

THE NEUTRAL VACANCY IN SILICON AND DIAMOND:
GENERALIZED VALENCE BOND STUDIES*

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Self-consistent ab initio generalized valence bond and configuration interaction calculations are presented for molecular cluster models of the electronic states of the neutral vacancy in diamond and silicon. In each case the ground state of the vacancy is found to be 1E (T_d designation) with the 3T_1 and 5A_2 states slightly higher (0.18 eV and 0.60 eV for Si and 0.33 eV and 1.2 eV for C). The first excited singlet state is 1T_2 in each case. The $^1E-^1T_2$ excitation energy is found to be 1.7 ± 0.7 eV for diamond and 1.3 ± 0.5 eV in silicon, the range being due to uncertainty in the model used for estimating the polarization effects due to the remainder of the infinite crystal.

Introduction

The vacancy in silicon and diamond has been studied extensively both from the theoretical^{1,2} and experimental^{3,4} viewpoints. Through these studies, the Coulson-Kearsley (C-K) defect molecule⁵ has emerged as a useful framework for the study of the electronic states of the vacancy. Nevertheless, calculations to date using the C-K model are uniform in their lack of agreement as to the ordering of the electronic states.^{5,6} This fact is largely attributable to the semi-empirical nature of these calculations, but it is also due to the molecular orbital starting point used in the C-K model and the calculations.

In this communication we present the results of ab initio calculations including the dominant electron correlation (many-body) effects for models of the vacancy in Si and diamond. The technique employed is the generalized valence bond (GVB) method⁷ which has the advantages: (i) the dominant electron correlation effects are included self-consistently, (ii) the wavefunctions lead to localized defect orbitals allowing simple interpretations in terms of bonds, lone pairs, etc., (iii) the localized nature of the states allows one to predict (before explicit calculations) the ordering of the various electronic states, and (iv) residual electron correlation effects not included in the GVB wavefunction can be readily included via small configuration interaction (CI) calculations with these residual correlation effects easily interpreted. These points will be described at length elsewhere.⁸

Calculational Details

The vacancy in an infinite diamond lattice is modeled by a cluster of four AH_3 groups ($A =$

C, Si) surrounding the vacancy site and having full tetrahedral symmetry. The four atoms around the vacancy were positioned slightly outward from the bulk positions in accordance with separate surface relaxation calculations reported elsewhere.⁹ (The 12 second-nearest-neighbor hydrogens were positioned using the normal AH bond length.) In the case of silicon, the core electrons were replaced by an ab initio effective potential.¹⁰ The basis sets on the carbon¹³ and silicon¹⁰ atoms were valence double zeta sets of contracted gaussian functions; the basis on the H atoms was a single contracted gaussian.¹⁴

The Hartree-Fock (HF) wavefunction has the form

$$\mathcal{A} [\phi_1 \phi_1 \alpha \beta \dots \phi_n \phi_n \alpha \beta] \quad (1)$$

(\mathcal{A} is the antisymmetrizer or determinant operator) where each orbital is doubly-occupied and solved for self-consistently. This wavefunction is adequate for the ground state of molecules with geometries close to equilibrium; however, it is well-known that this wavefunction leads to a poor description of broken bonds. For example, the energy of a closed-shell HF wavefunction for the Si_4H_{12} cluster model of the Si vacancy is 2.9 eV above the energy of the HF quintet ($S=2$) state, whereas the singlet state should be the ground state.

Starting with the HF wavefunction (1), we can form the GVB wavefunction by replacing each doubly-occupied orbital $\phi_a \phi_a \alpha \beta$ with the correlated pair function

$$\frac{1}{\sqrt{2}} [(\phi_a \phi_b + \phi_b \phi_a)(\alpha \beta - \beta \alpha)], \quad (2)$$

where ϕ_a and ϕ_b are nonorthogonal. In this

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work the four electrons associated with the vacancy were correlated (two GVB pairs) while the remainder of the orbitals (corresponding to the AH bond) were uncorrelated (doubly-occupied as in the HF wavefunction). All 16 orbitals were solved for self-consistently.

The GVB orbitals (augmented with a small set of virtual or unoccupied orbitals) were used as the basis for a series of GVB-CI calculations in order to account for residual correlation effects and to obtain the spectrum of excited states.

Results and Discussion

Covalent States

In Figure 1 we present the GVB orbitals for the 1E ground state of diamond (the silicon orbitals are similar). The ground state has a singly-occupied dangling bond orbital on each of the four carbons surrounding the vacancy (as in the CK model) but each orbital is slightly distorted to form bond pairs. Other allowed spin coupling of four localized singly-occupied orbitals lead to the 3T_1 and 5A_2 states. As indicated in Figure 1, the 1E state involves two weakly bonding pairs; similarly, the 3T_1 and 5A_2 states lead to one pair and zero pairs. Thus simple valence bond arguments⁸ explain the ordering $^1E < ^3T_1 < ^5A_2$ for these covalent states (i.e., the states with one electron per dangling bond

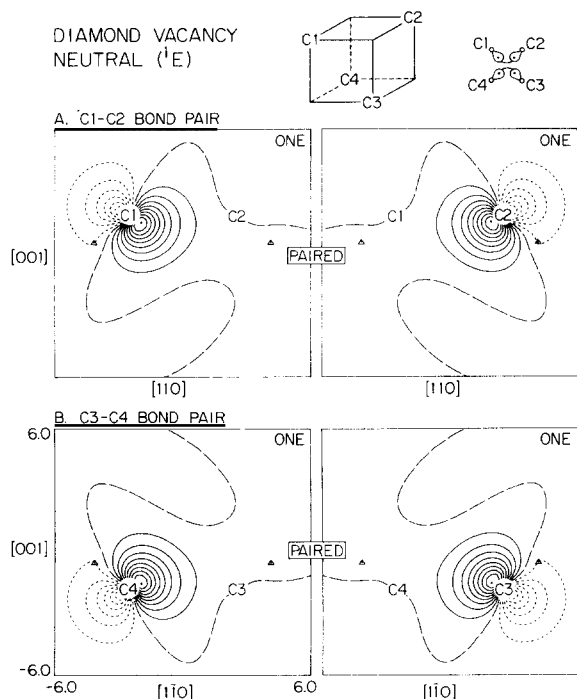


Fig. 1. Amplitudes of the GVB orbitals for the 1E ground state of the neutral vacancy in diamond. Each orbital contains one electron. The spacing of the contour lines is 0.05 a.u., with solid lines indicating positive contours, short dashed lines the negative contours, and long dashes the nodal surface. The axes are labelled by their crystallographic directions. Positions of hydrogen nuclei in the plane are denoted by triangles.

orbital). The separations are small, 0.2 to 1.0 eV (see Table 1) due to the small value (0.1) for the overlap of neighboring dangling bond orbitals.

Fully self-consistent GVB calculations on the 1E and 3T_1 states lead to the same excitation energy as the CI calculations (based on the 1E orbitals), indicating that the GVB description contains the important electron correlation effects. On the other hand, the HF wavefunction (1) leads to a singlet energy 3.56 eV higher than the GVB wavefunction for the 1E state. Indeed the HF description leads to a quintet ($S=2$) ground state (in contrast to experiment and to our calculations)! This indicates how essential it is to include correlation effects in studying defect states.

Ionic (Neutral) Excited States

Starting with the 1E or 3T_1 state and exciting the electron from an orbital on one center to an orbital on another gives rise to five excited singlet and five excited triplet states which we refer to as ionic (since one dangling bond orbital is doubly-occupied while another is empty). (There are no such ionic quintet states.) A simple valence bond argument⁸ predicts 1T_2 to be the lowest of these states; hence the first (dipole-allowed) excitation for the neutral vacancy will be $^1E \rightarrow ^1T_2$. The CI results for the above-mentioned low-lying states of the neutral vacancy in diamond and silicon are given in Table 1. The CI calculations were carried out using the GVB orbitals for the 1E state in each case. Fully self-consistent GVB calculations for the 1T_2 state in Si lowers the excitation energy for ($^1E \rightarrow ^1T_2$) by 0.2 eV, justifying the use of the 1E orbitals for even the ionic states.

Experimentally, it has been well established that the GR1 spectrum in diamond is associated with transitions at the neutral defect.³ The main line of the spectrum at 1.673 eV has been shown to be due to an $E \rightarrow T_2$ transition while the weaker line at 1.665 eV has been assigned $A_1 \rightarrow T_2$. Our results show that there is no low-lying 1A_1 state that could give rise to this transition. However, including spin-orbit coupling, the covalent 3T_1 state contains a component with total A_1 symmetry that could well be the lower state of the 1.665 eV transition (such an assignment was previously conjectured by Clark and Walker⁹).

On first inspection of Figure 2, the character of the orbitals for the 1T_2 ionic state may not be obvious. Note, however, that there are three electrons in orbitals localized between centers C3 and C4, while only one electron is in an orbital localized between centers C1 and C2. Thus, relative to the 1E state, the 1T_2 state represents the transfer of an electron from a bonding orbital in the C1-C2 region to an antibonding orbital in the C3-C4 region. The valence bond description of this state is illustrated by the series of "lobe diagrams" indicated in Figure 2.

For the covalent states, the charge distribution is quite symmetric, and the major flaws in using the finite cluster involve effects which should decrease exponentially (like overlaps) with cluster size. Thus we expect our cluster to give results in reasonable agreement with those of the infinite system. Certain of the

Table 1. GVB-CI results for the neutral vacancy in silicon and diamond.

Symmetry (T_d)	Character	Silicon (Si_4H_{12})		Diamond (C_4H_{12})	
		Cluster	Infinite Solid	Cluster	Infinite Solid
1^1E	Covalent	0.00 ^a	0.0	0.0 ^b	0.0
1^1T_2	Ionic	4.08	1.32 ± 0.54	6.06	1.70 ± 0.67
1^1A_1	Ionic	5.31		7.74	
1^1T_1	Ionic	6.20		9.62	
2^1E	Ionic	6.78		10.61	
2^1T_2	Ionic	7.90		12.09	
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1^3T_1	Covalent	0.18	0.18	0.33	0.33
2^3T_1	Ionic	4.74	1.98 ± 0.54	7.18	2.82 ± 0.67
3^3T_2	Ionic	6.29		9.68	
3^3E	Ionic	6.45		9.60	
3^3A_2	Ionic	6.58		9.56	
3^3T_1	Ionic	8.59		13.28	
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5^3A_2	Covalent	0.60	0.60	1.20	1.20

^a Total energy = -21.48636 h.

^b Total energy = -158.143155 h.

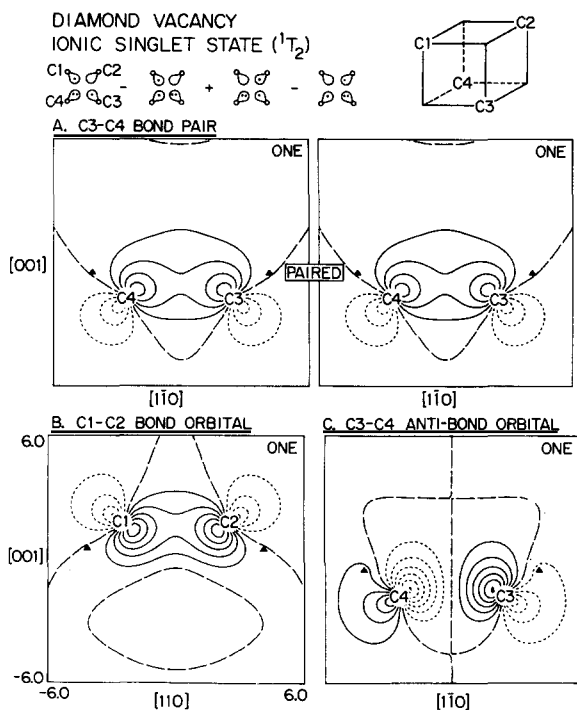


Fig. 2. The GVB orbitals for the 1^1T_2 ionic excited state of the neutral vacancy in diamond. All contour conventions are as in Figure 1.

ionic states, however, have quite unsymmetrical charge distributions, which in the infinite system will lead to a large polarization interaction with the surrounding medium, resulting in a large decrease in the excitation energy from that of the finite cluster. In order to estimate such excitation energies for the infinite solid, we calculated a polarization correction using the

classical model of a multipole field inside a spherical cavity in a dielectric medium.¹² This leads to a correction in diamond of 4.36 ± 0.67 eV for the 1^1T_2 ionic excited state while not affecting the 1^1E ground state. Thus the $1^1E-1^1T_2$ separation in diamond becomes 1.70 ± 0.67 eV for the infinite solid, in reasonable agreement with the experimental value of 1.67 eV. For silicon, the corresponding correction is 2.76 ± 0.54 eV, leading to an excitation energy of 1.32 ± 0.54 eV. This indicates that the vacancy excitation energy is higher than the energy gap, perhaps explaining the lack of an observed transition.

Clearly our cluster approach is deficient in examining the excitation energies to such ionic states. The energy corrections are large and the uncertainties are large.

Previous Calculations

The only previous nonempirical calculation for the vacancy is the scattered wave $X\alpha$ calculation for the diamond vacancy reported by Watkins and Messmer.¹¹ In these MO calculations, the orbital configuration is $a_1^2t_1^2$. Using triplet coupling of the t_1 orbitals leads to a pure 3^3T_1 state while the corresponding singlet calculation (doubly-occupied t_1) leads to a mixture of 3^3T_1 , 1^1E , 1^1A_1 , and 1^1T_2 states. Indeed, the MO singlet energy is given by

$$\bar{E}_S = \frac{1}{9}(3E_{3^3T_1} + 3E_{1^1T_2} + 2E_{1^1E} + E_{1^1A_1}), \quad (3)$$

in terms of the energies of the various component states. As a result the $X\alpha$ calculations lead to a triplet ground state (the quintet would, of course, have been even lower) with the singlet state approximately 1 eV higher. Even for an infinite cluster, such MO calculations would lead to the singlet state above the triplet.

Letting Δ be the excitation energy to the ionic singlet states, the limit of

$$\bar{E}_S - E_{3T_1}$$

is $\frac{2}{3}\Delta \approx 1.1$ eV (using the GR1 energy for Δ). This illustrates the kind of difficulty that arises in using uncorrelated wavefunctions to describe the electronic states of the vacancy.

Assuming the

$$\bar{E}_S - E_{3T_1}$$

would go to zero for infinite complexes, Watkins and Messmer argue that Jahn-Teller distortions are much greater than electron-electron effects (i.e., electron correlation). However, our results show that electron correlation effects are of the order of electron volts even for the infinite cluster. Thus, although agreeing that one must include Jahn-Teller distortions in the

final explanation of the states and spectra of these systems, we conclude that the electron correlation effects must be included before or simultaneous with investigating geometric distortions.

Summary

Using self-consistent GVB and GVB-CI calculations for molecular cluster models of the vacancy in diamond and silicon, we have found that in each case the ground state is a 1E state with the 3T_1 state slightly higher (0.18 eV for Si and 0.33 eV for C) while the 1A_2 state is somewhat above both the 3T_1 and 1E states (0.60 eV and 1.2 eV for Si and C relative to the 1E). The first excited state in each case is found to be a charge-transfer or ionic state, 1T_2 . The ${}^1E-{}^1T_2$ excitation energy for Si is found to be 1.3 ± 0.5 eV while for diamond it is 1.7 ± 0.7 eV, the variation being due to some uncertainty in the (necessary) inclusion of polarization corrections due to the remainder of the infinite crystal.

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