Electronic states of silicon vacancy. I. Covalent states*

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Self-consistent generalized valence bond (GVB) and configuration-interaction calculations have been performed for a cluster model of the neutral vacancy in silicon. Three low-lying states (^1E, $^3T_1$, $^5A_2$) are found to possess one electron in dangling-bond orbitals on each of the four silicon atoms around the defect. Of these three covalent states, the ^1E is found to be the ground state with the excitation energies to the $^3T_1$ and $^5A_2$ states being 0.17 and 0.60 eV, respectively. The shapes of the GVB orbitals for all three states are found to be quite similar.

I. INTRODUCTION

The electronic structure of vacancies in silicon has been the subject of numerous experimental[1] and theoretical[2] investigations. From a conceptual viewpoint, the most useful model of an isolated vacancy is the Coulson-Kearsley[3] defect molecule. This model has been used as the basis for a number of approximate calculations of the electronic structure of the vacancy, as well as used to explain the EPR spectra of the positive and negative charge states of the vacancy. However, the model is inherently a molecular orbital (MO) model and as such contains inadequacies.

First, the calculations to date using the MO approach lack a predictive capability. That is, similar calculations give different orderings for the electronic states, thus not conclusively predicting whether the ground state of the vacancy is a singlet or triplet.[4] Second, the resulting wave functions provide little information as to the nature of the states (e.g., what the bonds look like). Furthermore, the effects of correlation are hard to include and interpret. These problems are inherent in an MO description of virtually any system, but can be eliminated by using a better description.

Our approach to eliminating these problems in the MO description is with the generalized valence-bond[5] (GVB) description. In the GVB method the orbitals are solved self-consistently, while simultaneously including the dominant electron correlation effects. Inclusion of such correlation effects self-consistently is most important for cases, such as the silicon vacancy, for which there are very weak or broken bonds. The GVB wave function results in a description with localized dangling-bond orbitals at the vacancy, leading to a simple valence-bond model that correctly predicts the nature and ordering of the states of the vacancy.

First (Sec. II), we will present a qualitative description of the states expected for the neutral vacancy based on the simple valence-bond picture. Second (Sec. III), the computational details will be presented. Then we present the results (Sec. IV) followed by a discussion (Sec. V) and our conclusions (Sec. VI).

II. QUALITATIVE DESCRIPTION OF THE STATES

A. Covalent states

In the valence-bond (VB) description of the vacancy there is a singly occupied "dangling-bond orbital" on each of the four neighboring Si atoms, pointed at the vacancy site. In the zero-order description of the vacancy, these four localized orbitals, ϕ_a, ϕ_b, ϕ_c, and ϕ_d, are combined with an appropriate spin function χ and antisymmetrized,

$$\mathcal{C}(\phi_a\phi_b\phi_c\phi_d\chi)$$

($\mathcal{C}$ is the antisymmetrizer or determinant operator). This leads to two singlet states, three triplet states, and a quintet state.[6] A typical singlet state will be represented[7] as

$$\tag{1}$$
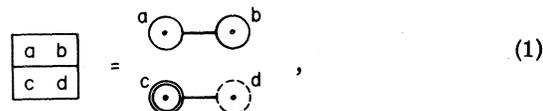
indicating a bond between orbitals a and b (in the plane of the paper) and a bond between orbitals c and d (c above the plane, d below). A typical triplet state has the form

$$\tag{2}$$
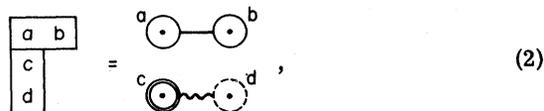
where the wavy line indicates a triplet-coupled pair of orbitals. The quintet state can be represented

$$
\begin{array}{|c|}
\hline
a \\
\hline
b \\
\hline
c \\
\hline
d \\
\hline
\end{array} \quad , \tag{3}
$$

indicating high-spin coupling of all four orbitals.

As discussed later, for tetrahedral symmetry the two singlet states are degenerate, leading to a ^1E state; the three triplet states are degenerate, leading to a $^3T_1$ state, while the quintet is a $^5A_2$ state. These six states are collectively referred to as the *covalent* states, since each has one electron on each of the four silicon atoms surrounding the vacancy.

The overlaps of the vacancy orbitals are small $(S = 0.08)^8$ and hence the ^1E, $^3T_1$, and $^5A_2$ states are expected to be close in energy. However, the overlap is large enough for the bonding effects to dominate the electron-electron exchange interactions leading to a ^1E ground state, the $^3T_1$ state at 0.18 eV (relative to the ^1E) and the $^5A_2$ state at 0.60 eV. (Recall that the ^1E state has two weak bonds, the $^3T_1$ one, and the $^5A_2$ none.)

B. Ionic states

Retaining the simple picture in which there are only four localized orbitals for the electrons, additional excited states must involve two electrons in at least one dangling-bond orbital, e.g.,

$$
\begin{array}{|c|c|}
\hline
a & a \\
\hline
c & d \\
\hline
\end{array} \quad = \quad \text{(diagram)} \quad . \tag{4}
$$
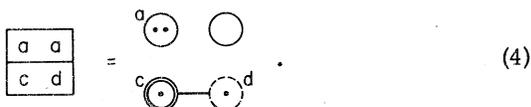
There are 12 such singlet states, leading (in T_d symmetry) to $^1A_1$, ^1E, $^1T_1$, $^1T_2$, and $^1T_2$ states. Similarly, we obtain triplet states of the form

$$
\begin{array}{|c|c|}
\hline
a & a \\
\hline
c & \\
\hline
d & \\
\hline
\end{array} \quad = \quad \text{(diagram)} \quad , \tag{5}
$$
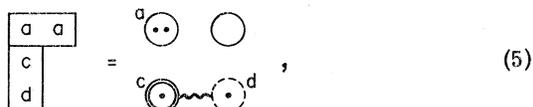
leading to $^3A_2$, ^3E, $^3T_2$, $^3T_1$, and $^3T_1$ states. There are no corresponding quintet states.

Similar states with two doubly occupied orbitals would be approximately twice as high in energy as (4) and (5). Excited states involving $4s$, $4p$, or $3d$ character are also expected to be high lying. Neither of these types of states will be considered.

In this paper we will be concerned only with the covalent states of the vacancy. As noted, these states are all essentially symmetric, having one electron per center. Thus, any polarization effects from the interaction of the vacancy electrons with the remainder of the crystal should provide a slight uniform shift in the energy of the covalent

states with little effect upon the energy separations among these covalent states. On the other hand, for the ionic states the polarization effects should lead to large corrections for some states, leading to large effects upon the excitation energies, as will be discussed in a subsequent paper.

C. Molecular-orbital description

The more common model for the vacancy in silicon is the Coulson-Kearsley^3 MO model. Therein one constructs a hybrid orbital (pointing at the vacancy site) on each of the four Si atoms and combines these into four molecular orbitals $(a_1, t_{1x}, t_{1y}, t_{1z})$ delocalized over the defect. The MO configuration for the singlet state, then is $\alpha(a_1^2 t_1^2 \alpha\beta\alpha\beta)$, where t_1 is some linear combination of t_{1x}, t_{1y}, t_{1z}. This MO configuration is a mixture of the states ^1E, $^1A_1$, $^1T_2$. Since the MO singlet state is forced to contain components ($^1A_1$ and $^1T_2$) corresponding to high-lying ionic states, whereas the MO triplet state is properly described as a low-lying covalent state ($^3T_1$), the MO picture can be expected to predict a triplet ground state for the vacancy.

III. CALCULATIONAL DETAILS

Silicon occurs in the diamond structure,^{9} which is a face-centered-cubic lattice with two atoms per unit cell. The calculations in this work involve clusters of atoms that extend only to the second-nearest-neighbor position. Starting with the vacancy site at the origin, the nearest-neighbor positions are $\frac{1}{4}a(1,1,1)$, $\frac{1}{4}a(1,-1,-1)$, $\frac{1}{4}a(-1,1,-1)$, and $\frac{1}{4}a(-1,-1,1)$ while the 12 second-nearest-neighbor positions are $\frac{1}{2}a(\pm 1, \pm 1, 0)$,
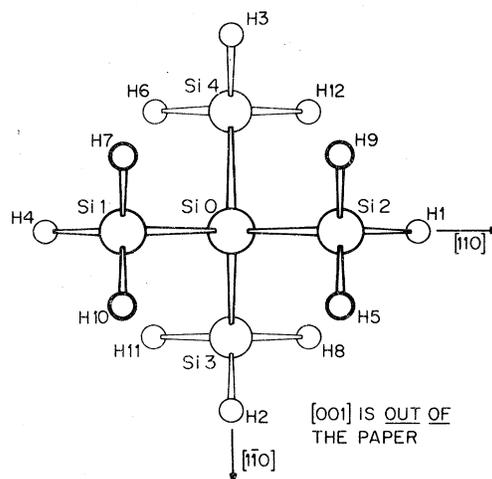
FIG. 1. Vacancy cluster for silicon as viewed from the [001] direction. Si 0 is the vacancy site.

TABLE I. Coordinates (in a.u.) for the tetrahedral cluster for silicon. Si 0 is the vacancy site. The centers are numbered with reference to Fig. 1. As described in the text, Si 1, Si 2, Si 3, and Si 4 have all been displaced by 0.084 Å away from Si 0.

Si 0	(0.0, 0.0, 0.0)
Si 1	(−2.65775, −2.65775, 2.65775)
Si 2	(2.65775, 2.65775, 2.65775)
Si 3	(2.65775, −2.65775, −2.65775)
Si 4	(−2.65775, 2.65775, −2.65775)
H 1	(4.23229, 4.23229, 0.96614)
H 2	(4.23229, −4.23229, 0.96614)
H 3	(−4.23229, 4.23229, −0.96614)
H 4	(−4.23229, −4.23229, 0.96614)
H 5	(4.23229, 0.96614, 4.23229)
H 6	(−4.23229, 0.96614, −4.23229)
H 7	(−4.23229, −0.96614, 4.23229)
H 8	(4.23229, −0.96614, −4.23229)
H 9	(0.96614, 4.23229, 4.23229)
H 10	(−0.96614, −4.23229, 4.23229)
H 11	(0.96614, −4.23229, −4.23229)
H 12	(−0.96114, 4.23229, −4.23229)

$\frac{1}{2}a(\pm 1, 0, \pm 1)$, and $\frac{1}{2}a(0, \pm 1, \pm 1)$. Here a is the cubic lattice constant, $a = 5.43$ Å for silicon. In the calculations reported here, the second-nearest-neighbor atoms were replaced with hydrogen atoms placed along the appropriate bond directions, but using an SiH bond length of 1.479 Å. This structure, shown in Fig. 1, retains tetrahedral symmetry.

With the removal of the central silicon atom to form the vacancy, some displacement is expected in the atoms ajacent to the vacancy site. For a silicon atom on the (111) surface, calculations using a Si-(SiH$_3$)$_3$ complex[10] led to a relaxation of the apical Si of 0.08 Å toward the bulk. Forcing the geometry of the vacancy to be tetrahedral, we expect the same relaxation of 0.08 Å away from the vacancy site for each of the four Si atoms, leading to the relaxed geometry of Table I. It is likely that the ^1E and $^3T_1$ states undergo other distortions of lower symmetry (Jahn-Teller distortions); however, such distortions are *not* treated in this paper.

A. Basis sets

Two types of calculations were performed, one type was to obtain geometries and qualitative information about states, while the second type was to obtain quantitative descriptions of the various states. For the former a minimum basis set (MBS) was used while for the latter a "valence" double-zeta basis was employed. In all cases the bases were of contracted Cartesian-Gaussian functions as given in Table II. The *ab initio* ef-

fective potential was used to replace the $(1s)^2$ $(2s)^2$ $(2p)^6$ core of each Si.[11]

The GVB wave function[5] for a bonding pair of electrons is represented as

$$(1/\sqrt{2})[(\phi_1\phi_2 + \phi_2\phi_1)(\alpha\beta - \beta\alpha)] , \qquad (6)$$

where ϕ_1 and ϕ_2 are solved for self-consistently (they are allowed to be nonorthogonal). The form for more than two electrons is

$$\mathcal{Q}(\phi_{a1}\phi_{b1}\phi_{a2}\phi_{b2}\cdots\chi) , \qquad (7)$$

where there is one orbital for each electron and the spin function χ is a general-spin eigenfunction. It is often computationally convenient to use a more restricted form for the wave function as follows: the spin function is taken as the product of singlet spin functions and the orbitals of *different* singlet pairs are required to be orthogonal.[12] These constraints are referred to as the perfect-pairing and strong orthogonality constraints, respectively, and the resulting self-consistent wave function is referred to as the GVB perfect-pairing (GVB-PP) wave function.

In solving for the GVB-PP wave function, it is advantageous to transform each GVB pair,

$$\phi_1\phi_2 + \phi_2\phi_1 , \qquad (8)$$

to the natural orbital (NO) representation,

$$\phi_1\phi_2 + \phi_2\phi_1 = C_g\phi_g\phi_g - C_u\phi_u\phi_u , \qquad (9)$$

where

$$\langle\phi_g|\phi_u\rangle = 0 ;$$

TABLE II. The basis functions for Si and H (each function is expanded in terms of $1s$ or $2p$ Cartesian-Gaussian functions with exponents and coefficients are given). All functions are used in the double-zeta basis. The minimum basis set is obtained by deleting the $2s$ and $2p$ functions of the Si. Only a minimum basis for H was used in either case.

	Function	Exponent	Coefficient
Silicon	$1s$	4.051	0.0436619
		1.484	−0.2748724
		0.2704	0.4527114
		0.09932	0.4247582
	$2s$	0.2704	−0.2004077
		0.09932	0.4247582
	$1p$	4.185	−0.0047173
		1.483	−0.0365421
		0.335	0.3147023
		0.09699	0.1447246
	$2p$	0.335	−0.0307458
		0.09699	0.1447246
Hydrogen	$1s$	5.663728	0.0871988
		0.857387	0.5046466
		0.190504	0.8087388

ϕ_g and ϕ_u are referred to as the first and second natural orbitals, respectively ($C_g > C_u > 0$). After solving for the self-consistent GVB natural orbitals (9), we transform back to the usual GVB form (8), in order to interpret and display the orbitals. Normally, the ϕ_g orbital has a form similar to a localized Hartree-Fock (HF) bonding molecular orbital while the ϕ_u orbital has a form similar to a localized HF antibonding orbital. In terms of the NO's, the GVB wave function can be thought of as a generalization of the HF wave function where each doubly occupied HF orbital is correlated (and thus allowed to localize). On the other hand, using the GVB form of the orbitals (6) or (8), the GVB wave function can be conceptualized as a generalization of the valence-bond (VB) wave function in which each orbital is solved for self-consistently and allowed to delocalize.

In our calculations, we have allowed only the valence orbitals associated with the defect to be correlated, that is, we did not correlate the doubly occupied orbitals corresponding to the SiH bonds. Initially a minimum basis set calculation for the $^5A_2$ state was performed. In this calculation the four dangling-bond orbitals are quite distinct from the SiH bonds. Subsequent double-zeta calculations were first performed using the SiH bond orbitals from the above calculation. Later these orbitals were allowed full variational freedom in solving for certain states.

After obtaining the optimum orbitals from the GVB-PP calculations, we carried out several types of configuration-interaction (CI) calculations designed to remove any effects arising from the perfect-pairing restriction and to include several small electron-correlation effects not included in the GVB-PP wave function. In describing the CI calculations it is convenient to consider three sets of orbitals:

(a) The *bulk* (or band) *orbitals*. In our complex these are the orbitals describing the Si–H bonds as obtained from the GVB-PP calculation.

(b) The *valence orbitals* of the vacancy. These are the four correlated orbitals obtained from the GVB-PP calculations; they can be thought as dangling-bond orbitals on each of the four Si atoms adjacent to the vacancy.

(c) The *virtual orbitals* of the vacancy. We constructed eight orbitals orthogonal to all the occupied orbitals of the GVB-PP wave function, which will be referred to as the virtual orbitals. These orbitals were obtained by selecting two orbitals on each of the four silicon atoms (the more expanded 2s function of Table II and the more expanded 2p orbital oriented along the axis to the vacancy site) and orthogonalizing to each of the occupied orbitals of sets a and b. These eight

virtual functions are suitable for allowing the hybridization and spatial extent of the valence orbitals of set b to change and are necessary for describing the orbitals of the ionic excited states.

Three types of CI calculations were considered, all of which kept the orbitals of set a fixed. That is, the bulk or band states were not allowed to readjust. For each state we constructed the dominant configuration by allowing various appropriate occupations of the orbitals of set b and then included the following types of excitations.

(i) GVB-restricted CI (RCI): Double excitations are allowed within each of the two sets of natural orbitals of the GVB-PP wave function. This allows relaxation of the perfect-pairing form of the spin function. (The orbitals of set c are not used.)

(ii) GVB-CI: All possible excitations among the orbitals of set b are allowed. This serves to relax both the perfect-pairing and strong orthogonality restrictions of the GVB-PP wave function. (The orbitals of set c are not used; GVB-CI includes all configurations of GVB-RCI.)

(iii) SD-CI (singles and doubles CI): Starting with each configuration of the GVB-RCI, all single and double excitations among the orbital sets b and c are allowed. In addition, all configurations of the GVB-CI are included. This allows additional correlation effects not included in the previous CI's.

The integrals were done using the Caltech version of POLYATOM incorporating effective potentials.[13] The SCF calculations were carried out using GVBTWO (Bobrowicz,[14,15] Wadt and Goddard), the integral transformations using the Bobrowicz-Huestis-Goddard transformation program[14,16] and the CI calculations using CIONE (Bobrowicz,[14] Winter, Ladner,[17] Walch, Harding, Olafson, Goddard). The properties were calculated using the Ermler version of the NYU properties program (Moskowitz).

IV. RESULTS

We found a ^1E ground state with the $^3T_1$ state slightly higher (0.18 eV) and the $^5A_2$ at 0.60 eV. This is to be expected from (1)–(3) since the ^1E state has two weak bonds, the $^3T_1$ one, and the $^5A_2$ none. The lowest ionic state ($^1T_2$) was found at 4 eV. (See Tables III and IV.)

The self-consistent orbitals for the ground state are shown in Fig. 2. As expected, each of the four electrons of the vacancy is associated with one of the four Si atoms and is very similar to a dangling-bond orbital of the (111) surface.[10] The overlap between the two GVB orbitals of each bond pair is $S_{ab} = 0.23$, indicating a very weak bond. Two localized dangling-bond orbitals would have an overlap of 0.08,[18] the self-consistent orbitals re-

TABLE III. GVB calculations for the covalent states of the vacancy in silicon. All quantities are in Hartree atomic units.

State	SiH[d]	Energy	C_1^a	C_2^a	ΔE^b	S_{ab}^c	Comments
^1E	Fixed[d]	−21.476647	0.846215	−0.532842	0.071860	0.226495	Relaxed Si positions
^1E	Fixed	−21.471674	0.862486	−0.506080	0.065916	0.260423	Tetrahedral Si positions
^1E	Free	−21.491605	0.848504	−0.529188	0.073275	0.231775	Relaxed Si positions
$^3T_1$	Fixed	−21.470127	0.871873	−0.489733	0.062499	0.280053	Relaxed Si positions
$^5A_2$	Fixed	−21.460531	...	...	...	...	

[a]Coefficients of the natural orbitals: $\phi_a\phi_b + \phi_b\phi_a = C_1\phi_1\phi_2 + C_2\phi_2\phi_2$.

[b]Energy lowering due to the presence of the second NO. This is the amount the energy would *increase* if the second term in the NO expansion were deleted (to obtain a HF pair) with the other orbitals held constant.

[c]Overlap of the GVB orbitals, $S_{ab} = (\phi_a|\phi_b)$.

[d]Fixed implies that the SiH bond orbitals come from a MBS calculation of the $^5A_2$ state.

adjust to maximize bonding leading to an increase to $S_{ab} = 0.23$.

Transforming one of the GVB pairs to natural orbitals leads to the two orbitals of Fig. 3. The left one resembles a bondinglike HF orbital, while the right one resembles an antibondinglike HF orbital. In the GVB calculation the left orbital has an occupation of 1.44 electrons while the right one has an occupation of 0.56 electrons. Deleting the second natural orbitals to obtain a HF description of the bond pairs leads to an energy increase of 0.073 hartree = 2.0 eV! Thus electron correlation is of great importance in describing the states of the vacancy.

The self-consistent GVB orbitals of the $^3T_1$ state are shown in Fig. 4. The bond pairs [Fig. 4(a)] is very similar to that of the ^1E state. The triplet bond pair [Fig. 4(b)] appears to have changed greatly from the singlet pair [Fig. 2(b)] of the ^1E state. This change is mostly just apparent. The two triplet orbitals can be recombined via arbitrary (nonsingular) transformations without changing the total energy of the wave function and could be recombined to obtain orbitals very similar to the bonding pairs. This can be seen by comparing the triplet orbitals [Fig. 4(b)] with the

TABLE IV. Energy separations for the covalent states of the Si vacancy.[a]

Type of calculation	Total energy (h) ^1E	Excitation energy (eV) $^3T_1$	$^5A_2$
GVB	−21.47665	0.177	0.439
	−21.49161[b]	...	0.846
GVB−RCI	−21.48546	...	0.678
SD−CI	−21.48636	0.171	0.605

[a]SiH bond orbitals fixed from the $^5A_2$ MBS HF calculation except as noted.

[b]SiH bond orbitals relaxed.

NO's of a single bond pair (Fig. 3).

The dominant terms in the CI wave function for the first two singlet states are given in Table V. The two components of the ^1E state correspond to the two possible spin couplings for the orbitals. The $^1E(A_1)$ component corresponds to the case, where the GVB orbitals are singlet coupled into two bond pairs which are coupled together into an overall singlet state.
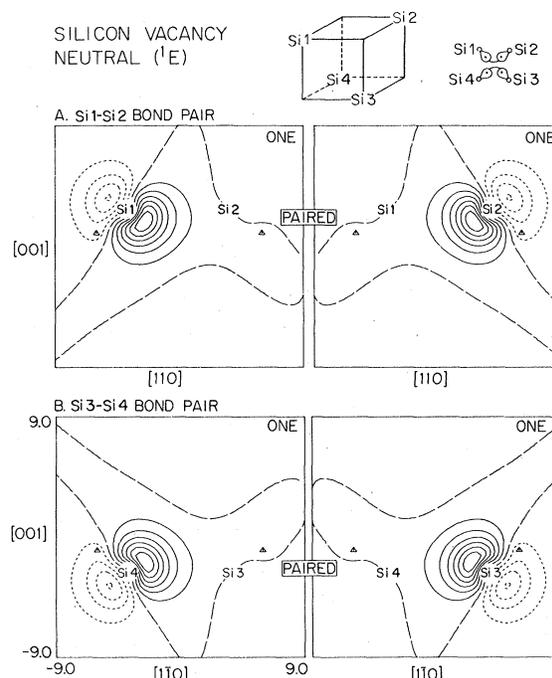
FIG. 2. Amplitudes of the GVB orbitals for the ^1E state of the neutral vacancy (silicon). The long dashes indicate nodal surfaces. The spacing of the contour lines is 0.03 a.u. with the dashed lines being negative. This spacing is used for all of the silicon orbitals. The centers are labeled according to Table I and Fig. 1. These conventions are used for all other plots.
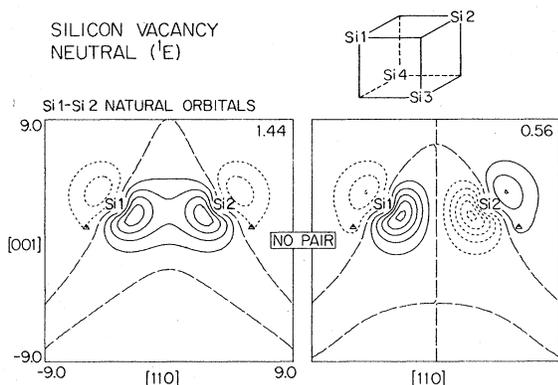
FIG. 3. The natural orbitals of one bond pair of the ^1E state of neutral vacancy (silicon).

The $^1E(A_2)$ component corresponds to the second orthogonal spin coupling in which the GVB orbitals of each bond are triplet coupled and then the two triplet bonds are coupled into a singlet. This can be seen most clearly by reordering the orbitals in the dominant configuration to be $\sigma_1\sigma_1^*\sigma_2\sigma_2^*$. In this case the spin eigenfunction becomes $-(0.04\chi_1 + 0.935\chi_2)$.[19] In terms of VB structures, the $^1E(A_2)$ state corresponds to the resonant combination of two structures (10b),

(10a)

(10b)
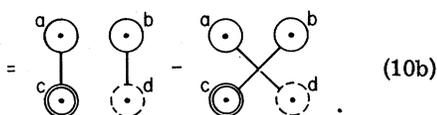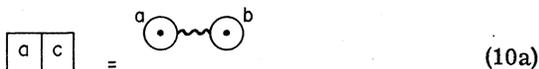
The dominant contributions to the CI wave functions for the triplet states are also given in Table V. The $^3T_1(B_1)$ component is just the VB structure (2) described in Sec. II.

The $^3T_1(B_2)$ component is the similar state

(11)
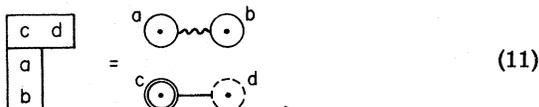
The $^3T_1(A_2)$ component is more complicated. Again reordering the orbitals as $\sigma_1\sigma_1^*\,\sigma_2\sigma_2^*$ leads to a dominant configuration for the $^3T_1(A_2)$ of the form

$$-0.07\chi_1 + 0.809\chi_2 - 0.48\chi_3 ,$$

which corresponds closely to coupling two triplet pairs into one overall triplet state. (The coefficients must be

$$\sqrt{\tfrac{2}{3}}\,\chi_2 - \sqrt{\tfrac{1}{3}}\,\chi_3 = 0.816\chi_2 - 0.577\chi_3$$

in order to correspond exactly to this spin-coupling).

In addition, starting off with two triplet states, we can couple them into a quintet state ($^5A_2$).

To a first approximation, the separations between the ^1E, $^3T_1$, and $^5A_2$ states are described by the eigenstates of the Heisenberg-Hamiltonian

$$\mathcal{H} = -2K \sum_{j<k=1}^{4} (\vec{S}_j \cdot \vec{S}_k) ,$$

leading to

$$[E(^5A_2) - E(^1E)]/[E(^3T_1) - E(^1E)] = 3 . \tag{12}$$

In fact we find the calculated ratio to be 3.5, indicating the validity of this simple description of the states. The calculated exchange term is

$$K = 0.09 \text{ eV} = 714 \text{ cm}^{-1} .$$

V. DISCUSSION

While our calculations include the major correlation effects involving the four vacancy electrons, we have ignored several important effects. Only symmetric relaxation of the vacancy was included, and we used a small finite complex.
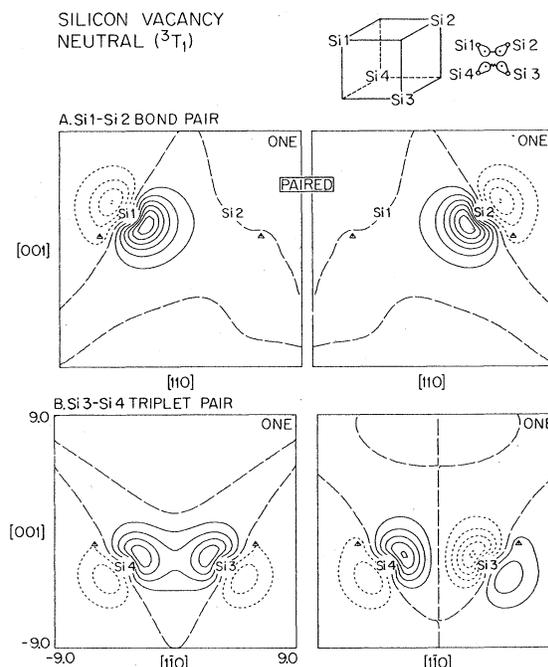
FIG. 4. The GVB orbitals of the $^3T_1$ state of the neutral vacancy (silicon).

TABLE V. Dominant terms in the configuration interaction wave function for the covalent states of the neutral vacancy in silicon. The components of the ^1E and $^3T_1$ are also denoted (in parentheses) by their C_{2v} symmetry. Included are all configurations with energy lowerings of ≥ 0.001 hartree. The numbers 0, 1, or 2 indicate the occupation number for each orbital.

State configuration [a] $\sigma_1\sigma_2\sigma_1^*\sigma_2^*$		Spin eigenfunction coefficient [b]			Energy lowering [c] millihartree [d]
		C_{χ_1}	C_{χ_2}	C_{χ_3}	ΔE
$^1E(A_1)$	2 2 0 0	0.682	$\cdots$	$\cdots$	$\cdots$
	0 2 2 0	-0.456	$\cdots$	$\cdots$	68.9
	2 0 0 2	-0.456	$\cdots$	$\cdots$	68.9
	0 0 2 2	0.277	$\cdots$	$\cdots$	31.0
	1 1 0 2	-0.140	$\cdots$	$\cdots$	5.4
	1 1 2 0	-0.140	$\cdots$	$\cdots$	5.4
$^1E(A_2)$	1 1 1 1	-0.830	0.433	$\cdots$	$\cdots$
	0 2 1 1	-0.245	$\cdots$	$\cdots$	16.5
	2 0 1 1	-0.244	$\cdots$	$\cdots$	16.5
$1^3T_1(A_2)$	1 1 1 1	0.736	-0.344	-0.486	$\cdots$
	0 2 1 1	0.225	$\cdots$	$\cdots$	13.3
	2 0 1 1	0.225	$\cdots$	$\cdots$	13.3
$1^3T_1(B_1)$	1 2 1 0	0.826	$\cdots$	$\cdots$	$\cdots$
	1 0 1 2	-0.504	$\cdots$	$\cdots$	66.3
	2 1 1 0	-0.229	$\cdots$	$\cdots$	11.1
	0 1 1 2	-0.088	$\cdots$	$\cdots$	2.4
$1^3T_1(B_2)$	1 2 0 1	0.826	$\cdots$	$\cdots$	$\cdots$
	1 0 2 1	-0.504	$\cdots$	$\cdots$	66.3
	2 1 0 1	-0.229	$\cdots$	$\cdots$	11.1
	0 1 2 1	-0.088	$\cdots$	$\cdots$	2.4
1^5A_2	1 1 1 1	1.0	$\cdots$	$\cdots$	$\cdots$

[a]The orbitals are as follows: σ_1, σ_2, GVB 1st NO's, corresponding to $\phi_a+\phi_b$ and $\phi_c+\phi_d$, respectively; σ_1^*, σ_2^* GVB 2nd NO's, corresponding to $\phi_a-\phi_b$ and $\phi_c-\phi_d$, respectively. In C_{2v} symmetry, these orbitals σ_1, σ_2, σ_1^*, σ_2^* have symmetries a_1, a_1, b_1, and b_2, respectively.

[b]The spin eigenfunctions for four electrons are $\chi_1=\frac{1}{2}(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)$, $\chi_2 = -(1/\sqrt{12})(2\alpha\alpha\beta\beta - \beta\alpha\beta\alpha - \alpha\beta\beta\alpha + 2\beta\beta\alpha\alpha - \beta\alpha\alpha\beta - \alpha\beta\alpha\beta)$, for singlet states; $\chi_1 = -(1/\sqrt{2})(\alpha\beta\alpha\alpha - \beta\alpha\alpha\beta)$, $\chi_2 = -(1/\sqrt{6})(2\alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$, $\chi_3 = -(1/\sqrt{12})(3\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$, for triplet states; and $\chi_1 = \alpha\alpha\alpha\alpha$, for the quintet state.

[c]The energy lowering is the change in the energy upon deleting a particular configuration while all other CI coefficients are fixed. The contribution from the dominant configuration is not meaningful.

[d]1 millihartree $= 10^{-3}$ hartree $= 0.0272$ eV.

A. Nontetrahedral distortions

Given the character of the ^1E state as in (1), we expect that the complex would distort so as to move atoms a and b closer and atoms c and d closer, while moving a and b away from c and d. Thus, in the ^1E state the system should distort to D_{2d} symmetry. This distortion, while lowering the energy of the $^1E(A_1)$, will increase the energy of the $^1E(A_2)$, thereby leading to a splitting of these levels. Such distortions are referred to as Jahn-Teller distortions.

Starting with the $^3T_1(B_2)$ component of (2), one would expect the optimal distortion to move a and b closer together, while moving c and d farther apart. This C_{2v} distortion would stabilize the $^3T_1(B_2)$ component, destabilize the $^3T_1(B_1)$ compo-

nent, but would lead to only second-order effects in the $^3T_1(A_2)$.

Recombining the $^3T_1(B_1)$ and $^3T_1(A_2)$ states into the form

$$\begin{array}{|c|c|} \hline a & d \\ \hline b & \\ \hline c & \\ \hline \end{array} \tag{13}$$
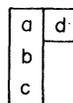
(where ϕ_a, ϕ_b, and ϕ_c are coupled into a quartet and ϕ_d coupled to form an overall triplet) leads to a state that could be stabilized by C_{3v} distortions. Here atom d would move closer to the other three while atoms a, b, and c would all move farther from each other.

Assuming that the Jahn-Teller splitting does not

effect the average energy of a degenerate set of states, the optimum direction for distortion should be the one for which one state does down while the others all go up. For $^3T_1$, this criterion suggests that the C_{3v} distortion is better than C_{2v}.

B. Effects of a finite complex

The use of a finite complex can lead to large errors if one is describing a system in which there is a net charge or a large dipole moment contained in the complex. However, for the covalent states described herein there is one electron in each of the four dangling bond orbitals associated with each of four silicon atoms adjacent to the vacancy. Thus, the charge distribution is neutral and symmetric. Indeed, calculations of the shape of the (111) surface dangling bond orbital have shown that this orbital is insensitive to increases in cluster size.[20] As a result, we believe the separations of the ^1E, ^3T, and $^5A_2$ states should be accurate. Proceeding to infinite cluster size would probably lead to a slight decrease in the separations between these states but without affecting the order.

Since our wave functions include many-body or electron-correlation effects, we do not get a band spectrum of states out of a single calculation as one would in a molecular-orbital or standard-band description. Rather, one must solve individually and self-consistently for each electronic state to be considered. Of course, with such a small complex we would obtain a quite inadequate description of the band states should we solve for them. As a result, our calculations do not provide direct information on the location of the vacancy states relative to the band edges in silicon. In order to obtain such information from finite cluster studies, we determine the ionization potential or electron affinity for the finite complex description of the neutral vacancy (as described within our many-electron formalism) and compare with the ionization potential or electron affinity for the bulk electronic states. This point will be discussed in conjunction with the ionic states.[21] On the other hand, due to the large localized electron-correlation effects in the vacancy, a standard band-type calculation should lead to large errors in the location of the vacancy levels, despite the use of an infinite system.

C. Other calculations

There have been several calculations of the silicon vacancy, using a variety of methods. Each method, ours included, has both strong and weak points. The calculations of Larkins[4] is close to ours in approach, yet the results are dramatically dif-

ferent. A major difference is that we calculate all integrals, *ab initio*, while Larkins used parametrized integrals. For the neutral vacancy, the Larkins calculation never obtains the ^1E ground state, a result we cannot understand.

Using a larger cluster but employing an extended Hückel-theory-type MO approach, Yip[22] has studied the vacancy for diamond, Si, and Ge. He does not report ground states for any system but finds very large symmetric distortions for the vacancy. For the neutral (V^0), his outward distortion is 0.50 Å, while we find a 0.08-Å outward distortion. In addition, Yip finds Jahn-Teller coupling coefficients an order magnitude less than the values estimated from experiments by Watkins,[1] leading to a Jahn-Teller energy of 0.0025 eV for V^0 as opposed to Watkins value of 1.5 eV. While Messmer and Watkins[23] obtained good results using extended Hückel theory on diamond, Yip's extended Hückel-theory calculations seem suspect.

Recently, self-consistent empirical pseudopotential calculations have been performed by Louie *et al.*,[24] based on an approach similar to the molecular unit-cell approach of Messmer and Watkins.[25] For the undistorted vacancy they find a triply degenerate MO at about the middle of the band gap. They also study the effect of inward and outward [100] distortions of the vacancy. While they do find a splitting of the degenerate levels, their distortion is quite large (1.13 Å in the [001] direction), and thus, may not relate to any physical situation. Their calculation does show that such large distortions of the vacancy leads to effects upon the second-nearest bonds, and perhaps farther. Their calculation seems to indicate that the vacancy electronic states are well localized in the vacancy.

VI. CONCLUSIONS

The covalent electronic states of the neutral vacancy V^0 have been studied using the generalized valence bond and configuration-interaction wave functions. We find that the nature and ordering of the states of the system can be described *a priori* using simple valence-bond arguments. These predictions are found to be correct on the basis of GVB and CI calculations. Specifically, the ground state of V^0 is a ^1E with low-lying $^3T_1$ and $^5A_2$ states at 0.17 and 0.60 eV, respectively. These numbers should be insensitive to the use of a finite complex.

In addition to finding the proper ordering of the states, we find that the Jahn-Teller distortions of the system can be understood from the form of the many-electron wave function in each case.

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[7] The tableaux indicate the spin coupling of the orbitals; thus a and b in the same row indicates two singlet-coupled orbitals, while a and b in the same column indicates two orbitals of the same spin coupled to have maximum spin projection $\hat{S}_z$. The orbital pictures use solid and wavy lines to indicate this same singlet and triplet coupling, respectively. Here, a single circle indicates an orbital in the plane of the paper while a double circle and a dashed circle indicate orbitals above and below the plane of the paper, respectively.

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[19] See Ref. b of Table V for the spin eigenfunctions.

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