Semiempirical electronic-structure calculations of the hydrogen-phosphorus pair in silicon

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(Received 29 September 1989)

We report the results of electronic-structure calculations on the hydrogen-phosphorus pair in silicon using the modified neglect of diatomic differential overlap (MNDO) method with a finite cluster. We find that the stable geometry for the defect has C_{3v} point-group symmetry with the hydrogen located at the antibonding position of the silicon, which is, in turn, adjacent to the substitutional phosphorus. This prediction is consistent with a model inferred on the basis of infrared spectroscopy. We also calculate hydrogen vibrational frequencies of 2140 and 630 cm^{-1}, respectively, for the axial and perpendicular motions. These are considerably different than the values of 1555 and 809 cm^{-1}, assigned on the basis of infrared experiments. The physical characteristics of the defect and these differences are discussed.

I. INTRODUCTION

The tendency of hydrogen to form defect complexes with impurities in semiconductors has been a subject of intense recent interest and controversy.[1,2] A common manifestation of such defect-complex formation is the disappearance of preexisting electrical activity, or "passivation." In most recent studies, the focus has been on the formation of hydrogen–shallow-acceptor and hydrogen–shallow-donor pairs in semiconductors. We report here the results of semiempirical electronic-structure calculations on the hydrogen-phosphorus (shallow donor) pair in silicon. We use the self-consistent MNDO (modified neglect of diatomic differential overlap) -cluster method.[3]

The formation of H-P pairs in silicon was first identified experimentally in a study by Johnson *et al.*[4] In this treatment, the resistivity and Hall voltage were measured to determine the effect of deuteration on both the electron concentration and Hall mobility in P-doped silicon. It was found that the electron concentration went down and the mobility went up with increasing deuteration. This supported the formation of neutral pairs which have a lower (non-Coulombic) scattering cross section than the normally ionized, isolated P donors. Therefore, the reduction in free carriers with deuteration is not simply due to compensation without the formation of pairs. Furthermore, SIMS (secondary-ion mass spectroscopy) studies have also supported the trapping of hydrogen by phosphorus donors.

One of the most successful experimental techniques for establishing the identity of a hydrogen-related complex in a semiconductor is infrared (or Raman) spectroscopy. The hydrogen absorption is readily identified as the only signal in the 2000-cm^{-1} range; hence, a perturbation due to a nearby acceptor or donor can be resolved. In the well-studied H-B defect in silicon, the hydrogen stretching frequency was found[5-8] to be about 1900 cm^{-1}, and, based on stress studies, there is evidence that the defect has C_{3v} point-group symmetry.[9] Furthermore, it was found to be sensitive to acceptor identity, shifting to about 2200 cm^{-1} for the H-Al pair.[10] These results suggest a stable geometry with hydrogen in either the B-AB (boron antibonding) position or the BC (bond centered) position, as shown schematically in Fig. 1. As we describe shortly, most theoretical calculations favor the BC site; the B-AB site is found to be a saddle point.

Returning to the H-P pair, the hydrogen vibrational modes were examined by Bergman *et al.* using infrared spectroscopy.[11] For the H-P pair, stretching (A_1) and perpendicular (E) modes were identified at 1555 and 809 cm^{-1}, respectively. Furthermore, it was found that the symmetry was C_{3v}, like that of the H-B pair.[12] However, unlike the H-B pair, the frequency was found to be insensitive to the donor's chemical identity (1555, 1561, and 1562 cm^{-1} for H-P, H-As, and H-Sb, respectively). This supports the Si-AB site (see Fig. 1), first suggested on the basis of a tight-binding electronic-structure calculation.[4]

Electronic-structure calculations have played a critical role in understanding the H-acceptor and -donor pairs, especially since these defect systems are electrically inactive and nonparamagnetic. Computational studies began with the treatment of the H-B pairs, where the BC site was supported as the stable location for the passivating hydrogen.[13] With the exception of a scattered-wave $X\alpha$ cluster study,[14] all other theoretical treatments have supported the BC site.[15-18]

Electronic-structure calculations on the H-donor pairs have been performed more recently. In the original tight-binding study of Johnson *et al.*,[4] the Si-AB site was found to be stable over the P-AB site by 0.41 eV. Since this first study, both semiempirical and *ab initio* calculations have predicted a stable Si-AB site.[16,18-20] However, atomic relaxations, degree of stability, possible metastability, and vibrational frequencies are issues of current discussion.

We begin with a description of electronic-structure methods as they pertain to the study of hydrogen-related complexes. We then present our computational results and discuss them in the light of experiment and other calculations.

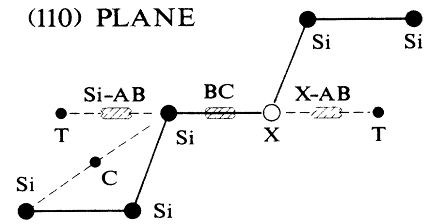

FIG. 1. Likely sites with axial symmetry for the hydrogen impurity in H-acceptor or H-donor pairs. The sites BC, Si-AB, and *X*-AB refer to the bond-centered, silicon antibonding, and *X* (donor or acceptor) -antibonding sites, respectively.

II. COMPUTATIONAL METHODS

The defect and its environment are simulated in this treatment by a finite fragment of the solid and terminated by hydrogen atoms.[21] The clusters used in this study are designed to properly represent the environments of both the interstitial hydrogen and the substitutional phosphorus. Bond-centered interstitial impurities have been treated using clusters such as ZSi_5H_{12} and ZSi_8H_{18}, where Z is the BC atom. Expanded so that the connections are clear, we have respectively, H_3-Si-Z-Si-Si_3-H_9 and H_9-Si_3-Si-Z-Si-Si_3-H_9. Notice that the BC site is symmetrically located in the latter cluster. Both of these cluster types have been used previously to treat the H-B pair[13,22] (i.e., H_3-Si-H-B-Si_3-H_9 and H_9-Si_3-Si-H-B-Si_3-H_9), and the latter cluster has been used to treat the isolated interstitial hydrogen.[23]

These clusters would be appropriate for the treatment of a H-P pair with hydrogen located at the BC site; however, although this may turn out to be a metastable configuration, it is not believed to be the equilibrium geometry. In order to properly explore the other two configurations, where hydrogen is either at the Si-AB or P-AB sites (see Fig. 1), a larger cluster is required. We have, therefore, constructed a larger cluster which contains both satisfactory BC and Si-AB, or P-AB, sites. This cluster, $HPSi_{19}H_{36}$, is shown with atoms relaxed in Fig. 2, containing 20 silicon atoms in the absence of the defect. Essentially, we have extended one side of the ZSi_8H_{18} cluster so as to close an adjacent interstitial cage; hence, we now have on one side -Si-Si_3-Si_{12}-H_{27}. Also, each silicon in this Si_3 group is fourfold coordinated by silicon atoms.

It is well known that the stability of many defects, particularly BC-type interstitials, depends strongly on the relaxation of the host atoms surrounding the defect. A direct approach to model these relaxations involves the displacements of some "inner" set of atoms in a fixed framework of "outer" silicons. Usually, the fixed silicons would be located at the crystalline rigid-lattice sites. A common problem with this approach is that the frozen cage can overly restrict the motions of the inner atoms in the cluster; silicon is quite flexible when all atoms are allowed to relax.[21] Therefore, in many earlier studies involving well-known substitutional impurities, the best results using the MNDO-cluster method were produced with small clusters, such as ZSi_5H_{12}, where the outer silicon atoms were also permitted to relax.

In these "hybrid" calculations,[21] the outer silicon atoms of the ZSi_5H_{12} cluster were connected to "springs" which served to simulate the response of the missing silicon atoms outside the cluster. The hydrogen terminators were constrained to rigidly follow the outer silicon atoms, maintaining bond lengths and angles of 1.48 Å and 109.47°, respectively. The optimal spring parameters for each outer atom were identified by using the ZSi_5H_{12} cluster to simulate three well-studied defects in silicon: substitutional oxygen and nitrogen, and the lattice vacancy. Accordingly, the spring origin was set 0.3 Å from each outer silicon atom along a line which connects this silicon to the next inner silicon atom; parallel and perpendicular spring constants of 6.9 and 0.8 eV/Å^2 with respect to this line were established as optimal. This was later extended to the ZSi_8H_{18} cluster, where the springs were connected to the outer six silicon atoms.[23]

Recognizing the value of the small ZSi_8H_{18} cluster with springs attached to outer silicon atoms, we proceed here with a three-step approach for determining relaxed geometries in our $HPSi_{19}H_{36}$ cluster: We (i) use the ZSi_8H_{18} cluster with "springs" to relax the H, P, Si, and the shell of six Si neighbors, (ii) use these coordinates in the larger $HPSi_{19}H_{36}$ cluster, but keep farther silicons fixed at rigid-lattice sites, and (iii) rerelax the H, P, and (innermost) Si in the framework of surrounding nearby-relaxed and farther-unrelaxed silicons.

The electronic structures for these clusters are calculated using the semiempirical MNDO method.[3] Accordingly, three- and four-center integrals in this Hartree-Fock framework are set to zero. The one- and two-center integrals are parametrized from atomic spectroscopy and characteristics (heats of formation, bond lengths, electric dipole moments, etc.) of small molecules. The detailed approximations and results for many molecules have been reported in the literature. The most important results of these calculations are the total energies as functions of atomic positions. These total energies can be used, in principle, to establish the stable geometry, metastability, migration, and reorientation energies, and vibrational frequencies.

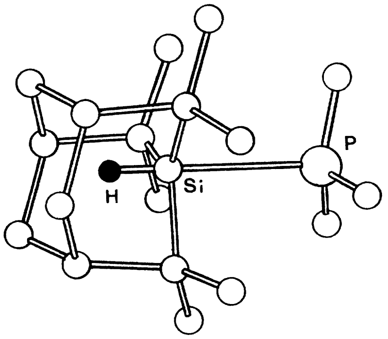

FIG. 2. View of the cluster $HPSi_{19}H_{36}$ with atoms relaxed. Hydrogen terminators are not shown in the figure.

TABLE I. Computed interatomic distances and displacements, total energies, and vibrational frequencies using cluster $HPSi_{19}H_{36}$. Distances are in angstroms, cluster energies (relative scale) and site energies in eV, and vibrational frequencies ('Freq.") in cm^{-1}. The sites labeled Si-AB, P-AB, and BC are identified in Fig. 1. Since we use an asymmetric cluster, there are two types of clusters with H at the BC site, one with the large cage on the Si side, BC(Si), and one with the large cage on the P side, BC(P). Both are needed to produce the BC "Site energy," indicated between the two BC columns, relative to that of the Si-AB site (see text).

Quantity	Si-AB	P-AB	BC(Si)	BC(P)
P origin	0.54	0.72	0.67	1.05
Si origin	0.74	0.13	0.66	0.48
Si-H	1.44		1.43	1.42
P-H		1.35		
P-Si	3.63	3.20	3.68	3.88
Cluster energy	0.00	1.62	1.48	2.48
Site energy	0.00	0.62	1.48	
Freq. (A_1)	2140	2550	2200	2280
Freq. (E)	630	700	510	570

III. COMPUTATIONAL RESULTS

We show in Table I the results of our calculations using the $HPSi_{19}H_{36}$ clusters as described in the preceding section; hence, the H, P, and opposing Si atoms are allowed to fully relax, the surrounding six silicon atoms are relaxed appropriate to the ZSi_8H_{18} starting cluster, and farther silicon atoms are frozen at rigid-lattice sites. Views of the relaxed atoms in the cluster are also provided by Figs. 2 and 3.

Notice that, due to the asymmetry of the $HPSi_{19}H_{36}$ cluster, there are two distinct BC clusters: one with P connected to the large cage of silicon atoms [call it BC(P)], and one with Si connected to the large cage of silicon atoms [call it BC(Si); this one is shown in Fig. 2]. These are equivalent in ZSi_8H_{18} and real crystalline silicon. In order to extract relative total energies for the three sites, all four cluster energies are required (row labeled "Cluster energy" in Table I). The energy difference between Si-AB (large cage on Si) and BC(Si) gives the energy difference between the relaxed Si-AB and BC structures; the energy difference between P-AB (large cage on P) and BC(P) gives the energy difference between the P-AB and BC structures (row labeled "Site energy" in Table I). From this, we see that the Si-AB site has the lowest energy, with the P-AB site higher by about 0.6 eV and the BC site higher by about 1.5 eV.

As a test, we used the $HPSi_{19}H_{36}$ cluster to calculate the corresponding relative total energies of these three sites for the H-B pair. We find that here the BC site has the lowest energy, consistent with the earlier studies, and the Si-AB and B-AB energies are higher by 0.95 and 1.73 eV, respectively. We have also explored the energy surface for the H-P pair with respect to H-only motion, and we find that all three sites are stable, suggesting that the BC and P-AB sites might be metastable. This is in contrast to the H-B pair, where the B-AB site is found by these and earlier calculations to be a saddle point for reorientation.

Selected atomic displacements and separations are also provided in the table and in Figs. 2 and 3. In Fig. 3 we show the coordinates of the relaxed atoms in a (110) plane. Also, on the figure we show schematically the phosphorus *p* orbital and the strong bond between the hydrogen and the silicon. Note that the H-Si unit is rigidly displaced substantially away from the phosphorus. Focusing on the Si-AB configuration, we note that the P and central Si atoms are displaced outward by substantial amounts. We also note that the Si-H distance of 1.44 Å is close to the conventional molecular distance of 1.48 Å for tetrahedrally bonded silicon. We return to this point in the following section.

The vibrational frequencies both parallel and perpendicular to the P-Si axis have been calculated for hydrogen in the $HPSi_{19}H_{36}$ cluster; these are also shown in Table I. The axial and perpendicular vibrational frequencies are predicted for the Si-AB geometry to be 2140 and 630 cm^{-1}, respectively. Here it is clear that there is a significant discrepancy between the reported experimentally determined frequencies (1555 and 809 cm^{-1}) (Ref. 11) and the results of these calculations.

For the purpose of a comparison which we describe in the following section, we also calculate the hydrogen location and frequency for the Si-AB geometry where all other atoms are frozen at their rigid-lattice sites. In this configuration the vibrational frequency was found to be 1800 cm^{-1}. Furthermore, the Si-H distance increased to 1.52 Å.

This substantial frequency reduction was brought about by a rather large change in the coordinates of the atoms which form the environment of the hydrogen. As a follow-up to this, we raise the obvious question: How sensitive is the frequency to cluster geometry and other factors pertaining to a frequency prediction? First, we have examined the adiabatic potential-energy surface for evidence of anharmonicity which would significantly affect these predictions. We find that the potential is adequately harmonic for H displacements up to about 0.3 Å, so that no corrections are necessary. Next, we varied the locations of the second-near-neighbor silicon atoms in relation to the phosphorus atoms by 0.1 Å and found frequency variations of only 10–20 cm^{-1}. Using the small-

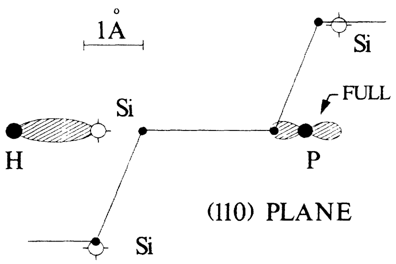

FIG. 3. Computed locations of atoms in a (110) plane for the H-P pair in the Si-AB geometry.

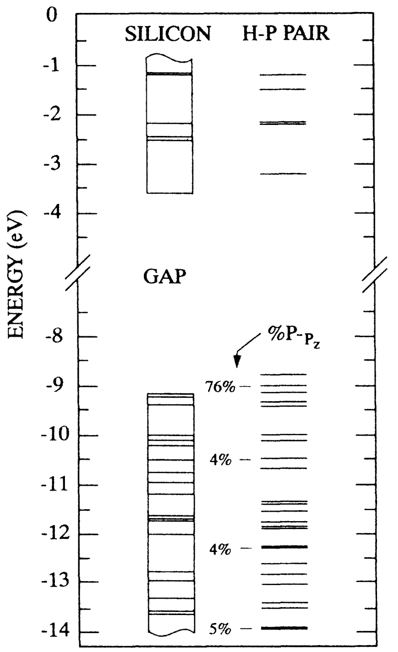

FIG. 4. Single-particle electronic structures of silicon and the H-P pair using cluster $ZSi_{19}H_{36}$. %P-p_z refers to the ⟨111⟩-oriented phosphorus p orbital.

er cluster, $PHSi_{16}H_{36}$, we computed a frequency of 2150 cm^{-1}, again only a small change. Other related changes similarly produce only small shifts in the predicted frequencies. Also, for the BC configuration, the frequency is relatively insensitive to these cluster changes (e.g., $HPSi_{19}H_{36}$ versus ZSi_8H_{18}), in contrast to what we have recently discovered for the H-B pair.[24]

Finally, the single-particle electronic structures appropriate to the $ZSi_{19}H_{36}$ cluster with and without the H-P defect pair are shown in Fig. 4. The band gap is simulated in this model calculation by the difference between the last occupied state and the first unoccupied state for the host. The exaggerated gap is an expected consequence of a Hartree-Fock-like method used in a cluster framework. This has been described in the literature.[21] The main point provided by the figure is that the gap is clear of states when the H-P pair is introduced; hence, no electrical activity is expected. The filled phosphorus p orbital is located just below the top of the valence band.

IV. DISCUSSION

We begin this discussion by first comparing our computed results for the H-P pair with those of other calculations and with experiment. The results of the current investigation appear in Table I. In Tables II and III we have collected relevant distances, energies, and frequencies appropriate to our calculations and those reported by others. We see that in all cases the Si-AB site is predicted to be the lowest in energy (Table III). Although the relative energies of the metastable configurations vary, most predict that the P-AB configuration is lower than the BC configuration. Also common among these calculations is a substantial relaxation of the Si adjacent to the hydrogen for the stable configuration (Table II). The predicted structural features are consistent with the observations of axial symmetry[25] and frequency insensitivity to donor identity.

The most significant discrepancies between predictions appear when we consider the vibrational frequencies. In our calculations, as well as in *ab initio* and semiempirical Hartree-Fock and tight-binding calculations of others, the axial frequency is predicted to be roughly 2150 cm^{-1}. This is considerably higher than the frequency of 1555 cm^{-1} assigned to the H-P pair. Our high-frequency prediction can be related to the strength of the Si—H bond, which is, in turn, related to the relaxed geometry. The relaxed defect is shown in Fig. 3 in the (110) plane, where it is clear that the Si atom has gone planar and, in fact, "puckered" a bit through the plane of the three neighboring silicon atoms. This silicon atom, according to our calculation, is attempting to tightly bond to the hydrogen as though it were a normal Si—H molecular bond. In fact, the Si—H bond length that we predict is 1.44 Å. This, in turn, produces a frequency in the 2000-cm^{-1} range, as expected for such a bond. It is this reversal or near reversal of the silicon position (i.e., silicon having moved through the plane of neighboring silicon atoms) that permits the formation of such a strong bond with what would otherwise be a weakly bound interstitial hydrogen.

TABLE II. Computed displacements and interatomic distances in angstroms for the H-P pair in silicon when in the Si-AB geometry.

Distance	Johnson[a]	Denteneer[b]	Amore-B.[c]	Estreicher[d]	Present
P origin		−0.14	0.09	0.19	0.54
Si origin		0.59	0.63	0.74	0.74
Si-H	1.6	1.66	1.41	1.40	1.44
P-Si		2.80	3.07	3.28	3.63

[a] Johnson *et al.*, Ref. 4.
[b] Denteneer *et al.*, Ref. 20.
[c] Amore-Bonapasta *et al.*, Ref. 19.
[d] Estreicher *et al.*, Ref. 18.

TABLE III. Computed energies in eV relative to the lowest-energy Si-AB configuration, E(site), and vibrational frequencies for the Si-AB configuration in cm^{-1}, ν(atom mode), for the H-P pair in silicon. A_1 refers to axial vibration and E refers to perpendicular twofold-degenerate vibration.

$X(\cdots)$	Johnson[a]	Denteneer[b]	Amore-B.[c]	Estreicher[d]	Present
E(BC)		0.45	0.19	1.33	1.48
E(P-AB)	0.41	0.35	2.37	0.92	0.62
ν(H-A_1)	2145	1460	2149		2140
ν(H-E)		740	908		630

[a] Johnson *et al.*, Ref. 4.
[b] Denteneer *et al.*, Ref. 20.
[c] Amore-Bonapasta *et al.*, Ref. 19.
[d] Estreicher *et al.*, Ref. 18.

If we freeze all atoms except the hydrogen at their rigid-lattice sites (i.e., if we do not permit the silicon atom to reverse its position to form an sp^3 bond with the hydrogen), then the hydrogen vibrational frequency is now reduced to 1800 cm^{-1}. This is still higher than the experimental value, but it is closer to it. This lower frequency is, of course, related to a weaker bond, as evidenced by the Si-H distance, which is now 1.52 Å instead of 1.44 Å. Notice how sensitive the frequency is to the Si-H separation. This configuration does not, however, produce a minimum in the total energy.

The local-density pseudopotential calculations, on the other hand, seem to produce a much weaker Si—H bond.[20] There, the Si—H bond length is greater, and the frequency is lower and therefore closer to the experimental value. Furthermore, we note that a metastable Si-AB geometry is produced in the local-density calculations with a still-lower frequency which is not produced in our calculations.

This brings us now to consider the experimental identification of the hydrogen vibrational frequency. The 1555-cm^{-1} band, reported by Bergman *et al.*,[11] is clearly related to a hydrogen atom and phosphorus, and has been identified with axial symmetry.[12] No H-P bands in the 2000-cm^{-1} range were observed in this study. In a more recent study,[26] the H-P pair has been identified with vibrations at about 2100 cm^{-1} and at 2340 cm^{-1}. In this treatment the symmetry was not identified by stress experiments, nor were other H-donor pairs considered as reported in the work of Bergman *et al.*[11,12]

In order to reconcile our theoretical predictions (and perhaps other Hartree-Fock predictions) with experiment, we consider the following alternative views: (i) the MNDO-cluster method overestimates the strength of the Si—H bond when Si is in a near-planar geometry, whereas local-density pseudopotential methods are more properly simulating this interaction; (ii) the MNDO-cluster method overestimates the degree to which the silicon relaxes away from the P so that the lower 1800-cm^{-1} result is more representative of the true H-P system; (iii) the MNDO-cluster method properly simulates this bond, but the actual configuration for the defect characterized by a 1555-cm^{-1} vibration is not the Si-AB geometry or any of the others considered here. Of course, this is where the new observation of a vibrational frequency at about 2100 cm^{-1} could play a role;[26] (iv) the frequencies are extremely sensitive to model-dependent approximations; hence, any of the reported computational results may be in error or accidentally correct.

We cannot at this time definitively rule out any of the above-mentioned alternatives. Further experiments to definitively rule out alternative (iii) and to search for metastable configurations would be helpful. Before statement (i) or (ii) could be considered definitive, the nature of the Hartree-Fock failure would have to be isolated; this has not been done. We do know, based on our MNDO and MINDO/3 (modified intermediate neglect of differential overlap, Ref. 27) simulations of a H-Si-Si_3-H_9 cluster, that the calculated H frequency is high (around 2200 cm^{-1}) for this simple cluster when the Si atom is in the plane of the other three silicon atoms. Hence, our resulting high frequency for the $\mathrm{HPSi}_{19}\mathrm{H}_{36}$ cluster is quite independent of the complications due to cluster geometry and the presence of phosphorus. In the meantime, we report our result and the corresponding discrepancy with the currently accepted experimental vibrational frequency.

V. SUMMARY

In summary, we have performed semiempirical electronic-structure calculations on the hydrogen-phosphorus pair in silicon using the MNDO method and the cluster $\mathrm{HPSi}_{19}\mathrm{H}_{36}$. We find that the Si-AB site is the most stable location for the hydrogen. This is consistent with other calculations, and an experimental model which explains the insensitivity of H vibrational frequency to donor type and the observation of axial symmetry. Furthermore, we find that the P-AB and BC sites could be metastable, with energies of 0.62 and 1.48 eV, respectively, relative to that of the Si-AB geometry.

The computed vibrational frequencies of 2140 and 630 cm^{-1} for axial and perpendicular motion, respectively, can be compared with the experimentally determined values of 1555 and 809 cm^{-1}. The predicted axial value is considerably higher than the assigned experimental value for reasons unknown at this time.

ACKNOWLEDGMENTS

The authors are grateful to Michael Stavola for helpful discussions, and to the Lehigh University Computing Center for the generous amounts of computer time and assistance which was made available. This research was supported by the U.S. Navy Office of Naval Research (Electronic and Solid State Sciences Program) under Contracts No. N00014-85-K-0460 and No. N00014-89-J-1223, and by the U.S. National Science Foundation (Research Experiences for Undergraduates Program) under Contract No. PHYS-89-00022.

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[24] We note as an aside that this is in contrast to what we have discovered recently for the H-B pair in a BC configuration. Here, the predicted frequency is found to change substantially from previous predictions when $ZSi_{19}H_{36}$ is used in the absence of a more thorough treatment of silicon relaxations, or when bond lengths or angles are changed even slightly. This sensitivity for small substitutional atoms next to BC hydrogen will be discussed more thoroughly in a subsequent publication. Meanwhile, we proceed since these effects are found to be small for the phosphorus-related systems we are considering here.

[25] Strictly speaking, we have not conclusively demonstrated that the defect has axial symmetry since the entire energy surface was not examined. However, axial symmetry is considered to be likely since sample calculations with H off-axis and full silicon and phosphorus relaxations produce higher energies.

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