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Ground-state configuration of double acceptors in silicon and germanium

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The ground-state manifold of double-acceptor impurities in Si and Ge shows small splittings. An explanation of this fine structure is presented. It is based on a calculation containing tight-binding p functions at the top of the valence band. The approach takes spin-orbit coupling and hole-hole interaction fully into account. The results indicate that the various experimentally observed orderings of levels may be explained by a short-range hole-hole nearest-neighbor intersite interaction that, because of dynamical effects, may in some cases be attractive.

I. INTRODUCTION

Infrared spectra of double-acceptor (DA) impurities in germanium and silicon show, in general, main features similar to those of single acceptors. Even though the double-acceptor levels are much deeper, the $(1s)^2 \rightarrow (1s2p)$ transitions are, for the two-hole case, very similar to the one-hole $(1s) \rightarrow (2p)$ transitions not only with respect to the spacing of the lines but also in what concerns oscillator strengths. This fact indicates that the $1s$ hole in the two-hole excited state screens the doubly charged central cell, but exchange and correlation effects between holes in the $(1s)$ and $(2p)$ orbitals are negligible because of their small overlap. Transitions in many-electron systems that resemble one-electron atoms are known as the Rydberg limit in atomic physics. Fiorentini and Baldereschi[1] described the DA excited states by means of a semiempirical approach. They modified their very successful single-acceptor calculations by introducing an additional Hartree screening potential arising from the remaining $(1s)$ hole in the $(1s2p)$ states.

However, there is a remarkable difference between double- and single-acceptor spectra in high resolution. All DA spectra in germanium[2-4] and in silicon[5-8] show small splittings with peak heights which are temperature dependent. These features and their temperature dependence indicate a split ground-state manifold *and* excited states which are split as well.

The purpose of the present contribution is to analyze the physical factors[9] that contribute to the splittings of the ground-state manifold. The magnitude of the various effects is paramount here. Table I contains the first and second ionization potentials of Be and Zn in both Ge and Si. The ionization potentials of various single acceptors in both semiconductors are listed for the sake of comparison. Also listed in Table I is the number of semiconductor atoms enclosed in a sphere of the radius equal to the Bohr radius of that particular energy. The latter was calculated using values for hydrogen or helium, with the semiconductor dielectric constant and the ionization potentials as sole input. The numbers in Table I point out that although double acceptors in Ge can be envisioned as shallow-level impurities, and treated in the first approximation by means of an effective-mass theory,[10,11] the same impurities in Si are much deeper and therefore atomiclike, i.e., related to the properties of only a few unit cells.

The observed splittings[2-8] of levels in the DA are in the range of 0.3–0.6 meV. These numbers are 2 orders of magnitude smaller than the first ionization potential for the Ge-based impurities, and 3 orders of magnitude for the Si-based impurities. The understanding of these disparate numbers has been a puzzlement for several years, and the central focus of the present work.

Section II provides a cluster calculation for an impurity surrounded by 16 semiconductor atoms. The approach includes all one-particle effects capable of splitting the ground-state manifold and Sec. III provides a detailed study of hole-hole correlations. The results are analyzed in Sec. IV, and Sec. V contains the conclusions.

II. CLUSTER CALCULATION FOR DOUBLE ACCEPTORS

As indicated by Table I, the acceptor states of deep impurities are confined to a few semiconductor unit cells surrounding the impurity central cell. The Zn- and Be-related impurities in Si are examples of this kind. In order to discuss the splitting of their DA ground-state manifold, we calculate two-hole DA states for a cluster with tetrahedral symmetry that consists of the impurity atom, four nearest (NN) and 12 next-nearest (NNN) semiconductor atom neighbors.

Our calculation is based on atomic np functions $|\alpha_{ij},\sigma\rangle$ only. The p orbitals are labeled $\alpha=x,y,z$ according to the cubic axes of the diamond lattice and σ denotes the spin. The index $ij=00$ specifies the impurity site. The four NN are specified by $i=1,2,3,4$ and $j=0$. The 12 NNN outer atoms are indicated by $i=1,2,3,4$ and $j=1,2,3$, corresponding to the three j neighbors of the four i NN's. (When detailed identification is not necessary the single letter i label is supposed to run over the 17 sites of the cluster.) The top of the semiconductor valence band, because of symmetry, contains only p states; inclusion of other symmetries is not necessary. If we were interested in the overall position of the ground-state man-

TABLE I. Ionization energies E_i (meV) and the number N_B of semiconductor atoms contained in a sphere of the effective Bohr radius of various acceptors in Ge and Si.

	Ge		Si	
Impurity	E_i	N_B	E_i	N_B
Be^0	25	1120	192	6.9
Be^-	58	717		
Zn^0	33	487	320	1.5
Zn^-	87	212	620	1.6
Mg^0	36	375		
Cd^0	55	105		
Hg^0	92	22		
B	11	13 100	46	500
Al	10	17 500	57	263
Ga	11	13 100	65	177
In	11	13 100	158	12

TABLE II. Two single-particle total angular momenta j_1, j_2 combined to antisymmetric two-particle states of total angular momentum F.

j_1	j_2		F	
$\frac{3}{2}$	$\frac{3}{2}$	$\Gamma_8\otimes\Gamma_8$	2	$\Gamma_3\oplus\Gamma_5$
			0	Γ_1
$\frac{3}{2}$	$\frac{1}{2}$	$\Gamma_8\otimes\Gamma_7$	1	Γ_4
			2	$\Gamma_3\oplus\Gamma_5$
$\frac{1}{2}$	$\frac{1}{2}$	$\Gamma_7\otimes\Gamma_7$	0	Γ_1

ifold relative to the semiconductor valence band, we would have to include at least the *s* orbitals as well. However, our goal is to understand small splittings in the energy range of a few meV, for which the inclusion of only *p* functions is sufficient.

For the same reason we may take into account only those terms of the DA Hamiltonian that are capable of splitting the two-hole states built up from only the *p* orbitals. We study the influence of spin-orbit coupling, and intrasite and nearest-neighbor-site Coulomb and exchange interactions. All other mechanisms either only shift the entire manifold or are considered to be negligible. We mention explicitly the tetrahedral crystal field. This contribution to the Hamiltonian acts only on the orbital degrees of freedom of the states. However, the one-particle orbital degrees of freedom are all *p* states that do *not* split in the tetrahedral crystal field.

The following six (three α orbital and two σ spin degrees of freedom) linear combinations:

$$|\alpha,\sigma\rangle \equiv \sum_{ij} c_{ij}|\alpha_{ij},\sigma\rangle \tag{1}$$

form the single-particle basis of this approach. The coefficients c_{00}, $c_{i0}=-c_{00}\exp(-\sqrt{3}/a_0)$ for $i\neq 0$, and $c_{ij}=c_{00}\exp(-2\sqrt{2}/a_0)$ for $i,j\neq 0$ model an *s*-like envelope function of these acceptor states. The magnitude of the effective Bohr radius a_0 determines the extent of the acceptor state. We do not make explicit use of the exponential form of the coefficients given above. The theory described below is valid for any value of the coefficients that corresponds to a fully symmetric function with only three real parameters c_{00}, $c_{i0}=-c_{NN}$ for $i\neq 0$, and $c_{ij}=c_{NNN}$ for $i,j\neq 0$. Normalization requires that $c_{00}^2+4c_{\rm NN}^2+12c_{\rm NNN}^2=1$.

Based on these single-particle states, we construct a convenient antisymmetrized (Pauli principle) two-particle basis in three steps.

(i) Taking spin-orbit coupling into account requires the one-particle basis to be written in terms of the total angular momentum of the single-hole state $j=\frac{3}{2}$, $m_j=\frac{3}{2},\ldots,-\frac{3}{2}$ and $j=\frac{1}{2}$, $m_j=\pm\frac{1}{2}$. This is at the same time the proper symmetry classification of the single-hole states: The symmetry group of the 17-atom cluster is T_d. States with $j=\frac{3}{2}$ ($j=\frac{1}{2}$) transform according to the representation Γ_8 (Γ_7) of the double group $\overline{T}_d$.

(2) The six single-hole states are now combined to yield 15 antisymmetrized two-particle states with total angular-momentum quantum numbers F and M_F. They are listed in Table II together with their point-group symmetries.

(3) The tetrahedral symmetry splits the $F=2$ states into Γ_3 and Γ_5 components. These components may be calculated by the usual projection-operator technique:

$$\Gamma_3\!: \begin{cases} \sqrt{1/2}\,|F=2,\ M_F=2\rangle+\sqrt{1/2}\,|F=2,\ M_F=-2\rangle \\ |F=2,\ M_F=0\rangle\ , \end{cases} \tag{2a}$$

$$\Gamma_5\!: \begin{cases} \sqrt{1/2}\,|F=2,\ M_F=2\rangle-\sqrt{1/2}\,|F=2,\ M_F=-2\rangle \\ |F=2,\ M_F=1\rangle \\ |F=2,\ M_F=-1\rangle\ . \end{cases} \tag{2b}$$

These successive steps provide the unitary transformation between the 15 antisymmetric states $|\alpha,\sigma;\beta,\sigma'\rangle$ and the basis with proper symmetry quantum numbers.

The Hamiltonian matrix written in this basis has a very simple structure: The *spin-orbit coupling* matrix is diagonal. It has a sixfold eigenvalue equal to 0 (both particles have $j=\frac{3}{2}$), an eightfold eigenvalue Δ (one particle has $j=\frac{3}{2}$, the other $j=\frac{1}{2}$), and a nondegenerate eigenvalue 2Δ (both particles have $j=\frac{1}{2}$). The spin-orbit coupling parameter is given by

$$\Delta=\sum_{i=0}^{16} c_i^2\Delta_i \tag{3}$$

where Δ_i is the atomiclike spin-orbit splitting of an $(np)^2$ configuration of atom i. The *Coulomb interaction* only mixes two-hole states with identical symmetry, with a resulting 2×2 matrix for the Γ_1 states, two identical 2×2 matrices for the Γ_3 states, and three identical 2×2 matrices for the Γ_5 states. The Γ_4 states occur only once and do not couple to any other state.

III. THE COULOMB INTERACTION

Some remarks on the calculation of the Coulomb contribution are in order. The matrix elements of the Coulomb repulsion $\hat{V}$ are a linear combination of matrix elements of the following type:

$$\langle \alpha,\sigma;\beta,\sigma'|\hat{V}|\gamma,\sigma'';\delta,\sigma'''\rangle = \sum_{i,j,l,m=0}^{16} c_i^* c_j^* c_l c_m \langle \alpha_i,\sigma;\beta_j,\sigma'|\hat{V}|\gamma_l,\sigma'';\delta_m,\sigma'''\rangle \; . \tag{4}$$

They contain a complicated fourfold sum over all sites. However, only two types of terms contribute significantly to this sum:

(1) The *intrasite* correlation matrix elements consist of those terms of Eq. (4) with $i=j=l=m$. They reduce to a simple site sum of expressions I_i:

$$(\langle \alpha,\sigma;\beta,\sigma'|\hat{V}|\gamma,\sigma'';\delta\sigma'''\rangle)_{\text{intra}} = \sum_{i=0}^{16} c_i^4 I_i \tag{5}$$

with

$$I_i = \delta_{\sigma,\sigma''}\delta_{\sigma',\sigma'''}\int d\mathbf{r}_1 d\mathbf{r}_2 \hat{V}(r_1-r_2)\phi^*_{\alpha,i}(\mathbf{r}_1)\phi^*_{\beta,i}(\mathbf{r}_2)\phi_{\gamma,i}(\mathbf{r}_1)\phi_{\delta,i}(\mathbf{r}_2)$$
$$-\delta_{\sigma,\sigma'''}\delta_{\sigma',\sigma''}\int d\mathbf{r}_1 d\mathbf{r}_2 \hat{V}(r_1-r_2)\phi^*_{\alpha,i}(\mathbf{r}_1)\phi^*_{\beta,i}(\mathbf{r}_2)\phi_{\delta,i}(\mathbf{r}_1)\phi_{\gamma,i}(\mathbf{r}_2) \; . \tag{6}$$

[$\phi_{\alpha,i}(\mathbf{r})$ denotes a p function of the atom at site i, $\alpha=x,y,z$.] The integrals in I_i are well known in atomic physics. They take three different nonvanishing values:

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \hat{V}(r_1-r_2)\phi^*_{\alpha,i}(\mathbf{r}_1)\phi^*_{\beta,i}(\mathbf{r}_2)\phi_{\gamma,i}(\mathbf{r}_1)\phi_{\delta,i}(\mathbf{r}_2) = \begin{cases} U_i & \text{if } \alpha=\beta=\gamma=\delta \\ U_i-2J_i & \text{if } \alpha=\gamma\neq\beta=\delta \\ J_i & \text{if } \alpha=\delta\neq\beta=\gamma \text{ or } \alpha=\beta\neq\gamma=\delta \; . \end{cases} \tag{7}$$

The largest of these integrals, U_i, appears in all the diagonal elements of the Hamiltonian matrix and therefore contributes only a uniform shift, but not to the splitting of the energy levels. Hence all splittings due to intra-atomic correlations depend on one single parameter

$$J = \sum_{i=0}^{16} c_i^4 J_i \tag{8}$$

which may be estimated from atomic J_i values ($J_{\text{Ge}} \approx J_{\text{Si}} \approx 380$ meV). It is worth mentioning that restricting ourselves to the study of only intrasite correlations, the Hamiltonian matrix becomes exactly equivalent to the problem of two electrons in an atomic p shell. The resulting splittings satisfy Hund's rule: Nine states in the triplet ^3P term with energy ($-J$), five states in the singlet ^1D term with energy ($+J$) and one state in the singlet ^1S term with energy ($+4J$). The splitting parameter for intra-atomic correlations may be interpreted in the following way: c_i^4 is the probability for the two holes both being at the particular site i. For extended states where the c_i's are not too different, J scales like N_B^{-1}, where N_B is the number of atoms involved in the single-particle state (see Table I). It is obvious that our approach for the 17-atom cluster may be easily generalized to systems of any size. Every additional "shell" of outer atoms adds an additional term to (8), which defines the parameter J.

(2) The nearest-neighbor *intersite* correlations consist of those terms of Eq. (4) where two of the indices i,j,l,m correspond to the 00 site (impurity) and the remaining two to one of the four NN $i0$ sites, and the four analog ($i0$-ij)-pair sum for the NN and NNN atoms. We consider only contributions of bonding neighboring orbitals with large overlap. These states are projections onto the p-state manifold of the four bonding sp hybrids which make up the valence band of the tetrahedrally coordinated semiconductors. Further details may be found in the Appendix, where we discuss briefly the details of the calculation for the impurity site and one of its NN's. Generalization to the bonds between NN and NNN sites is straightforward.

The intersite contributions of the Coulomb interaction are

$$(\langle \alpha,\sigma;\beta,\sigma'|\hat{V}|\gamma,\sigma'';\delta,\sigma'''\rangle)_{\text{inter}} = (\delta_{\sigma,\sigma'''}\delta_{\sigma',\sigma''} - \delta_{\sigma,\sigma'''}\delta_{\sigma',\sigma''})W \quad \text{if} \quad \begin{cases} \alpha=\beta=\gamma=\delta \\ \alpha=\beta\neq\gamma=\delta \\ \alpha=\gamma\neq\beta=\delta \\ \alpha=\delta\neq\beta=\gamma \end{cases}$$
$$=0 \text{ otherwise.} \tag{9}$$

The quantity W, which depends on the explicit form of the p orbitals, on their overlap, and on the c_{ij}, is defined in the Appendix. [Generalization of these results to larger clusters is, once again, straightforward. This generalization changes the parameter W only, and not the structure of (9). The parameter W scales like N_B^{-1}, i.e., with the probability of finding both particles on the same bond.]

IV. RESULTS AND DISCUSSION

The diagonalization of the 15×15 Hamiltonian matrix is straightforward. It has a block structure of six 2×2

matrices (only three different ones, corresponding to the three symmetries Γ_1, Γ_3, and Γ_5), and three (identical, Γ_4) diagonal eigenvalues. The eigenvalues and multiplicities are listed in Table III. The last two columns list the values of the two limiting cases, where either the spin-orbit coupling or the hole-hole Coulomb interaction vanishes. These two limits correspond, respectively, to very deep and very shallow acceptors.

In the deep-impurity limit, where J and W are much larger than Δ, W is probably the largest parameter in the system. It contains direct Coulomb integrals in addition to exchange terms, whereas J consists of exchange terms only. However, screening and dynamic effects may have a significant impact on the magnitude, and even on the sign of W.

If the intersite interaction and the spin-orbit coupling are assumed to vanish ($W=0$ and $\Delta=0$), then, as mentioned above, the problem is atomiclike, and the states may be labeled according to the energy levels of an atomic $(np)^2$ configuration. The eigenvalues E_3 and E_5 correspond to ${}^3P_2$; E_4 corresponds to ${}^3P_1$; E_1 corresponds to ${}^3P_0$. These are the nine lowest states, which satisfy Hund's rules and constitute the ${}^3P$ term. The energy levels E_3' and E_5' of Table III correspond to the term${}^1D_2$, and E_1' constitutes the nondegenerate ${}^1S_0$ term.

Other interactions produce additional splittings.

(1) A crystal field of tetrahedral symmetry acting on the one-particle orbitals. It does *not,* contrary to expectations, split the $F=2$ levels into their Γ_3 and Γ_5 components.

(2) Interatomic hole-hole interactions. On the one hand these are very important since they are a major contribution to the hole-hole interaction. On the other hand, these interatomic Coulomb interactions yield a coupling mechanism of tetrahedral symmetry. This is important as well because, as seen above, the crystal field acting on the single-particle orbitals does not change the fine structure of the states. In contrast to the crystal field, the interatomic interaction is a *two*-particle term. But, similarly to the crystal field, this two-particle interaction acts only on the orbital degrees of freedom. As a result the ${}^1D_2$ states are split by an energy $2W$. The ${}^3P_2$ manifold, however, remains degenerate because the orbital degrees of freedom are still P-like, and the spin degrees of freedom are not affected by this interaction.

(3) Spin-oprbit coupling. The ${}^3P_2$ manifold splits, but only through a combined effect of intersite interactions *and* spin-orbit coupling. Only when Δ and W are *both* nonvanishing are the ${}^3P_2$ states split. This is a remarkable effect which explains the large discrepancies in orders of magnitude of the splittings. The intersite interaction W is, for deep impurities, most likely to be the largest parameter in the problem. It represents the major contribution with tetrahedral, i.e., nonspherical symmetry. Nevertheless the splitting that it causes on the $F=2$, P (ground state) manifold can be very small, because it needs a nonvanishing spin-orbit coupling. For reasonably deep impurities in Si the combined effect of large W and small Δ result in a Γ_3-Γ_5 splitting which is neither too large nor too small, i.e., a few tenths of a meV. This mechanism may answer the puzzling question of how an interaction of the order of 10^2 meV might cause a splitting of less than 1 meV.

It is important to discuss the value (or at least the order of magnitude) of the parameters. For DA in silicon, $\Delta=44$ meV if the contribution arises mostly from the silicon host. It should be smaller for the Be impurity, and considerably larger for Zn and Cd impurities. The values of J and W are much more difficult to estimate, since they depend on a variety of factors: the extent and shape of the impurity p orbitals, the overlap between adjacent Wannier functions, and the extent of the s-like envelope function (the values of the c_{ij} coefficients). An arbitrary but reasonable choice is $J=100$ meV, and $W=300$ meV. This choice yields the following energies (relative to the lowest-energy eigenvalue): $E_3=0.000$, $E_5=1.458$, $E_4=31.319$, $E_1=44.731$, $E_3'=218.638$, $E_5'=817.180$, and $E_1'=1417.907$ meV.

The only levels which can be thermally populated at the low temperatures of the experiments are the *two* lowest ones, one twofold Γ_3 level and a threefold Γ_5 level, separated, in this example, by 1.458 meV. It should be possible to study some of the higher levels (Γ_4 and Γ_1) by far-infrared spectroscopy. The present theory is, however, only applicable to the energy range below the free-hole continuum. Therefore the values for the higher-energy states (resonances in fact, not hydrogenic bound states) are not meaningful in the framework of this approach.

In contrast to Si, the DA's in Ge have a strong spin-orbit coupling. If the magnitude of the effective spin-orbit parameter comes mostly from the Ge atoms, Δ will

TABLE III. Eigenvalues of the 15×15 Hamiltonian matrix as a function of the intrasite correlation parameter J, the intersite correlation parameter W, and the spin-orbit coupling parameter Δ. The first column lists the symmetry of the states and their degeneracy, the third and fourth column list the eigenvalues for two limiting cases.

Symmetry	Eigenvalue	$\Delta=0$	$W=0$ $J=0$
$\Gamma_1(1)$	$E_1'=\frac{3}{2}(J+W)+\Delta+[\frac{1}{4}(\frac{5}{3}J+W-2\Delta)^2+2(\frac{5}{3}J+W)^2]^{1/2}$	$4J+3W$	2Δ
$\Gamma_5(3)$	$E_5'=W+\frac{1}{2}\Delta+\{[\frac{1}{3}(J+W)+\frac{1}{2}\Delta]^2+\frac{8}{9}(J+W)^2\}^{1/2}$	$J+2W$	Δ
$\Gamma_3(2)$	$E_3'=\frac{1}{2}\Delta+[(\frac{1}{3}J+\frac{1}{2}\Delta)^2+\frac{8}{9}J^2]^{1/2}$	$+J$	Δ
$\Gamma_4(3)$	$E_4=\Delta-J$	$-J$	Δ
$\Gamma_1(1)$	$E_1=\frac{3}{2}(J+W)+\Delta-[\frac{1}{4}(\frac{5}{3}J+W-2\Delta)^2+2(\frac{5}{3}J+W)^2]^{1/2}$	$-J$	0
$\Gamma_5(3)$	$E_5=W+\frac{1}{2}\Delta-\{[\frac{1}{3}(J+W)+\frac{1}{2}\Delta]^2+\frac{8}{9}(J+W)^2\}^{1/2}$	$-J$	0
$\Gamma_3(2)$	$E_3=\frac{1}{2}\Delta-[(\frac{1}{3}J+\frac{1}{2}\Delta)^2+\frac{8}{9}J^2]^{1/2}$	$-J$	0

take an approximate value of 290 meV. Additionally DA states in Ge are very extended (except for Hg, see Table I). As a result, the Coulomb interaction parameters are much smaller than Δ. The limiting case of vanishing J and W leads to the well-known analogy between very shallow DA states and a "helium atom" with a negatively charged nucleus and two spin-$\frac{3}{2}$ holes bound to it. Such a very shallow system may be treated in a spherical approximation, because the ground-state splitting due to tetrahedral symmetry can only be observed if the Coulomb interaction is not negligible. However, DA states in Ge show a fine structure, thus they belong to a regime somewhere in between deep and very shallow heliumlike acceptors. As an arbitrary choice, based on atomic properties, the following parameters were chosen: $J=0.4$ meV, $W=0.6$ meV, and $\Delta=290$ meV. They yield the following energies: $E_3=0.000$, $E_5=0.397$, $E_1=2.262$, $E_4=289.734$, $E'_3=290.268$, $E'_5=291.070$, $E'_1=581.006$ meV. Here, as observed experimentally,[2] the *three* lowest levels are very closely spaced (less than 3 meV from each other) and may be thermally populated at the low temperatures of the experiments.

So far, the discussion of the DA-ground-state manifold is based on the assumption that the parameters J and W are essentially determined by single-particle atomic orbitals. This assumption provides the correct order of magnitude in general. However, it is certainly not correct if dynamical many-body and screening effects become important. It is well known that screening effects may change the particle-particle interaction parameters drastically. For shallow DA systems, where the average distance between the quasiparticles is very large, their mutual interaction may be well described by a $1/r$-Coulomb potential screened by a static dielectric function of the host material. At short distances, however, the static "host" screening is no longer effective, and the carriers interact via a bare Coulomb repulsion. At intermediate distances, the details of the dielectric function are more difficult to assess.[12,13] For DA holes it is possible that the nearest-neighbor Coulomb repulsion may be overcompensated by dynamic many-body effects, i.e., the rearrangement of the lattice when two holes are in nearest-neighbor sites (a covalent bond) results in a *decrease* of the total energy, an effective attraction between same-charge carriers. Therefore it might be justified to consider the parameter W as variable not only in magnitude, but also in sign. An attractive nearest-neighbor interaction (negative W values) on the DA ground-state configuration results in a reversed ordering of the energy levels close to the ground state. The regions in the parameter space with various orderings of the energy levels E_3, E_5, and E_1 are shown in Fig. 1. The particular situations described above for Si and Ge DA corresponding to region (a).

The set of parameters $\Delta=44$ meV, $J=100$ meV, and $W=-25$ meV corresponds to region (b) in Fig. 1 and leads to the following energies: $E_5=0.000$, $E_3=0.587$, $E_4=31.906$, $E_1=42.270$, $E'_5=169.812$, $E'_3=219.225$, and $E'_1=446.542$ meV. For this set of parameters the ground-state level is the lowest threefold Γ_5 state. This ordering seems to be the one observed experimentally[7] in Si:Be by analysis of the intensity ratios of the various lines at different temperatures, extrapolated to $T\rightarrow\infty$. This method is based on the premise that all transitions have similar oscillator strengths.

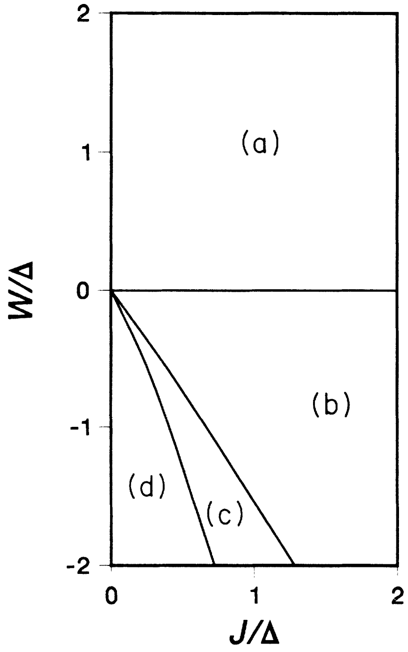

FIG. 1. Various orderings of the two lowest-energy levels corresponding to the symmetries Γ_3, Γ_5, and Γ_1 in the J/Δ-W/Δ parameter plane. The regions (a)–(d) correspond to the following orderings of the two lowest levels: (a) $E_3<E_5$; (b) $E_5<E_3$; (c) $E_5<E_1$; (d) $E_1<E_5$.

Thewalt *et al.*[2] report an inverse level ordering for DA's in Ge, with the Γ_1 level being the ground state. This inversion may be explained in a similar fashion. For $J=0.4$ meV, $W=-1.2$ meV, and $\Delta=290$ meV [region (d) in Fig. 1] the energies take the values $E_1=0.000$, $E_5=0.532$, $E_3=1.334$, $E'_5=290.003$, $E_4=291.068$, $E'_3=291.601$, and $E'_1=580.535$ meV, in agreement with the observations.

The situation for Si:Zn is not completely clear. Dörnen *et al.*[8] report that the ground state of this DA has Γ_1 symmetry. However, recent measurements by Merk *et al.*[5,14] show that the ground state of Si:Zn splits under $\langle 100\rangle$ uniaxial stresses, a fact that is not possible for the nondegenerate Γ_1 level. These authors also observe no splitting for stresses along $\langle 111\rangle$ directions, which seems to indicate that the ground state has Γ_3 symmetry, which exhibits these characteristics, and not Γ_5 symmetry, which splits under *any* uniaxial stress. A Γ_1 ground state would correspond to region (d); a Γ_3 ground state, to region (a) of Fig. 1.

V. SUMMARY AND CONCLUSIONS

This paper provides a simple calculation of double-acceptor ground-state configurations that is capable of explaining the fine structure of many DA states, both deep and shallow. The approach is based on a two-hole calculation in a cluster of arbitrary extent. The one-particle orbitals are taken to be a proper linear combination of atomiclike p states, i.e., the tight-binding p states at the top of the group-IV semiconductor valence band (the fourfold Γ_8 symmetry and the twofold Γ_7 split-off band). This linear combination contains, in its approximately exponentially decaying coefficients, the s-like envelope characteristic of the ground state of these impurities.

The qualitative results of the calculation are very general and revealing.

(a) The particle-particle repulsion decreases in importance as the impurities become shallower; the effect decreases proportionally to the number of host atoms encompassed in the impurity envelopes.

(b) Without inclusion of spin-orbit interaction the particle-particle interaction leaves the ninefold ^3P ground level unsplit.

(c) When the spin-orbit interaction is included, the particle-particle intrasite interaction only splits the sixfold ground-state manifold into an unsplit ("accidentally" degenerate) quintet $\Gamma_3 \oplus \Gamma_5$ and a singlet Γ_1.

(d) The single-particle effects of the tetrahedral crystal field cannot, under any circumstances, split the Γ_3 and Γ_5 levels; this fact can be easily understood based on the fact that the tetrahedral crystal field does not split the Γ_8 quartet at the top of the valence band.

(e) The combined effect of the spin-orbit coupling and the intersite particle-particle interaction *do* split the Γ_3 and the Γ_5 levels; the ordering of the levels depends on the signs of the parameters, but the effect is very small, with splittings of the order of 0.5 meV for interaction and spin-orbit parameters of the order of 50 meV.

Quantitative analysis indicates that for *normal, repulsive* intersite particle-particle interaction, the phenomenological Hund's rules apply, and the higher multiplicity and higher-angular-momentum $\Gamma_3 \oplus \Gamma_5$ manifold should be lower in energy than the Γ_1 level. Reversed level ordering might be explained by many-body lattice effects, leading to an *attractive* hole-hole intersite interaction W. The attractive character would result from a displacement of the nuclei when the two holes are in neighboring sites, so as to produce a lowering of the total energy. This effect, a net attractive interaction mediated by lattice distortions, is the main cause of superconductivity in metals[15] and has been explored in semiconductors under the name of negative-U centers.[16,17] This phenomenon of inverted level ordering deserves further investigation, both theoretical and experimental.

It should be emphasized that the analysis presented here for an attractive W neither explains nor justifies the existence of such an attractive interaction. It has simply been assumed, for the current purposes, that such a sign reversal may take place, and thereafter its consequences explored. The sign and the explicit value of W must depend on the details of the electronic structure of the impurity center, on the local vibrational modes of the system, and on the dynamics of the electron-phonon interaction. Such study is beyond the scope of the present paper. It is nonetheless important to realize that such effective attraction is possible, that it has been proposed before in a variety of contexts, and that it explains in a natural way the reverse ordering of levels reported experimentally. It is also possible (although neither necessary nor likely) that the same strong electron-lattice interaction that is responsible for the sign reversal of W may produce a lattice distortion with a consequent lowering of the point symmetry; if such is the case the problem should be reexamined taking into account the new group-theoretical properties of the system.

The study of DA spectra under uniaxial stress is a very powerful experimental tool. The theoretical analysis of spectra under uniaxial stress requires a further extension of this approach. Some general results can be stated.

(i) Under uniaxial stress all levels are nondegenerate, with the possible exception of stresses along symmetry directions, where a maximum degeneracy of 2 is allowed for some representations.

(ii) As a consequence of (i) all levels with Γ_4 and Γ_5 symmetry should split under *any* stress.

(iii) The Γ_3-symmetry levels should split in general, except for uniaxial stresses along $\langle 111 \rangle$.

(iv) The Γ_4- and Γ_5-symmetry levels should split in general into three nondegenerate levels, except for uniaxial stresses along $\langle 100 \rangle$ and $\langle 111 \rangle$, where they split into a singlet and a doublet.

It should be emphasized that, in any case, the maximum number of lines is the dimension of the space under consideration, i.e., 15. The problem is therefore always susceptible to easy numerical handling, assuming that the relevant parameters (spin-orbit coupling, particle-particle interactions, and stress-induced energies) are known.

In addition, in order to understand the spectra of DA states fully, a more detailed analysis of the excited states is required. The Si:Be and Si:Zn double-acceptor[2,3,7,14] spectra clearly indicate additional splittings of the excited states. These splittings are most likely caused by the interaction between the outer hole with the remaining 1s hole, which cannot be explained by the single-particle approach of Fiorentini and Baldereschi.[1]

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APPENDIX

This appendix provides some brief remarks on the calculation of the important intersite contributions to the matrix elements (4). To determine the importance of the various contributions, the atomic p functions are written in terms of *directed* orbitals, which are simpler to interpret. For each (00-i0) site pair, the p functions on each site are expressed as linear combinations of the directed p orbitals, i.e., one p function which lies along the bond and two perpendicular p functions. For example, for the sites

00 at the origin (the impurity) and the host site 10 along the [1, −1, −1] direction, the directed orbitals at the host atom 10 are $\Phi_{10\to00}=\sqrt{1/3}(-\phi_{x,10}+\phi_{y,10}+\phi_{z,10})$ which points toward the center of the cluster, and

$$\Psi_{10\to00}=\sqrt{1/2}(\phi_{x,10}+\phi_{y,10})$$

and

$$\Theta_{10\to00}=\sqrt{1/6}(-\phi_{x,10}+\phi_{y,10}-2\phi_{z,10})$$

which are orthogonal to $\Phi_{10\to00}$ and to each other. Notice that the functions $\Phi_{ij\to kl}$ are just the *p* component of the familiar *sp* hybrids, commonly used in building the group-IV element valence states. Since the *s* components are neglected—only the top of the valence band contributes to the studied effects—it is not possible to build four orthogonal tetrahedral lobes at once. Thus each [00-*i*0] pair has to be expressed in terms of a different set of linear combinations of the same three functions.

For the three central atomic function $\phi_{\alpha,00}$, four transformations are used. In considering the (00-10) pair the three linear combinations are $\Phi_{00\to10}=\sqrt{1/3}(\phi_{x,00}-\phi_{y,00}-\phi_{z,00})$, which points toward the 10 site, and $\Psi_{00\to10}=\sqrt{1/2}(\phi_{x,00}+\phi_{y,00})$ and $\Theta_{00\to10}=\sqrt{1/6}(\phi_{x,00}-\phi_{y,00}+2\phi_{z,00})$, which are orthogonal to $\Phi_{00\to10}$ and to each other.

For every integral corresponding to a (00-*i*0) pair [and similarly to (*i*0-*ij*) pairs] the Cartesian *p* functions are expressed in terms of these new rotated *p* functions. This procedure yields in principle 81 "new" integrals for each Cartesian term. However, only *one single term* is kept in the calculations: that contains only two $\Phi_{ij\to kl}$ functions and two $\Phi_{kl\to ij}$ functions. These are the only states having a significant overlap; all other integrals may be neglected.

The sum over the four bonds (12 bonds for the outer "shell") simplifies the matrix elements significantly: for all cases $\alpha,\beta,\gamma,\delta$ except those listed in (9), the signs of the terms alternate and the sum over sites cancels exactly. The result (9) contains a constant *W*, which is given by

$$\begin{aligned}W=\tfrac{8}{9}c_{00}^2c_{\mathrm{NN}}^2\Bigg[&\int d\mathbf{r}_1d\mathbf{r}_2\hat{V}(r_1-r_2)|\Phi_{00\to10}(\mathbf{r}_1)|^2|\Phi_{10\to00}(\mathbf{r}_2-\mathbf{R}_{10})|^2\\&+2\int d\mathbf{r}_1d\mathbf{r}_2\hat{V}(r_1-r_2)\Phi^*_{00\to10}(\mathbf{r}_1)\phi^*_{10\to00}(\mathbf{r}_2-\mathbf{R}_{10})\Phi_{10\to00}(\mathbf{r}_1-\mathbf{R}_{10})\Phi_{00\to10}(\mathbf{r}_2)\Bigg]\\+\tfrac{8}{3}c_{\mathrm{NN}}^2c_{\mathrm{NNN}}^2\Bigg[&\int d\mathbf{r}_1d\mathbf{r}_2\hat{V}(\mathbf{r}_1-\mathbf{r}_2)|\Phi_{10\to11}(\mathbf{r}_1-\mathbf{R}_{10})|^2|\Phi_{11\to10}(\mathbf{r}_2-\mathbf{R}_{11})|^2\\&+2\int d\mathbf{r}_1d\mathbf{r}_2\hat{V}(r_1-r_2)\Phi^*_{10\to11}(\mathbf{r}_1-\mathbf{R}_{10})\Phi^*_{11\to10}(\mathbf{r}_2-\mathbf{R}_{11})\Phi_{11\to10}(\mathbf{r}_1-\mathbf{R}_{11})\Phi_{10\to11}(\mathbf{r}_2-\mathbf{R}_{10})\Bigg]\,.\end{aligned}\tag{A1}$$

This parameter *W*, as is obvious from (A1), contains both direct Coulomb integrals and exchange terms.

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[1] V. Fiorentini and A. Baldereschi, Solid State Commun. **69**, 953 (1989).

[2] M. L. W. Thewalt, D. Labrie, I. J. Booth, B. P. Clayman, E. C. Lightowlers, and E. E. Haller, Physica B&C **146B**, 47 (1987); M. L. Thewalt, B. P. Clayman, and D. Labrie, Phys. Rev. B **32**, 2663 (1985).

[3] W. J. Moore, J. Chem. Phys. Solids **32**, 93 (1971); Phys. Rev. B **29**, 7062 (1984).

[4] T. A. Callot and J. W. MacKay, Phys. Rev. **161**, 698 (1967).

[5] E. Merk, J. Heyman, and E. E. Haller, Solid State Commun. **72**, 851 (1989), and private communication.

[6] R. K. Crough, J. B. Robertson, and T. E. Cilimer, Phys. Rev. B **5**, 3111 (1972).

[7] J. Heyman, A. Giesekus, L. M. Falicov, and E. E. Haller, Bull. Am. Phys. Soc. **35**, 279 (1990), and private communication.

[8] A. Dörnen, R. Kienle, K. Thonke, P. Stolz, G. Pensl, D. Grünebaum, and N. A. Stolwijk, Phys. Rev. B **40**, 12 005 (1989).

[9] N. Binggeli, Doctoral Thesis, Institut de Physique Appliquée Ecole Polytechnique Fédérale de Lausanne, 1985 (unpublished).

[10] C. Kittel and A. H. Mitchell, Phys. Rev. **96**, 1488 (1954).

[11] C. Kittel, *Introduction to Solid State Physics,* 6th ed. (Wiley, New York, 1986), Chap. 8.

[12] J. S.-Y. Wang and C. Kittel, Phys. Rev. B **7**, 713 (1973).

[13] W. E. Pickett, M. L. Cohen, and C. Kittel, Phys. Rev. B **20**, 5050 (1979).

[14] E. Merk (private communication).

[15] See, for instance, C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), Chap. 8.

[16] P. Pincus, P. Chaikin, and C. F. Coll III, Solid State Commun. **12**, 1265 (1973).

[17] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).