2\,|\,v\,|\,\vec{k}'_1\vec{k}'_2\rangle$ describes the mutual interaction between two electrons. To solve Eq. (5), we expand the total envelope function $D(\vec{k}_1,\vec{k}_2)$ in terms of a set of basis functions. Since the single-particle Hamiltonians $h_e(1)$ and $h_e(2)$ and the mutual interaction $v(1,2)$ are invariant under the operations of the point group T_d, it is convenient to choose basis functions that transform according to the irreducible representations of T_d. We can choose these basis functions as linear combinations of products of single-particle wave functions, while also transform according to the irreducible representations of T_d. To avoid confusion, we will use τ to label the irreducible representation associated with single-particle states and Γ_e label the irreducible representation associated with the two electron product states. If we denote the single-particle states as $|\,m;\tau_1\mu_1\rangle$ and $|\,n;\tau_2\mu_2\rangle$ for particles 1 and 2, respectively (where μ_1 and μ_2 label the partners of the representations τ_1 and τ_2; m and n label the remaining quantum numbers for the two particles), then we can write the product basis states (transforming as a basis vector μ_e of the representation Γ_e) as

$$\begin{aligned} |\,mn;(\tau_1\tau_2)\Gamma_e\mu_e\rangle=\sum_{\mu_1\mu_2} & C_{\tau_1\tau_2}(\mu_1\mu_2,\Gamma_e\mu_e)\\ &\times|\,m;\tau_1\mu_1\rangle\,|\,n;\tau_2\mu_2\rangle\ . \end{aligned} \tag{7}$$

$C_{\tau_1\tau_2}(\mu_1\mu_2;\Gamma_e\mu_e)$ are the coupling coefficients for the group T_d, and can be found in Ref. 14. For Si, τ_1,τ_2 can be any of the representations Γ_1, Γ_3, Γ_5, and Γ_e can be any of the representations Γ_1, Γ_2, Γ_3, Γ_4, or Γ_5.[14] For Ge, τ_1,τ_2 can be either Γ_1, or Γ_5, and Γ_e can be Γ_1, Γ_3, Γ_4, or Γ_5.[14] Since the total Hamiltonian is spin independent, we may choose the basis states to be eigenstates of the total spin operator. This can be accomplished by using symmetric (labeled by $+$) or antisymmetric (labeled by $-$) (if the two electrons are in different orbitals) combinations of the states defined in Eq. (7). Namely,

$$|mn;(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e\rangle=\frac{f_{mn}^{\tau_1\tau_2}}{\sqrt{2}}[\,|mn;(\tau_1\tau_2)\Gamma_e\mu_e\rangle \pm |nm;(\tau_2\tau_1)\Gamma_e\mu_e\rangle]$$

with

$$f_{mn}^{\tau_1\tau_2}=\begin{cases}1/\sqrt{2} & \text{if } m=n \text{ and } \tau_1=\tau_2\\ 1 & \text{otherwise},\end{cases} \tag{9}$$

where we have assumed implicitly that a singlet (triplet) two-electron spinor is multiplied by a symmetric (antisymmetric) space state to make the total wave function antisymmetric under the exchange of the two electrons.

The total envelope function $D(\vec{k}_1,\vec{k}_2)$ can be expanded in terms of the above basis states. Then, the expansion coefficients $C(mn,(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e)$ will be determined by the standard configuration-interaction matrix equation

$$\sum_{\substack{mn\\ \tau_1\tau_2}}\langle m'n';(\tau_1'\tau_2')\Gamma_e^{\pm}\mu_e\,|H_{D^-}|\,mn;(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e\rangle C(mn,(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e)=EC(m'n',(\tau_1'\tau_2')\Gamma_e^{\pm}\mu_e)\,, \tag{10}$$

where the states of different symmetries have been decoupled. The Hamiltonian matrix elements in Eq. (10) involve the matrix elements of the single-particle Hamiltonians [$h_e(1)$ and $h_e(2)$] for the two electron interacting with donor and the matrix elements for the mutual interaction, viz.,

$$\begin{aligned}\langle m'n';(\tau_1'\tau_2')\Gamma_e^{\pm}\mu_e\,|H_{D^-}|\,mn;(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e\rangle=f_{mn}^{\tau_1\tau_2}f_{m'n'}^{\tau_1'\tau_2'}[\,&{}_{\tau_1}\langle m'|h_e(1)|m\rangle_{\tau_1}\delta_{nn'}\delta_{\tau_1\tau_1'}\delta_{\tau_2\tau_2'}\\ &+{}_{\tau_2}\langle n'|h_e(2)|n\rangle_{\tau_2}\delta_{mm'}\delta_{\tau_1\tau_1'}\delta_{\tau_2\tau_2'}\\ &\pm{}_{\tau_1}\langle n'|h_e(1)|m\rangle_{\tau_1}\delta_{m'n}\delta_{\tau_1\tau_2'}\delta_{\tau_2\tau_1'}\\ &\pm{}_{\tau_2}\langle m'|h_e(2)|n\rangle_{\tau_2}\delta_{mn'}\delta_{\tau_1'\tau_2}\delta_{\tau_1\tau_2'}]\\ &+\langle m'n';(\tau_1'\tau_2')\Gamma_e^{\pm}\mu_e\,|v(1,2)|\,mn;(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e\rangle\,,\end{aligned} \tag{11a}$$

where we have used the relations

$$\begin{aligned}\langle m';\tau_1'\mu_1'\,|h_e(1)|\,m;\tau_1\mu_1\rangle&={}_{\tau_1}\langle m'|h_e(1)|m\rangle_{\tau_1}\delta_{\mu_1\mu_1'}\delta_{\tau_1\tau_1'}\,,\\ \langle n';\tau_2'\mu_2'\,|h_e(2)|\,n;\tau_2\mu_2\rangle&={}_{\tau_2}\langle n'|h_e(2)|n\rangle_{\tau_2}\delta_{\mu_2\mu_2'}\delta_{\tau_2\tau_2'}\,,\end{aligned} \tag{11b}$$

and the orthonormalization property of the coupling coefficients $C_{\tau_1\tau_2}(\mu_1\mu_2,\Gamma_e\mu_e)$. We shall classify the states associated with the same single-particle symmetries $(\tau_1\tau_2)$ as belonging to the crystalline configuration labeled by $(\tau_1\tau_2)$. From Eqs. (11), it is noted that the states of different configurations are coupled together through the mutual interaction term only. In the following subsections, we will discuss the matrix elements for the single-particle Hamiltonian h_e and the mutual interaction separately.

B. Interaction of an electron with the donor

The single-particle Hamiltonian h_e for the electron in the D^- system, interacting with the donor is the same as that for a neutral donor system.

The solutions for neutral donors in Si and Ge have been studied by several authors[15–18] and are briefly reviewed here. In indirect materials, the conduction band has several equivalent minima. The number of equivalent minima N is 4 in Ge and 6 in Si. The bound eigenstates of the donor Hamiltonian are constructed from linear combinations of wave functions localized at the N equivalent minima, the expansion coefficients being determined by group theory. The bound states for donors in Ge are then classified as Γ_1 (singlet) states and Γ_5 (triplet) states, and those in Si are classified as Γ_1 (singlet), Γ_3 (doublet), and Γ_5 (triplet) states.[14] If we denote the single-particle basis functions $|m;\tau\mu\rangle$ in $\vec{\mathrm{k}}$ representation as $\beta_m^{\tau\mu}(\vec{\mathrm{k}})$, then $\beta_m^{\tau\mu}(\vec{\mathrm{k}})$ can be written as linear combinations of wave functions localized at the N equivalent minima denoted by $\vec{\mathrm{k}}_i$, $i=1,\ldots,N$, viz.,

$$\beta_m^{\tau\mu}(\vec{\mathrm{k}})=\sum_{i=l}^{N}\alpha_i^{\tau}(\mu)\beta_m^{i}(\vec{\mathrm{k}}-\vec{\mathrm{k}}_i)\ , \tag{12}$$

where the wave functions $\beta_m^{i}(\vec{\mathrm{k}}-\vec{\mathrm{k}}_i)$, $i=1,\ldots,N$, are transformed into each other under certain operations of T_d, and the coefficients $\alpha_i^{\tau}(\mu)$ are determined entirely by group theory. Substituting Eq. (12) into Eq. (11b), we obtain after application of symmetry,

$${}_{\tau}\langle m\,|h_e|\,m'\rangle_{\tau}=\sum_{\lambda=1}^{3}g_{\lambda}(\tau)\langle\beta_m^{i}\,|h_e|\,\beta_{m'}^{j}\rangle\ , \tag{13}$$

where $\lambda=1$, 2, and 3 for the intravalley ($\vec{\mathrm{k}}_i=\vec{\mathrm{k}}_j$), intertransverse ($\vec{\mathrm{k}}_i$ and $\vec{\mathrm{k}}_j$ along different axes) and interlongitudinal ($\vec{\mathrm{k}}_i$ and $\vec{\mathrm{k}}_j$ along the same axis) scattering terms, respectively. The coefficients $g_{\lambda}(\tau)$ can be found in Ref. 17 for Si and Ref. 18 for Ge. Each matrix element in Eq. (13) can be written as the sum of the kinetic energy (KE) and potential energy (PE) matrix elements. The KE matrix elements may be evaluated by carrying out the integral

$$\int\beta_m^{i}(\vec{\mathrm{k}}-\vec{\mathrm{k}}_i)E_c(\vec{\mathrm{k}})\beta_{m'}^{j}(\vec{\mathrm{k}}-\vec{\mathrm{k}}_j)\frac{d^3k}{(2\pi)^3}$$

in $\vec{\mathrm{k}}$ space. The conduction-band energy expression $E_c(\vec{\mathrm{k}})$ may be approximated by the sum of several truncated valleys, each valley being described by an ellipsoidal expression.[12] The PE matrix elements may be evaluated in real space, where the kernel associated with the PE operator is written approximately as[12]

$$\langle\vec{\mathrm{k}}\,|V_{\phi}|\,\vec{\mathrm{k}}'\rangle\sim J_{\lambda}+V_{\mathrm{PC}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')R_{\lambda}\ , \tag{14}$$

with $\vec{\mathrm{k}}$ and $\vec{\mathrm{k}}'$ restricted in the neighborhood of the center of the ith and jth valleys, respectively. The J_{λ}'s represent the short-range interaction strength factors as defined in Ref. 12. For nonisocoric impurities, they are taken as empirical parameters fitted to the binding energies of the donor ground states. The values of J_{λ} have been previously given in Ref. 12. However, in the calculation of D^- states, we have adjusted the J_{λ} parameters so that the use of a smaller set of basis functions reproduce the ionization energies for the lowest-lying donor states for various sysmmetries. The adjusted values are given in Table I.

The R_{λ};s are umklapp renormalization factors as defined in Ref. 16; the index $\lambda=1$, 2, and 3 corresponds to the intravalley, intertransverse and interlongitudinal valley terms, respectively. Their values are given in Ref. 12. The function $V_{\mathrm{PC}}(\vec{\mathrm{q}})$ is the Fourier transform of the screened point charge potential.[17]

C. Mutual interaction between two electrons in the D^- system

The mutual interaction for electrons in multivalley semiconductors are complicated by two factors.

(1) Electron states are described by the sum of

TABLE I. Values of semiempirical parameters, J_{λ} ($\lambda=1,2,3$), for Si and Ge doped with various impurities. The unit of J_{λ} is 10^{-3} Ry bohr^3.

Material Parameter	Si:P	Si:As	Si:Sb	Si:Li	Ge:P	Ge:As	Ge:Sb
J_1	1.53	18.52	36.33	54.01	−8.95	−7.69	0.55
J_2	5.83	−4.98	−3.92	88.17	4.05	2.31	10.55
J_3	6.13	2.52	25.83	80.37			

envelope functions localized in $\vec{k}$ space near the N equivalent minima. The mutual interactions between these electron states result in terms coupling electrons in the various valleys, the intra-intra, intra-inter, and inter-inter scattering terms. In the intra-intra scattering term, the final states of the two mutually interacting electrons remain in the same valleys as those of the initial states. In the intra-inter scattering term, one electron is scattered into a valley other than the original one (occupied by the initial state) while the other electron remains in the same valley. In the inter-inter scattering term, both electrons are scattered into valleys which differ from the original valleys. These envelope functions are well localized in the N valleys, separated by some wave vectors that are large compared to the spreading of the envelope functions in $\vec{k}$ space. Therefore, the mutual interaction is appreciable only for the scattering processes in which the wave vector is conserved, e.g., the intra-intra term and some inter-inter scattering terms. The intra-inter scattering term does not satisfy the wave-vector conservation and hence can be neglected. For the D^- states in Si and Ge, it can be shown that the intra-intra term is about 2 orders of magnitude larger than the sum of the remaining scattering terms, and therefore dominates the mutual interaction.

(2) Since the constant energy surfaces in Si and Ge are ellipsoids near the N equivalent minima, the envelope function localized in each valley for a given electron will also be ellipsoidal. The intra-intra term of the mutual interaction between two electrons with ellipsoidally distributed charge densities takes on two different values depending on whether or not the major axes of the ellipsoids associated with the two electrons are oriented parallel to each other. We shall refer to these two values as the "parallel" and "nonparallel" mutual interactions, respectively. The difference between the parallel and nonparallel mutual interactions is about a few percent of the total mutual interaction. However, this difference determines the coupling of states associated with the same overall symmetry but different crystalline configurations labeled by $(\tau_1\tau_2)$. We will return to this point below. Based on the above discussions, we can derive an expression for the matrix elements for the interaction between the two-electron product states, $|mn;(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e\rangle$ and $|m'n';(\tau_1'\tau_2')\Gamma_e^{\pm}\mu_e\rangle$. We obtain (see Appendix A for the details of this derivation)

$$\langle m'n';(\tau_1'\tau_2')\Gamma_e^{\pm}\mu_e\,|\,v(1,2)\,|\,mn;(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e\rangle$$

$$\simeq\Big[U_0(m'n',mn)\delta_{\tau_1\tau_1'}\delta_{\tau_2\tau_2'}+\sum_{\lambda=1}^{4}U_\lambda(m'n',mn)G_\lambda^{\Gamma_e}(\tau_1\tau_2,\tau_1'\tau_2')\Big]f_{mn}^{\tau_1\tau_2}f_{m'n'}^{\tau_1'\tau_2'}\pm\cdots\;, \tag{15}$$

where the ellipsis represents an exchange term, U_0 represents the intra-intra parallel mutual-interaction term, and U_1 represents the difference between the intra-intra parallel and nonparallel mutual interaction terms; U_2 and U_3 represent the contributions from the wave-vector conserving inter-inter scattering schemes (longitudinal and transverse) and U_4 the contribution from momentum nonconserving intervalley scattering schemes. For Si, the U_4 term is negligibly small. For Ge, there is no U_2 term, and the U_3 and U_4 terms are found to be negligibly small. The exchange term is obtained from the direct term by exchanging the roles of the two electrons in the final state. The G matrices describing the electron-electron couplings are listed in Tables V and VI for Si and Ge, respectively. As will be shown in Sec. III, the total contribution of U_1, U_2, U_3, and U_4 is less than 5% of the total energy. In the zeroth-order approximation, the terms involving U_1, U_2, U_3, and U_4 are neglected, hence the states of different configurations are decoupled. The energy levels can then be labeled by the symmetry representation of single-particle states $(\tau_1\tau_2)$.

In the absence of the coupling terms U_1, U_2, U_3, and U_4, the spin singlet and triplet states for the mixed configurations [i.e., $(\Gamma_1\Gamma_3)$, $(\Gamma_1\Gamma_5)$, and $(\Gamma_5\Gamma_3)$] are degenerate. For the symmetric configurations [i.e., $(\Gamma_1\Gamma_1)$, $(\Gamma_5\Gamma_5)$, and $(\Gamma_3\Gamma_3)$], the spin triplet states lie at much higher energies than the spin singlet states in analogy to the $2S_{3/2}$ and $1S_{1/2}$ states in the He system.[1] When the coupling terms (U_λ; $\lambda \geq 1$) are included, the states originally labeled by the symmetry representation of single-particle states are now split into several states labeled by the symmetry representation of the total Hamiltonian. For the mixed configurations, these states are also split into spin singlet and triplet states.

The above symmetry arguments can also be applied to the donor bound exciton (D^0X) system, which we will discuss in a future publication. However, the D^0X is further complicated by the presence of a Γ_8-symmetry hole.

III. CALCULATION METHOD

The present calculation is based on the configuration-interaction (CI) method. The procedure of our calculation is divided into two steps. In the first step (zeroth-order approximation), all the electron-electron coupling terms (U_λ; $\lambda=1,\ldots,4$) are neglected. The effect of these coupling terms are included in the second step using the first-order degenerate perturbation theory. In the zeroth-order approximation, Eqs. (11) are decoupled for various crystalline configurations; therefore, we can perform the CI calculation for each crystalline configuration ($\tau_1\tau_2$) separately. For convenience, we introduce normalized units in which distance and energy are measured in units of $\epsilon_0 h^2/m_t e^2$ (the bohr), and $e^4 m_t/2\epsilon_0^2\hbar^2$ (the rydberg), respectively, where ϵ_0 and m_t are the macroscopic dielectric constant and the transverse effective mass, respectively.

A. Basic functions

We choose the single-particle basis functions of symmetry ($\tau\mu$) to be the linear combination of Slater-type orbitals (STO) defined in an ellipsoidal coordinate system, viz.,

$$\beta_{nlm}^{\tau\mu}(\vec{r})=\sum_{j=1}^{N}\alpha_j^{\tau}(\mu)e^{i\vec{k}_j\cdot\vec{r}}f_{nl}(r')Y_{lm}(\Omega')\ , \tag{16a}$$

with

$$f_{nl}(r')\equiv\sum_{p}(r')^l e^{-b_{pl}r'}A_{pn}^{l}\ , \tag{16b}$$

and

$$\vec{r}\,'\equiv(x,y,z/\zeta)\ ,$$

where ζ is the eccentricity factor used for describing the donor states,[12] $\vec{k}_j$ denotes the positions of the N equivalent minima in $\vec{k}$ space, and $\alpha_j^{\tau}(\mu)$ are coefficients determined by group theory. The exponents b_{pl} are selected to be

$$b_{pl}=b_0/Z_p,\quad p=1,\ldots,7 \tag{17a}$$

with $b_0=2$ bohr^{-1} for Si and 4 bohr^{-1} for Ge and

$$Z_{pl}=(1,2,4,8,16,\tfrac{1}{2},\tfrac{1}{4})\ \text{ for }\ l=0,1,2\ . \tag{17b}$$

The A_{pn}^{l}'s are the transformation matrix elements, which make the orbitals $f_{nl}(r')$ orthogonalized to each other. The intervalley overlap matrix elements are negligibly small for the exponents chosen here and are neglected.[12]

The basis functions for the D^- states are constructed from the linear combinations of the products of the single-particle basis functions for the two electrons. These two-electron product basis functions can be selected to be eigenstates of the total angular momentum $L=l_1+l_2$, labeled by the quantum number (LM). It should be noted that these angular momenta are defined in an ellipsoidal coordinate system. According to the symmetry of the total Hamiltonian, these two-electron product states with L differing by an even integer but the same M are coupled together. Since we are concerned with the lowest-lying states for each crystalline configuration only, we can restrict these basis functions to have $M=0$ and $L=$even integers. If we denote these states by the notation $|l_1,l_2;L,M\rangle$, then the product basis functions are classified as the $|0,0;0,0\rangle$, $|0,2;2,0\rangle$, $|1,1;0,0\rangle$, $|1,1;2,0\rangle$, $|1,2;2,0\rangle$, $|2,2;0,0\rangle$, $|2,2;2,0\rangle$, and $|2,2;4,0\rangle$ states when the single-particle states with $l=0,1,2$ are used. The states constructed from two non-s-like single-particle states (e.g., $|1,1;0,0\rangle$, $|2,2;0,0\rangle$, and $|2,2;2,0\rangle$, etc.) are coupled to the state $|00;00\rangle$ only through the mutual-interaction term. In Appendix B, we derive a general expression for the parallel mutual-interaction term. We find that the contribution to the ground-state energy due to the mixing with $L\neq0$ states (i.e., the $|1,1;2,0\rangle$, $|1,2;2,0\rangle$, $|2,2;2,0\rangle$, and $|2,2;,4,0\rangle$ states) are only a few percent of that due to the mixing with the $|1,1;0,0\rangle$ and $|2,2;0,0\rangle$ states. The state $|0,2;2,0\rangle$ is coupled to the state $|00;00\rangle$ mainly through the single-particle Hamiltonian h_e. The contribution of this state to the total energy of the D^- ground state can be included in large part by adjusting the empirical parameters, J_λ's in the single-particle Hamiltonian h_e, such that the use of seven s-like ellipsodial STO's yields the same binding energies for the lowest-lying donor states as the experimental values. Therefore, we select the product states with total angular momentum $L=0$ (i.e., $|ll;00\rangle$; $l=0,1,2$) as our basis functions. We define

$$|(n_1n_2)l;\tau_1\mu_1,\tau_2\mu_2\rangle \equiv\frac{(-1)^l}{(2l+1)^{1/2}}\sum_m \beta_{n_1lm}^{\tau_1\mu_1}(\vec{r}_1)\beta_{n_2lm}^{\tau_2\mu_2^*}(\vec{r}_2)\ , \tag{18}$$

where $\beta^{\tau\mu}_{nlm}(\vec{r})$ is defined in Eq. (16). The product basis functions which transform according to the irreducible representation Γ_e, denoted $|(n_1n_2)l;(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e\rangle$, are taken as linear combinations of the states $|(n_1n_2)l;\tau_1\mu_1,\tau_2\mu_2\rangle$ according to Eqs. (7) and (8). The total number of product basis states constructed from seven single-particle states for $l=0$, 1, and 2 is 147 for mixed configurations [i.e., $(\Gamma_1\Gamma_3)$, $(\Gamma_1\Gamma_5)$, and $(\Gamma_3\Gamma_5)$] and 84 for symmetric configurations [i.e., $(\Gamma_1\Gamma_1)$, $(\Gamma_3\Gamma_3)$, and $(\Gamma_5\Gamma_5)$].

B. Matrix elements

The matrix elements of H_{D^-} within the zeroth-order approximation for each configuration $(\tau_1\tau_2)$ is given by

$$\begin{aligned}\langle(n_1n_2)l;(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e\,|H_{D^-}|\,(n_1'n_2')l';(\tau_1'\tau_2')\Gamma_e^{\pm}\mu_e\rangle\\ =f^{\tau_1\tau_2}_{n_1n_2}f^{\tau_1\tau_2}_{n_1'n_2'}\frac{\delta_{ll'}}{(2l+1)}\sum_m[{}_{\tau_1}\langle n_1lm\,|h_e(1)|\,n_1'lm\rangle_{\tau_1}\delta_{n_2n_2'}+{}_{\tau_2}\langle n_2lm\,|h_e(2)|\,n_2'lm\rangle_{\tau_2}\delta_{n_1n_1'}]\\ +U_0((n_1n_2)l,(n_1'n_2')l')\pm\cdots\ ,\end{aligned}\tag{19}$$

where the ellipsis represents an exchange term that is obtained from the direct term by exchanging the roles of the two electrons in the final state. The matrix elements for h_e is given by Eq. (13). For the s-like states, the expression of the matrix elements had been derived in Ref. 12. For the non-s-like states, we neglect the intervalley scattering terms and approximate the $\vec{q}$-dependent dielectric function $\epsilon(\vec{q})$ by the static dielectric constant ϵ_0; therefore the intravalley matrix elements are given by

$$\sum_m\langle nlm\,|h_e|\,n'lm\rangle=\sum_{pp'}\left[\frac{\sqrt{b_pb_{p'}}}{b}\right]^{2l+3}\left[B\left[b_pb_{p'}+\frac{b^2l}{l+1}\right]-\frac{2a_0b}{l+1}\right]A^l_{pn}A^l_{p'n'}\ ,\tag{20a}$$

where

$$B\equiv\frac{1}{3}\left[2+\frac{m_t}{m_l\zeta^2}\right]\tag{20b}$$

with m_t and m_l being the transverse and longitudinal masses, respectively,

$$a_0=(\sin^{-1}g)/g\ ,\tag{20c}$$

with

$$g\equiv(1-\zeta^2)^{1/2}\ ,\tag{20d}$$

and

$$b=(b_p+b_{p'})/2\ .$$

A general expression for the matrix elements for the parallel mutual interaction is derived in Appendix B. We find that these matrix elements for the $L=0$ states defined in an ellipsoidal coordinate system are simply that for the $L=0$ states defined in a spherical coordinate system multiplied by a factor a_0 [defined in Eq. (20c)]. Therefore, we have[19]

$$U_0((n_1n_2)l,(n_1'n_2')l')=2(-1)^{l+l'}[(2l+1)(2l'+1)]^{1/2}a_0\sum_L\left|\begin{pmatrix}l&l'&L\\0&0&0\end{pmatrix}\right|^2\zeta^{(L)}_{ll'}(b_{n_1}b_{n_2},b_{n_1'}b_{n_2'})\tag{21a}$$

where

$$\begin{aligned}\zeta^{(L)}_{ll'}(b_1b_2,b_1'b_2')\equiv\frac{(4b_1b_2)^{l+3/2}(4b_1'b_2')^{l'+3/2}}{(2l+2)!(2l'+2)!}\int\exp[-(b_1+b_1')r_1-(b_2+b_2')r_2]\\ \times\frac{r_<^L}{r_>^{L+1}}r_1^{2+(l+l')}r_2^{2+(l+l')}dr_1dr_2\end{aligned}\tag{21b}$$

and

$$\begin{bmatrix} l & l' & L \\ 0 & 0 & 0 \end{bmatrix}$$

is given in Ref. 20. In Eq. (21), we have approximated the $\vec{q}$-dependent dielectric function $\epsilon(\vec{q})$ by the macroscopic dielectric constant ϵ_0. This is a good approximation, since the Fourier transform (in $\vec{q}$ space) of the product of the electron wave functions is localized near $\vec{q}=0$.[21]

The Hamiltonian matrix given in Eq. (19) is diagonalized numerically with the lowest eigenvalue denoted by $E_0(\tau_1\tau_2)$ for each configuration $(\tau_1\tau_2)$. The electron-electron coupling terms (U_λ; $\lambda \geq 1$) are evaluated on the lowest-lying states for each configuration $(\tau_1\tau_2)$ obtained in the zeroth-order approximation. For simplicity, the non-s-like components ($l=1$ and 2) (about 1%) of these lowest-lying states are not included in the evaluation of the electron-electron couplings. In the evaluation of U_2 and U_3 terms for Si, we have used the Bloch function $\phi^c_{\vec{k}_i}$ ($\vec{k}_i$ denotes the position of the ith minimum of the conduction band) obtained from Altarelli and Hsu.[22] For Ge, we have only included the U_1 term for evaluating the electron-electron coupling. The sub-Hamiltonians, defined for each overall symmetry $\Gamma_e^\pm$ by

$$H^{\Gamma_e^\pm}(\tau_1\tau_2,\tau_1'\tau_2') = E_0(\tau_1\tau_2)\delta_{\tau_1\tau_1'}\delta_{\tau_2\tau_2'} + \sum_{\lambda=1}^{4} U_\lambda G^{\Gamma_e^\pm}(\tau_1\tau_2,\tau_1'\tau_2') \qquad (22)$$

are then diagonalized separately to obtain the final results for the energy values [denoted $E^{\Gamma_e^\pm}(\tau_1\tau_2)$].

IV. RESULTS AND DISCUSSION

A. H$^-$ system

To examine the convergence of the expansion for the ground state, we first compute the ground-state energy of the H$^-$ system using the present basis set. We obtain a ground-state energy of 1.0546 Ry, which is in good agreement with the experimental value of 1.0555 Ry.[1]

B. D^- states in Ge

In Table II, we list the total energies of the lowest-lying states for the donor (obtained experimentally)[23] and each configuration $(\tau_1\tau_2)$ of the D^- obtained in the zeroth-order approximation (ZOA) $E_0(\tau_1\tau_2)$ (upper half), and ZOA plus the electron-electron coupling, $E^{\Gamma_e^\pm}(\tau_1\tau_2)$ (lower half) for Ge:P, Ge:As and Ge:Sb. As defined in Sec. II C the ZOA includes only the interaction between the electrons when they are initially in valleys on the same axis and scatter into states in the original valleys. The additional electron-electron coupling terms are found to be small ($\sim$0.3 meV) compared to the total binding energies. Therefore the first-order perturbation method used to obtain $E^{\Gamma_e^\pm}(\tau_1\tau_2)$ is a good approximation. We find that the coupling between states of different configurations but the same overall symmetry is negligibly small ($\lesssim$0.2%) for Ge:P and Ge:As, but is substantial for Ge:Sb. For Ge:Sb, the mixing of $(\Gamma_5\Gamma_5)\Gamma_1^+$ state in the ground state is about 6% and the mixing of the $(\Gamma_5\Gamma_5)\Gamma_5^+$ in the $(\Gamma_1\Gamma_5)\Gamma_5^+$ state is about 26%. The theoretical and experimental values for the binding energies are presented in Table III. As shown in Table III, the theoretical values lie between the two sets of experimental values marked a and b. The set marked a is obtained at both higher temperature and higher impurity concentration than the other, and therefore includes more contribution from the D^- complexes.[8] This effect will shift the threshold of the photoconductivity spectrum up to higher energies. The set marked b is obtained at 0.38 K, with impurity concentration $\sim 5\times 10^{13}$ cm^{-3}, and D^- states under this condition were considered to be isolated.[7] However, although not mentioned in Ref. 7, it is reasonable to assume that the sample is slightly compensated with 10^{12} cm^{-3} D^+ and A^- charged centers. Although the average separation (R_{av}) between a D^- center and an A^- center is quite large (about 5000 Å), the Coulomb interaction ($e^2/\epsilon_0 R_{\text{av}}$) between them can be appreciable (about 0.2 meV). Hence, we might expect correction of this magnitude to the results in Ref. 7. This phenomenon is capable of explaining the differences in measured and theoretical values of the binding energy.

Considering the excited states of D^- listed in Table II, we find the $(\Gamma_1\Gamma_5)\Gamma_5^+$ and $(\Gamma_1\Gamma_5)\Gamma_5^+$ states are barely bound (by about 0.05 and 0.02 meV, respectively) for Ge:P. For Ge:As, no bound excited states are obtained. For Ge:Sb, the lowest-lying states of all possible configurations are bound. This is because the Γ_1 and Γ_5 donor states in Ge:Sb are separated by only 0.3 meV.[23] We find a group of excited states lying in the region of 0.10–0.25 meV above the ground state.

TABLE II. Total energies of the lowest-lying states for donors and for various configurations $(\tau_1\tau_2)$ of the D^- obtained in the zeroth-order approximation (ZOA), $E_0(\tau_1\tau_2)$ and ZOA plus the electron-electron coupling $E^{\Gamma_e^+}(\tau_1\tau_2)$ for Ge doped with P, As, and Sb. All energies are in meV.

	Configuration \ Dopant	P	As	Sb
Donor states	Γ_5	-10.1^a	-10.0^a	-10.0^a
	Γ_1	-12.9^a	-14.2^a	-10.3^a
Zeroth-order approximation $E_0(\tau_1\tau_2)$	$(\Gamma_5\Gamma_5)$	-10.75	-10.63	-10.63
	$(\Gamma_1\Gamma_5)$	-12.89	-14.14	-10.78
	$(\Gamma_1\Gamma_1)$	-13.65	-15.01	-10.91
Final $E^{\Gamma_e^{\pm}}(\tau_1\tau_2)$	$(\Gamma_5\Gamma_5)\Gamma_1^+$	-10.81	-10.69	-10.67
	$(\Gamma_5\Gamma_5)\Gamma_5^+$	-10.88	-10.76	-10.68
	$(\Gamma_5\Gamma_5)\Gamma_3^+$	-11.02	-10.90	-10.90
	$(\Gamma_5\Gamma_5)\Gamma_5^-$	-11.02	-10.90	-10.90
	$(\Gamma_1\Gamma_5)\Gamma_5^+$	-12.93	-14.16	-10.99
	$(\Gamma_1\Gamma_5)\Gamma_5^-$	-12.96	-14.16	-11.05
	$(\Gamma_1\Gamma_1)\Gamma_2^+$	-13.89	-15.25	-11.15

[a] Reuszer and Fisher (Ref. 23) [revised by Faulkner (Ref. 24)].

C. D^- state in Si

In Table IV, we list the total energies of the lowest-lying states for the donor (obtained experimentally)[25,26] and each configuration $(\tau_1\tau_2)$ of the D^- obtained in the zeroth-order approximation (ZOA) $E_0(\tau_1\tau_2)$ (upper half) and ZOA plus the electron-electron coupling, $E^{\Gamma_e^+}(\tau_1\tau_2)$ (lower half) for Si:P, Si:As, Si:Sb, and Si:Li, respectively. Again, the additional electron-electron coupling term is found to be small ($\sim$0.5 meV) compared to the total binding energies. This justifies the validity of the first-order perturbation method used to obtain $E^{\Gamma_e^{\pm}}(\tau_1\tau_2)$. The coupling between states of different configurations but the same overall symmetry is weak (3%) for Si:P, Si:As, and Si:Sb, but is substantial for Si:Li. The mixing between the $(\Gamma_3\Gamma_3)\Gamma_1^+$ and $(\Gamma_5\Gamma_5)\Gamma_1^+$ is about 40%, and similarly between the $(\Gamma_3\Gamma_3)\Gamma_3^+$ and $(\Gamma_5\Gamma_5)\Gamma_3^+$ states for Si:Li. This is due to the fact that the Γ_3 and Γ_5 donor states for Si:Li are nearly degenerate,[26] while these states for Si:P, Si:As, and Si:Sb are separated by about 2–3 meV.[25] If we included the q dependence of the dielectric function for the mutual-interaction term, these binding energies would be reduced to 2.6, 3.1, 2.5, and 2.1 meV, respectively. The photoconductivity spectra obtained by Taniguchi and Narita[5,9,10] suggest that the binding energies for D^- states for Si:P, Si:As, and Si:Li are 1.7, 2.0, and 1.7 meV, respectively. Hence, the experimental value for the binding is substantially smaller than that obtained theoretically. As in Ge, this difference in binding can be attributed to the existence of residual acceptors.

TABLE III. Binding energies of the D^- states for Ge doped with P, As, and Sb. All energies are in meV.

Materials	Theory	Experiment
Ge:P	0.99	1.2^a
Ge:As	1.05	$1.55,^a$ 0.75^b
Ge:Sb	0.85	$0.95,^a$ 0.625^b

[a] Gershenzon *et al.* (Ref. 3).
[b] Taniguchi and Narita (Ref. 7).

TABLE IV. The total energies of the lowest-lying states for donors and for various configurations $(\tau_1\tau_2)$ of the D^- obtained in the zeroth-order approximation (ZOA) $E_0(\tau_1\tau_2)$ and ZOA plus the electron-electron coupling, $E^{\Gamma_e^+}(\tau_1\tau_2)$ for Si doped with P, As, Sb, and Li. All energies are in meV.

	Impurity Configuration	P	As	Sb	Li
Donor states	Γ_3	-32.6^{a}	-31.2^{a}	-30.5^{a}	-33.0^{b}
	Γ_5	-33.9^{a}	-32.6^{a}	-32.9^{a}	-33.0^{b}
	Γ_1	-45.5^{a}	-53.7^{a}	-42.7^{a}	-31.2^{b}
Zeroth-order Approximation $E_0(\tau_1\tau_2)$	$(\Gamma_3\Gamma_3)$	−34.45	−33.04	−32.28	−34.88
	$(\Gamma_3\Gamma_5)$	−35.19	−33.82	−33.73	−34.89
	$(\Gamma_5\Gamma_5)$	−35.82	−34.47	−34.76	−34.91
	$(\Gamma_1\Gamma_3)$	−45.41	−53.60	−42.64	−34.10
	$(\Gamma_1\Gamma_5)$	−45.42	−53.60	−42.67	−34.12
	$(\Gamma_1\Gamma_1)$	−48.03	−56.82	−45.10	−33.12
Final $E^{\Gamma_e^\pm}(\tau_1\tau_2)$	$(\Gamma_3\Gamma_3)\Gamma_1^+$	−34.48	−33.08	−32.34	−35.14
	$(\Gamma_3\Gamma_3)\Gamma_3^+$	−34.63	−33.08	−32.48	−35.21
	$(\Gamma_3\Gamma_3)\Gamma_2^-$	−34.79	−33.38	−32.62	−35.22
	$(\Gamma_3\Gamma_5)\Gamma_5^+$	−35.08	−33.71	−33.63	−34.90
	$(\Gamma_3\Gamma_5)\Gamma_4^-$	−35.50	−34.12	−34.00	−35.20
	$(\Gamma_3\Gamma_5)\Gamma_4^+$	−35.53	−34.15	−34.03	−35.23
	$(\Gamma_3\Gamma_5)\Gamma_5^-$	−35.53	−34.16	−34.03	−35.24
	$(\Gamma_5\Gamma_5)\Gamma_1^+$	−35.81	−34.47	−34.78	−34.71
	$(\Gamma_5\Gamma_5)\Gamma_3^+$	−35.85	−34.47	−34.78	−34.88
	$(\Gamma_5\Gamma_5)\Gamma_5^+$	−36.13	−34.78	−35.08	−35.22
	$(\Gamma_5\Gamma_5)\Gamma_4^-$	−36.17	−34.81	−35.11	−35.25
	$(\Gamma_1\Gamma_3)\Gamma_3^+$	−45.41	−53.60	−42.65	−34.11
	$(\Gamma_1\Gamma_3)\Gamma_3^-$	−45.42	−53.61	−42.65	−34.42
	$(\Gamma_1\Gamma_5)\Gamma_5^+$	−45.42	−53.60	−42.68	−34.09
	$(\Gamma_1\Gamma_5)\Gamma_5^-$	−45.44	−53.61	−42.71	−34.44
	$(\Gamma_1\Gamma_1)\Gamma_1^+$	−48.23	−57.00	−45.31	−33.28

[a] Aggarwal and Ramdas (Ref. 25) [revised by Faulkner (Ref. 24)].

[b] Aggarwal *et al.* (Ref. 26) [revised by Faulkner (Ref. 24)].

Since the samples used in Refs. 9 and 10 are prepared with a concentration $\sim 10^{15}$ cm^{-3}, it is reasonable to assume the existence of $\sim 10^{13}$ cm^{3} A^- centers. With this assumption, a shift in energy of approximately 0.6 meV can occur in the photoconductivity spectrum due to the Coulomb repulsion between the D^- and the nearby A^- centers. This shift in energy brings the experimental data obtained in Ref. 10 in reasonable agreement with our theoretical results. In Ref. 9, it is also found that D^- states are bound by about 1.1 meV for both Si:P and Si:As under a high-stress limit. Theoretically, it is believed that under a high-stress limit the D^- system can be well described by a single-valley model,[11] and the binding energy should be about 1.7 meV.[2] This difference in binding can also be accounted for by the introduction of residual acceptors.

From Table IV, we see that the present calculation predicts that all the excited states for the D^-

system in Si:P, Si:As, and Si:Sb are not bound but that the lowest-lying states associated with all possible configurations for the D^- system in Si:Li are bound. The bound states for Si:Li are due to the fact that the Γ_3, Γ_5, and Γ_1 donor states are separated by only 1.8 meV, which is overcome by the binding energy for the D^- states (2.2 meV), hence, producing many bound states.

V. CONCLUSION

We have developed a theory for the D^- states in Ge and Si, including the effect of realistic band structures. By considering the valley-orbit interaction and mass anistropy for each electron interacting with the donor and the mutual interaction simultaneously, we obtain binding energy for the D^- states in Ge and Si, which are about twice as large as those obtained in a spherical model.[2] This enhancement in binding energy is in disagreement with the recent experimental data.[7–10] The difference between theory and experiment is accounted for by the existence of compensating (A^-) centers. We also find that the energy separation between the excited and ground donor states in Ge:Sb and Si:Li are smaller than the energy required to bind a D^- state, and hence, we obtain many bound excited states. Our study for the electron-electron mutual interaction can be applied to the electronic spectra of the donor bound exciton (D^0X) in Ge and Si, and provide an understanding for the electron-electron coupling scheme between the states belonging to different configurations in the D^0X. This application will be discussed in a future publication.

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APPENDIX A: MUTUAL INTERACTION BETWEEN TWO ELECTRONS IN D^-

In this appendix, we derive the expression for the matrix elements of the mutual interaction between two-electron product states denoted by

$$|mn;(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e\rangle \quad\text{and}\quad |m'n';(\tau_1'\tau_2')\Gamma_e^{\pm}\mu_e\rangle\;.$$

According to the definition of these states [see Eqs. (7) and (8)] we can write the matrix elements of the mutual interaction as

$$\begin{aligned}\langle m'n';(\tau_1'\tau_2')\Gamma_e^{\pm}\mu_e\,|\,v(1,2)\,|\,mn;(\tau_1\tau_2)\Gamma_e^{\pm}\mu_e\rangle\\ \equiv \sum_{\substack{\mu_1\mu_2\\ \mu_1'\mu_2'}} C_{\tau_1'\tau_2}(\mu_1'\mu_2',\Gamma\mu)C_{\tau_1\tau_2}(\mu_1\mu_2,\Gamma\mu)(\langle m'n',\mu_1'\mu_2'\,|\,W\,|\,mn,\mu_1\mu_2\rangle\\ \pm\langle m'n',\mu_1'\mu_2'\,|\,W\,|\,nm,\mu_2\mu_1\rangle)f_{mn}^{\tau_1\tau_2}f_{m'n'}^{\tau_1'\tau_2'}\end{aligned} \tag{A1}$$

$$\langle\mu_1'\mu_2'\,|\,W\,|\,\mu_1\mu_2\rangle\equiv\sum_{\substack{\vec{k}_1\vec{k}_1'\\ \vec{k}_2\vec{k}_2'}}\beta'^{*\mu_1'}(\vec{k}_1')\beta'^{*\mu_2'}(\vec{k}_2')\langle\vec{k}_1'\vec{k}_2'\,|\,v\,|\,\vec{k}_1\vec{k}_2\rangle\beta^{\mu_1}(\vec{k}_1)\beta^{\mu_2}(\vec{k}_2)\;. \tag{A2}$$

In Eq. (A2) the indices mn and $m'n'$ have been dropped for simplicity. Using the Fourier expansion in the reciprocal-lattice vector space for the product of the periodic parts of the Bloch functions $|\vec{k}_1'\rangle$ and $|\vec{k}_1\rangle$ (or $|\vec{k}_2'\rangle$ and $|\vec{k}_2\rangle$), with coefficients $c(\vec{k}_1,\vec{k}_1';\vec{G}_1)$ [or $c(\vec{k}_2,\vec{k}_2';\vec{G}_2)$], we can write the kernal for the mutual interaction as

$$\langle\vec{k}_1'\vec{k}_2'\,|\,v\,|\,\vec{k}_1\vec{k}_2\rangle=\sum_{\vec{G}_1\vec{G}_2}\tilde{v}(\vec{G}_1+\vec{k}_1-\vec{k}_1')c(\vec{k}_1,\vec{k}_1';\vec{G}_1)c^*(\vec{k}_2',\vec{k}_2;\vec{G}_2)\delta(\vec{G}+\vec{k}_1-\vec{k}_1'-\vec{G}_2+\vec{k}_2-\vec{k}_2')\;. \tag{A3}$$

Substituting Eq. (5) and Eq. (A3) into Eq. (A2), we obtain

$$\langle \mu_1'\mu_2' \,|\, W \,|\, \mu_1\mu_2 \rangle = \sum_{ii'jj'} \alpha_i'(\mu_1')\alpha_j'(\mu_2')\alpha_i(\mu_1)\alpha_j(\mu_2) W(i,i',j,j') \,, \tag{A4}$$

where

$$\begin{aligned} W(i,i',j,j') \equiv \sum_{\vec{G}_1\vec{G}_2} \sum_{\substack{\vec{k}_1\vec{k}_1' \\ \vec{k}_2\vec{k}_2'}} & \beta_{i'}'^*(\vec{k}_1' - \vec{k}_{i'})\beta_{j'}'^*(\vec{k}_2' - \vec{k}_{j'})\tilde{v}(\vec{G}_1 + \vec{k}_1 - \vec{k}_1')c(\vec{k}_1,\vec{k}_1';\vec{G}_1)c^*(\vec{k}_2',\vec{k}_2;\vec{G}_2) \\ & \times \delta(\vec{G}_1 + \vec{k}_1 - \vec{k}_1' - \vec{G}_2 + \vec{k}_2 - \vec{k}_2')\beta_i(\vec{k}_1 - \vec{k}_i)\beta_j(\vec{k}_2 - \vec{k}_j) \,. \end{aligned} \tag{A5}$$

The right-hand side of Eq. (A5) can be sorted into three classes: (1) $\Delta\vec{k}_1 = \Delta\vec{k}_2 = 0$, (2) $\Delta\vec{k}_1 = \Delta\vec{k}_2 \neq 0$, and (3) $\Delta\vec{k}_1 \neq \Delta\vec{k}_2$, where $\Delta\vec{k}_1 \equiv \vec{k}_{i'} - \vec{k}_i$ and $\Delta\vec{k}_2 \equiv \vec{k}_j - \vec{k}_{j'}$. We will discuss the three classes separately.

(1) $\Delta\vec{k}_1 = \Delta\vec{k}_2 = 0$ *(intra-intra).* Only the terms with $\vec{G}_1 = 0$ and $\vec{G}_2 = 0$ have appreciable contributions. Transforming Eq. (A5) into real space, we readily obtain

$$W(i,i,j,j) = \int d^3r_1 d^3r_2 \beta_i'^*(\vec{r}_1)\beta_j'^*(\vec{r}_2) v(r_{12})\beta_i(\vec{r}_1)\beta_j(\vec{r}_2) \,, \tag{A6}$$

which takes on two different values depending on whether the major axes of the ellipsoidal charge distributions of two particles are parallel to each other.

We define

$$W(i,i,j,j) \equiv \begin{cases} U_0 & \text{if } \vec{k}_i \,||\, \vec{k}_j \\ U_0 - U_1 & \text{if } \vec{k}_i \text{ not parallel } \vec{k}_j \,. \end{cases} \tag{A7}$$

This case contributes a term to $\langle \mu_1'\mu_2' \,|\, W \,|\, \mu_1\mu_2 \rangle$ as

$$W_1(\mu_1'\mu_2', \mu_1\mu_2) = U_0 \delta_{\mu_1\mu_1'} \delta_{\mu_2\mu_2'} + U_1 G_1(\mu_1'\mu_2', \mu_1\mu_2) \,, \tag{A8}$$

where

$$G_1(\mu_1'\mu_2', \mu_1\mu_2) \equiv -\delta_{\mu_1\mu_1'} \delta_{\mu_2\mu_2'} + \sum_{i||j} \alpha_i(\mu_1')\alpha_j(\mu_2')\alpha_i(\mu_1)\alpha_j(\mu_2) \,. \tag{A9}$$

The summation is over terms with $\vec{k}_i \,||\, \vec{k}_j$ only.

(2) $\Delta\vec{k}_1 = \Delta\vec{k}_2 \neq 0$ *(inter-inter).* We must have either ($\vec{k}_i = \vec{k}_{j'}$ and $\vec{k}_{i'} = \vec{k}_j$) or ($\vec{k}_i = -\vec{k}_j$ and $\vec{k}_{i'} = -\vec{k}_{j'}$). Only the terms with $\vec{G}_1 = \vec{G}_2$ have appreciable contribution, due to the restriction of the δ function in Eq. (A3). Analogous to the umklapp renormalization factor introduced for the single-particle potential energy term,[16] we define

$$R(i,i',j,j') \equiv \sum_{\vec{G}} c(\vec{k}_i, \vec{k}_{i'}, \vec{G}) c^*(\vec{k}_{j'}, \vec{k}_j; \vec{G}) \tilde{v}(\vec{G} + \vec{k}_i - \vec{k}_{i'}) / \tilde{v}(\vec{k}_i - \vec{k}_{i'}) \tag{A10}$$

as the renormalization factors for the mutual interaction term. With the restriction $\Delta\vec{k}_1 = \Delta\vec{k}_2$, it is easy to prove that $c(\vec{k}_{j'}, \vec{k}_j; \vec{G}) = c(\vec{k}_i, \vec{k}_{i'}, \vec{G})$, and Eq. (A10) is simplified to

$$R(i,i') = \sum_{\vec{G}} |\, c(\vec{k}_i, \vec{k}_{i'}; \vec{G}) \,|^2 v(\vec{G} - \Delta\vec{k}_1) / \tilde{v}(\Delta\vec{k}_1) \,, \tag{A11}$$

where we have dropped the dependence on j and j'. With the use of the renormalization factors $R(i,i')$ and transforming Eq. (A5) into real space, we readily obtain

$$W(i,i',j,j') = R(i,i') \int d^3r_1 d^3r_2 \, \beta_{i'}'^*(\vec{r}_1)\beta_i(\vec{r}_1) e^{i\Delta\vec{k}_1\cdot\vec{r}_1} v(r_{12}) \beta_{j'}'^*(\vec{r}_2)\beta_j(\vec{r}_2) e^{-i\Delta\vec{k}_2\cdot\vec{r}_2} \,. \tag{A12}$$

Introducing the Fourier transforms for the function $\beta_i'^*(\vec{r}_1)\beta_i(\vec{r}_1)e^{i\Delta\vec{k}_1\cdot\vec{r}_1}$ as $I_{i'i}(\vec{q} - \Delta\vec{k}_1)$ and similarly for

$\beta_{j'}^{*}(\vec{r}_2)\,\beta_j(\vec{r}_2)e^{-i\Delta\vec{k}_2\cdot\vec{r}_2}$, we can rewrite Eq. (A12) as

$$W(i,i',j,j')=R(i,i')\int\frac{d^3q}{(2\pi)^3}\tilde{v}(\vec{q})I_{i'i}(\vec{q}-\Delta\vec{k}_1)I^{*}_{j'j}(\vec{q}-\Delta\vec{k}_1)\ . \tag{A13}$$

The function $I_{i'i}(\vec{q}-\Delta\vec{k}_1)\ I^{*}_{j'j}(\vec{q}-\Delta k_1)$ is sharply peaked at $\vec{q}=\Delta\vec{k}_1$, and $\tilde{v}(\vec{q})$ is a smooth function there. Therefore, we can write approximately

$$W(i,i',j,j')=R(i,i',j,j')\tilde{v}(\Delta\vec{k}_1)\int\frac{d^3q}{(2\pi)^3}I_{i'i}(\vec{q})I^{*}_{j'j}(\vec{q})\ . \tag{A14}$$

We define

$$W(i,i',j,j')=\begin{cases}U_2 & \text{for longitudinal scattering scheme}\\ U_3 & \text{for transverse scattering scheme}\ .\end{cases}$$

For longitudinal scattering, we must have $\vec{k}_{i'}=-\vec{k}_i$ and $\vec{k}_{j'}=-\vec{k}_j$, and the restriction $\Delta\vec{k}_1=\Delta\vec{k}_2$ requires $\vec{k}_i=-\vec{k}_j$. This case contributes a term $U_2G_2(\mu_1'\mu_2',\mu_1\mu_2)$ to $W(\mu_1'\mu_2',\mu_1\mu_2)$, with

$$G_2(\mu_1'\mu_2',\mu_1\mu_2)\equiv\sum_i\alpha_{-i}(\mu_1')\alpha_i(\mu_2')\alpha_i(\mu_1)\alpha_{-i}(\mu_2)\ , \tag{A15}$$

where $\alpha_{-i}(\mu_1')$ is the component associated with $\vec{k}_{i'}=-\vec{k}_i$, similarly for $\alpha_{-i}(\mu_2)$. For the transverse scattering, we obtain a contribution $U_3G_3(\mu_1'\mu_2',\mu_1\mu_2)$ to $W(\mu_1'\mu_2',\mu_1\mu_2)$ with

$$G_3(\mu_1'\mu_2',\mu_1\mu_2)\equiv\sum\alpha_i(\mu_1')\alpha_j'(\mu_2')\alpha_i(\mu_1)\alpha_j(\mu_2)\ , \tag{A16}$$

where the sum is over all transverse scattering terms satisfying the restriction $\Delta\vec{k}_1=\Delta\vec{k}_2$.

(3) $\Delta\vec{k}_1\neq\Delta\vec{k}_2$. With the change of variables $\vec{k}_1\rightarrow\vec{k}_1-\ \vec{G}_1$ and $\vec{k}_2\rightarrow\vec{k}_2+\vec{G}_2$, Eq. (A5) can be rewritten as

$$\begin{aligned}W(i,i',j,j')=\sum_{\vec{G}_1\vec{G}_2}\ \sum_{\substack{\vec{k}_1\vec{k}_1'\\ \vec{k}_2\vec{k}_2}}&\beta_i'^{*}(\vec{k}_1'-\vec{k}_{i'})\beta_j'^{*}(\vec{k}_2'-\vec{k}_{j'})\tilde{v}(\vec{k}_1-\vec{k}_1')c(\vec{k}_1-\vec{G}_1,\vec{k}_l';\vec{G}_1)c^{*}(\vec{k}_2',\vec{k}_2+\vec{G}_2;\vec{G}_2)\\ &\times\delta(\vec{k}_1-\vec{k}_1'-\vec{k}_2-\vec{k}_2')\beta_i(\vec{k}_1-\vec{G}_1-\vec{k}_i)\beta_j(\vec{k}_2-\vec{k}_j+\vec{G}_2)\ .\end{aligned} \tag{A17}$$

Replacing $c(\vec{k}_1-\vec{G}_1,\ \vec{k}_1';\vec{G}_1)$ and $c^{*}(\vec{k}_2',\ \vec{k}_2+\vec{G}_2;\vec{G}_2)$ by their values at $\vec{k}_1-\vec{G}_1=\vec{k}_i$, $\vec{k}_1'=\vec{k}_{i'}$, $\vec{k}_2+\vec{G}_2=\vec{k}_j$, and $\vec{k}_2'=\vec{k}_{j'}$, respectively, and transforming Eq. (A17) into real space, we obtain

$$\begin{aligned}W(i,i',j,j')=&\sum_{\vec{G}_1\vec{G}_2}c(\vec{k}_i,\vec{k}_{j'};\vec{G}_1)c^{*}(\vec{k}_{j'},\vec{k}_j;\vec{G}_2)\\ &\times\int d^3r_1d^3r_2\beta_{i'}'^{*}(\vec{r})\beta_i(\vec{r}_1)e^{i(\Delta\vec{k}_1-\vec{G}_1)\cdot\vec{r}_1}v(r_{12}\beta_{j'}'^{*}(\vec{r}_2)\beta_j(\vec{r}_2)e^{-i(\Delta\vec{k}_2-\vec{G}_2)\cdot\vec{r}_2}\\ =&\sum_{\vec{G}_1\vec{G}_2}c(\vec{k}_i,\vec{k}_{i'};\vec{G}_1)c^{*}(\vec{k}_{j'},\vec{k}_j;\vec{G}_2)\int\frac{d^3q}{(2\pi)^3}I_{i'i}(\vec{q}-\Delta\vec{k}_1-\vec{G}_1)I^{*}_{j'j}(\vec{q}-\Delta\vec{k}_2+\vec{G}_2)\tilde{v}(\vec{q})\ ,\end{aligned} \tag{A18}$$

where $I_{i'i}(\vec{q})$ and $I_{j'j}(\vec{q})$ are the Fourier transforms of $\beta_{i'}'^{*}(\vec{r}_1)\beta_i(\vec{r}_1)$ and $\beta_{i'}'^{*}(\vec{r}_2)\beta_j(\vec{r}_2)$, respectively. Since $I_{i'i}(\vec{q}-\Delta\vec{k}_1+\vec{G}_1)$ and $I^{*}_{j'j}(\vec{q}-\Delta\vec{k}_2+\vec{G}_2)$ are sharply peaked at $\vec{q}=\vec{G}_1-\Delta\vec{k}_1$ and $q=\vec{G}_2-\Delta\vec{k}_2$, respectively. The integral appearing in the right-hand side of Eq. (A18) is negligibly small unless the momentum is approximately conserved, i.e.,

$$\vec{G}_1-\Delta\vec{k}_1=\vec{G}_2-\Delta\vec{k}_2\ . \tag{A19}$$

In Si, Eq. (A19) can be satisfied only for some very special cases. For example, if $\Delta\vec{k}_1=0$ and $\Delta\vec{k}_2=(0,0,2)k_0$, then the term with $\vec{G}_1=0$ and $\vec{G}_2=(0,0,2)(2\pi a)$ leads to appreciable contribution to the integral in Eq. (A18). However the coefficient $c^{*}(\vec{k}_{j'},\vec{k}_j;\vec{G}_2)$ in these cases happens to be nearly zero (less than

10^{-4}), which renders the net contribution to $W(i,i',j,j')$ negligible.

In Ge, the restriction $\Delta\vec{k}_1=\Delta\vec{k}_2$ and Eq. (A19) can be satisfied simultaneously only if $\vec{k}_i$, $\vec{k}_{i'}$, $\vec{k}_j$, and $k_{j'}$ are at four different minima. Combining Eq. (A18) and Eq. (A19), and replacing $\tilde{v}(\vec{q})$ by its value at $\vec{q}=\vec{G}_1-\Delta\vec{k}_1$, we obtain

$$W(i,i',j,j')=\sum_{G_1} c(\vec{k}_i,\vec{k}_{i'};\vec{G}_1)c^*(\vec{k}_j,\vec{k}_{j'};\vec{G}_1-\vec{k}_1+\vec{k}_2)\tilde{v}(\vec{G}_1-\vec{k}_1)\int \frac{d^3q}{(2\pi)^3} I_{ii'}(\vec{q})I_{j'j}(\vec{q})\equiv U_4 \, .$$

This class contributes a term $U_4G_4(\mu_1'\mu_2',\mu_1\mu_2)$ to $\langle \mu_1'\mu_2' \mid W \mid \mu_1\mu_2\rangle$ with

$$G_4(\mu_1'\mu_2',\mu_1\mu_2)\equiv \sum_{i\neq i'\neq j\neq j'} \alpha_i(\mu_1')\alpha_j'(\mu_2')\alpha_i(\mu_1)\alpha_j(\mu_2) \, . \tag{A20}$$

Collecting all the contributions to $\langle \mu_1'\mu_2' \mid W \mid \mu_1\mu_2\rangle$ from various terms, we obtain

$$\langle \mu_1'\mu_2' \mid W \mid \mu_1\mu_2\rangle = U_0\delta_{\mu_1\mu_1'}\delta_{\mu_2\mu_2'}+\sum_{\lambda=1}^{4} U_\lambda G_\lambda(\mu_1'\mu_2',\mu_1\mu_2) \, . \tag{A21}$$

Substituting this equation into (A1), we obtain the final expression with the indices mn and $m'n'$ written explicitly

$$\langle m'n';(\tau_1'\tau_2')\Gamma_e^{\pm}\mu_e \mid v(1,2) \mid (\tau_1\tau_2)\Gamma_e^{\pm}\mu_e;mn\rangle$$
$$=f_{mn}^{\tau_1\tau_2}f_{m'n'}^{\tau_1'\tau_2'}\left[U_0(m'n',mn)\delta_{\tau_1\tau_1'}\delta\tau_2\tau_2'+\sum_{\lambda=1}^{4} U_\lambda(m'n',mn)G_\lambda^{\Gamma_e}(\tau_1'\tau_2',\tau_1\tau_2)\right]\cdots \, , \tag{A22}$$

where the ellipsis represents an exchange term and where

$$G_\lambda^{\Gamma}(\tau_1'\tau_2',\tau_1\tau_2)\equiv \sum_{\substack{\mu_1\mu_2\\ \mu_{1'}\mu_{2'}}} C_{\tau_1'\tau_2'}(\mu_1'\mu_2',\Gamma\mu)C_{\tau_1\tau_2(\mu_1\mu_2\Gamma\mu)}G_\lambda(\mu_1'\mu_2',\mu_1\mu_2), \quad \lambda=1,2,3,4 \, . \tag{A23}$$

The exchange term is obtained from the direct term by exchanging the roles of the two electrons. The nonvanishing submatrices for the matrices G_λ^{Γ} are listed in Table V for Si and Table VI for Ge, respectively.

APPENDIX B: MATRIX ELEMENTS FOR THE PARALLEL MUTUAL INTERACTION

In this appendix, we derive the general expression of the matrix elements for the parallel mutual interaction U_0 between two-electron product states denoted by $\mid l_1l_2;L0\rangle$ and $\mid l_1'l_2';L'0\rangle$. We first introduce the notation $\omega(l_1l_2;LM)$ for a general two-electron product state, viz.,

$$\omega(l_1l_2;LM)\equiv \sum_{m_1m_2} C(l_1l_2L;m_1m_2M)Y_{l_1m_1}(\Omega_1)Y_{l_2m_2}(\Omega_2)R_{l_1}(r_1)R_{l_2}(r_2) \, , \tag{B1}$$

where $C(l_1l_2L;m_1m_2M)$ is the Clebsch-Gordon coefficient,[27] coupling the product of two spherical harmonics $\mid l_1,m_1\rangle$ and $\mid l_2,m_2\rangle$ with the state $\mid L,M\rangle$. $R_{l_1}(r_1)$ and $R_{l_2}(r_2)$ are the radial parts for the two-electron states. If $\vec{r}_1=\vec{r}_1\equiv\vec{r}$, we obtain a useful relation[20]

$$\omega(l_1l_2;LM)=f(l_1l_2,L)Y_{LM}(\Omega)R_{l_1}(r)R_{l_2}(r) \, , \tag{B2}$$

where

$$f(l_1l_2,L)=\left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}\right]^{1/2} C(l_1l_2L;000) \, . \tag{B3}$$

Then the matrix elements concerned here can be written as

$$\langle l_1l_2;L0 \mid v(1,2) \mid l_1'l_2';L'0\rangle=\int \omega(l_1l_2;L0)\frac{2}{\mid \vec{r}_1-\vec{r}_2\mid}\omega(l_1'l_2';L0)d^3r_1d^3r_2 \, , \tag{B4}$$

where the arguments for the two-electron product wave functions $\omega(l_1l_2;L0)$ and $\omega(l_1'l_2';L0)$ are $\vec{r}_1'$ and

TABLE V. The electron–electron-coupling matrices for Si; (ij) is the simplified notation for $(\Gamma_i\Gamma_j)$, the state in which the two electrons are transformed according to the representations Γ_i and Γ_j, respectively.

$G_1^{\Gamma_1}$	(11)	(33)	(55)
(11)	$-\frac{2}{3}$	$\sqrt{2}/3$	$1/\sqrt{3}$
(33)		$-\frac{1}{3}$	$\sqrt{2/3}$
(55)			0

$G_2^{\Gamma_1}$	(11)	(33)	(55)
(11)	$\frac{1}{6}$	$\sqrt{2}/6$	$-\sqrt{3}/6$
(33)		$\frac{1}{3}$	$-1/\sqrt{6}$
(55)			$\frac{1}{2}$

$G_3^{\Gamma_1}$	(11)	(33)	(55)
(11)	$\frac{4}{3}$	$\sqrt{2}/3$	$-2/\sqrt{3}$
(33)		$\frac{5}{3}$	$-2\sqrt{6}/3$
(55)			2

$G_1^{\Gamma_2}$	(33)
(33)	-1

$G_2^{\Gamma_2}$	(33)
(33)	0

$G_3^{\Gamma_2}$	(33)
(33)	-1

$G_1^{\Gamma_3}$	(13)	(31)	(33)	(55)
(13)	$-\frac{2}{3}$	$\frac{1}{3}$	0	$1/\sqrt{3}$
(31)		$-\frac{2}{3}$	0	$1/\sqrt{3}$
(33)			$-\frac{2}{3}$	$-1/\sqrt{3}$
(55)				0

$G_2^{\Gamma_3}$	(13)	(31)	(33)	(55)
(13)	$\frac{1}{6}$	0	0	$-\sqrt{3}/6$
(31)		$\frac{1}{6}$	0	$\sqrt{3}/6$
(33)			$\frac{1}{6}$	$\sqrt{3}/6$
(55)				$\frac{1}{2}$

$G_3^{\Gamma_2}$	(13)	(31)	(33)	(55)
(13)	$-\frac{2}{3}$	$\frac{1}{3}$	0	$1/\sqrt{3}$
(31)		$-\frac{2}{3}$	0	$1/\sqrt{3}$
(33)			$\frac{1}{3}$	$1/\sqrt{3}$
(55)				-1

$G_1^{\Gamma_4}$	(35)	(53)	(55)
(15)	-1	0	0
(53)		-1	0
(55)			-1

$G_2^{\Gamma_4}$	(35)	(53)	(55)
(35)	0	0	0
(53)		0	0
(55)			0

$G_3^{\Gamma_4}$	(35)	(53)	(55)
(35)	0	1	0
(53)		0	0
(55)			-1

$G_1^{\Gamma_5}$	(15)	(51)	(35)	(53)	(55)
(15)	$-\frac{2}{3}$	$\frac{1}{3}$	$\sqrt{2}/3$	$\sqrt{2}/3$	0
(51)		$-\frac{2}{3}$	$\sqrt{2}/3$	$\sqrt{2}/3$	0
(35)			$-\frac{1}{3}$	$\frac{2}{3}$	0
(53)				$-\frac{1}{3}$	0
(55)					-1

$G_2^{\Gamma_5}$	(15)	(51)	(35)	(53)	(55)
(15)	$-\frac{1}{6}$	$\frac{1}{6}$	$-\sqrt{2}/6$	$\sqrt{2}/6$	0
(51)		$-\frac{1}{6}$	$\sqrt{2}/6$	$\sqrt{2}/6$	0
(35)			$-\frac{1}{3}$	$\frac{1}{3}$	0
(53)				$-\frac{1}{3}$	0
(55)					0

$G_3^{\Gamma_5}$	(15)	(51)	(35)	(53)	(55)
(15)	0	$\frac{2}{3}$	0	$-\sqrt{2}/3$	0
(51)		0	$-\sqrt{2}/3$	0	0
(35)			0	$\frac{1}{3}$	0
(53)				0	0
(55)					1

TABLE VI. The electron-electron coupling matrices for Ge; the notation is the same as used in Table II.

$G_1^{\Gamma_1}$	(11)	(55)
(11)	$-\frac{3}{4}$	$\sqrt{3}/4$
(55)		$-\frac{1}{4}$

$G_3^{\Gamma_1}$	(11)	(55)
(11)	$\frac{7}{4}$	$-5\sqrt{3}/4$
(55)		$\frac{13}{4}$

$G_4^{\Gamma_1}$	(11)	(55)
(11)	$\frac{3}{2}$	$-\sqrt{3}/2$
		0

$G_1^{\Gamma_3}$	(55)
(55)	-1

$G_3^{\Gamma_3}$	(55)
(55)	1

$G_4^{\Gamma_3}$	(55)
(55)	$\frac{9}{4}$

$G_1^{\Gamma_4}$	(55)
(55)	-1

$G_3^{\Gamma_4}$	(55)
(55)	-1

$G_4^{\Gamma_4}$	(55)
(55)	0

$G_1^{\Gamma_5}$	(15)	(51)	(55)
(15)	$-\frac{3}{4}$	$\frac{1}{4}$	$\sqrt{2}/4$
(51)		$-\frac{3}{4}$	$\sqrt{2}/4$
(55)			$-\frac{1}{2}$

$G_3^{\Gamma_5}$	(15)	(51)	(55)
(15)	$-\frac{1}{4}$	$\frac{3}{4}$	$-\sqrt{2}/4$
(51)		$-\frac{1}{4}$	$-\sqrt{2}/4$
(55)			1/2

$G_4^{\Gamma_5}$	(15)	(51)	(55)
(15)	$-\frac{1}{2}$	$-\frac{1}{2}$	$1/\sqrt{2}$
(51)		$-\frac{1}{2}$	$1/\sqrt{2}$
(55)			$-\frac{3}{2}$

$\vec{r}_2{}'$, which are defined in an ellipsoidal coordinate system with an eccentricity factor ξ. It will be more convenient to express the product wave functions $\omega(l_1 l_2;L0)\ \omega(l'_1 l'_2;L0)$ in Eq. (B4) as linear combinations of product wave functions of the form $\omega(l_1 l'_1;L_1 M_1)\omega(l_2 l'_2;L_2 M_2)$ in which the two-electron states having the same coordinate are combined together. We use the relation[20]

$$\omega(l_1 l_2;L0)\omega(l'_1 l'_2;L'0)=\sum_{L_1 L_2 F} D(l_1 l_2 l'_1 l'_2 LL';L_1 L_2 F)\times\sum_{M_1 M_2}\omega(l_1 l'_1;L_1 M_1)\omega(l_2 l'_2;L_2 M_2)C(L_1 L_2 F;M_1 M_2 0)\,, \tag{B5}$$

where

$$D(l_1 l_2 l'_1 l'_2 LL';L_1 L_2 F)\equiv C(LL'F;000)[(2l+1)(2L'+1)(2L_1+1)(2L_2+1)]^{1/2}\begin{Bmatrix} l_1 & l_2 & L \\ l'_1 & l'_2 & L' \\ L_1 & L_2 & F \end{Bmatrix}. \tag{B6}$$

The last factor appearing in Eq. (B6) is the standard 9-j symbol.[20] Substituting Eq. (B5) into Eq. (B4), we find that these matrix elements can be expressed as linear combinations of the integrals

$$I\equiv\int\omega(l_1 l'_1;L_1 M_1)\frac{2}{|\vec{r}_1-\vec{r}_2|}\omega(l_2 l'_2;L_2 M_2)d^3r_1 d^3r_2\,. \tag{B7}$$

Equation (B7) can be readily carried out in momentum space ($\vec{q}$ space). Using Eq. (B2), we can express the Fourier transform of $\omega(l,l';LM)$ in $\vec{q}$ space as

$$\tilde{\omega}(ll';LM)=\phi_{ll'L}(q')Y_{LM}(\Omega'_q)\,, \tag{B8}$$

with

$$\phi_{ll'L}(q')\equiv 4\pi(i)^L\int R_l(r')R_{l'}(r')j_L(q'r')r'^2dr'f(ll',L)\,, \tag{B9}$$

where the coordinates $\vec{q}\,'$ are defined in an ellipsoidal system $\vec{q}\,'=(q_x,q_y,\zeta q_z)$ and j_L is the spherical Bessel function. Carrying out Eq. (B7) in $\vec{q}$ space, we find that

$$I=\int\tilde{\omega}(l_1 l'_1;L_1 M_1)\frac{8\pi}{q^2}\tilde{\omega}(l_2 l'_2;L_2 M_2)\frac{d^3q}{(2\pi)^3}=\xi(l_1 l'_1 L_1;l_2 l'_2 L_2)\int\frac{Y_{L_1 M_1}(\Omega)Y_{L_2 M_2}(\Omega)}{\zeta[1+(\zeta^{-2}-1)\cos^2\theta]}d\Omega\,, \tag{B10}$$

with

$$\xi(l_1l'_1L_1;l_2l'_2L_2)\equiv\int\phi_{l_1l'_1L_1}(q')\phi^*_{l_2l'_2L_2}(q')\frac{dq'}{\pi^2} \tag{B11}$$

Substituting Eqs. (B5) and (B10) into Eq. (B4), we find the final expression

$$\langle l_1l_2;L0\,|\,v(1,2)\,|\,l'_1l'_2;L'0\rangle=\sqrt{4\pi}\sum_{FL_1L_2}D(l_1l_2l'_1l'_2LL';L_1L_2F)f(L_1L_2,F)\xi(l_1l'_1L_1;l_2l'_2L_2)a_F(\zeta)\ , \tag{B12}$$

where we have used the relation [see Eqs. (B1) and (B2)]

$$\sum_{M_1M_2}C(L_1L_2F;M_1M_20)Y_{L_1M_1}(\Omega)Y_{L_2M_2}(\Omega)=f(L_1L_2,F)Y_{F0}(\Omega)$$

and defined the coefficients

$$a_F(\zeta)\equiv\int\frac{Y_{F0}(\Omega)}{\zeta[1+(\zeta^{-2}-1)\cos^2\theta]}\frac{d\Omega}{\sqrt{4\pi}}\ . \tag{B13}$$

Using Eq. (B12), we can estimate the ratio for the square of the coupling of the states $|\,ll;L0\rangle$ and $|\,ll;00\rangle$ with the state $|\,00;00\rangle$. We obtain

$$\left|\frac{\langle ll;L0\,|\,v(1,2)\,|\,00;00\rangle}{\langle ll;00\,|\,v(1,2)\,|\,00;00\rangle}\right|^2=\left|\frac{C(llL,000)}{C(ll0;000)[(2L+1)]^{1/2}}\frac{a_L(\zeta)}{a_0(\zeta)}\right|^2 .$$

Explicitly, we find

$$\left|\frac{\langle 11;20\,|\,v(1,2)\,|\,00;00\rangle}{\langle 11;00\,|\,v(1,2)\,|\,00;00\rangle}\right|^2\simeq\begin{cases}0.0408 & \text{for Si}\\ 0.1198 & \text{for Ge}\ ,\end{cases}$$

$$\left|\frac{\langle 22;20\,|\,v(1,2)\,|\,00;00\rangle}{\langle 22;00\,|\,v(1,2)\,|\,00;00\rangle}\right|^2\simeq\begin{cases}0.0291 & \text{for Si}\\ 0.0855 & \text{for Ge}\ ,\end{cases}$$

and

$$\left|\frac{\langle 22;40\,|\,v(1,2)\,|\,00;00\rangle}{\langle 22;00\,|\,v(1,2)\,|\,00;00\rangle}\right|^2\simeq\begin{cases}0.0032 & \text{for Si}\\ 0.0278 & \text{for Ge}\ ,\end{cases}$$

From Eq. (B12), we also find that

$$\langle 12;20\,|\,v(1,2)\,|\,00;20\rangle\propto C(122;000)=0\ .$$

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