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# Bond-centered interstitial hydrogen in silicon: Semiempirical electronic-structure calculations

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We report the results of electronic-structure calculations on interstitial hydrogen in silicon using the semiempirical modified neglect of diatomic overlap method with a finite cluster. We find that the interstitial hydrogen is stable at a bond-centered site, consistent with other, recent computational results. The barrier for migration between adjacent bond-centered sites is estimated to be $\lesssim 1$ eV. Furthermore, contrary to most other studies, we find the hydrogen to be asymmetrically located between the near-neighbor silicons. In a static picture, it is therefore bonded in a rather conventional way to one silicon, with the unpaired electron primarily located at the other silicon. However, we find that the barrier for inversion between neighboring silicons (along the bond) is quite small ($\lesssim 0.1$–$0.2$ eV); hence, motional effects are significant. Possible manifestations of this asymmetry are discussed.

## I. INTRODUCTION

As an impurity in covalent solids, atomic hydrogen has been a subject of scientific and technological interest for many years.[1] In silicon dioxide, for example, it has been identified as an impurity which attaches to ("satisfies") silicon dangling bonds at oxygen vacancies[2] and oxygen dangling bonds at silicon vacancies.[3] It has been found there as well in isolated form as an interstitial.[4] Hydrogen-containing defects are equally important in the tetrahedral semiconductors such as diamond, silicon, germanium, and gallium arsenide, where they are not as well understood.[1] In silicon, for example, hydrogen has been identified as a constituent in defect complexes and proposed as a passivator of dangling bonds in a lattice vacancy (see, for example, Refs. 5–7). In amorphous silicon, it clearly passivates silicon dangling bonds, thereby increasing the conductivity. In this study we treat theoretically the much more elusive isolated, interstitial hydrogen impurity in crystalline silicon. We concentrate on a particular location for the interstitial hydrogen which currently appears to be the most likely stable site.

Most of what is known about the hydrogen interstitial in tetrahedral semiconductors has been inferred from experimental studies of its pseudoisotope, muonium.[8–10] For our purposes, muonium can be considered to be a light ($\frac{1}{9}$ the mass of a proton) isotope of hydrogen with a short (2.2-$\mu$s) lifetime. Muonium is studied experimentally by the muon-spin-resonance ($\mu$SR) technique, which can provide essentially the same information as one normally extracts from electron paramagnetic resonance (EPR). The analogous hydrogen interstitial has proven to be much more elusive. As a consequence, the nature of the isolated interstitial has been a subject of particular controversy for many years.

There have been many theoretical treatments of hydrogen and/or muonium in silicon, including hydrogen at silicon-vacancy sites, hydrogen near other impurities, and the isolated interstitial. Based on computational studies which produce total energies, a number of locations have been proposed as being stable sites for the isolated hydrogen. Recently, some independent studies have revealed the bond-centered (BC) site as the lowest-energy position for atomic hydrogen in crystalline silicon and diamond.[10–15] Here, the hydrogen is located along the line joining near-neighbor silicon atoms. The impurity is found to be accompanied by substantial, outward relaxations of the neighboring silicons.

In this treatment we focus on the BC configuration of interstitial hydrogen. We examine the total energy and eigenstates as a function of hydrogen and silicon positions using semiempirical electronic-structure methods and a variety of cluster simulations of the environment. Based on the results we propose a simple model for the electronic structure and consequent stable geometry. We also examine the migration, reorientation, and vibrational characteristics, and speculate on possible, significant differences between hydrogen and muonium.

## II. BACKGROUND

The most complete experimental information is still that inferred from $\mu$SR studies of the hydrogen pseudoatom, muonium.[8–10] It is well known from these studies that the muonium pseudoatoms are located at two distinct sites in diamond and many semiconductors, including silicon. The defect is referred to as "normal muonium" (Mu) when the muon is located at the site observed to have tetrahedral ($T_d$) point-group symmetry. Geometries proposed for normal muonium include a stable tetrahedral interstitial ("$T$") site for the muon, and other models which produce the required symmetry through motional averaging.[10] Its isotropic hyperfine constant is found to be reduced from its free pseudoatom value by a factor of 0.44 when in silicon, for example. The other form, referred to as "anomalous muonium" (Mu*), has axial ($C_{3v}$) symmetry and is characterized by a highly anisotropic hyperfine interaction. This anisotropy indicates a substantial localization, but not on the muon, where only 2% or 3% of the unpaired spin is found. Silicon hyperfine has been resolved in a recent $\mu$SR experiment, where about 41% of the unpaired spin was identified with two equivalent silicons.[9] These hyperfine results confirm the BC model first suggested on the basis of chemical arguments[10] and computational studies.[11–15]

We begin the discussion of theoretical treatments with a brief description of some of the early computational studies involving hydrogen and/or muonium. In many of these studies electronic structures were reported for hydrogen located at a *T* site, and neither impurity nor host-atom displacements were explored. In a pioneering cavity-model study, Wang and Kittel[16] demonstrated how the hyperfine constant of Mu could be reduced when located in such a crystalline environment. Subsequently, the *T* site was examined using a supercell pseudopotential technique,[17] a cluster scattered-wave $X\alpha$ method,[12] and a spin-unrestricted, local-density, pseudopotential Green's-function method.[18] The first calculation with total-energy capabilities was an extended Hückel treatment by Singh, Weigel, Corbett, and Roth,[19] which located the isolated interstitial at the tetrahedral site when other defects were not present. In a later complete neglect of differential overlap (CNDO) treatment, Mainwood and Stoneham[20] also found a stable *T* site for hydrogen in silicon; however, it was very weakly bound. Using unrestricted Hartree-Fock methods, Sahoo *et al.*[21] and Estreicher *et al.*[22] found hydrogen to be stable in diamond at the *T* site. In a modified neglect of diatomic overlap (MNDO) study, Corbett *et al.*[23] found that the hydrogen was stable at the *M* site[24] when the silicon atoms were constrained to remain at their rigid-lattice sites.

We now describe recent theoretical treatments which focus on the BC site or the Mu* defect. The BC site was suggested as a possible location for the Mu* defect in a study by Cox and Symons.[10] There it was suggested that this site could be consistent with Mu* observations and that such a site was chemically reasonable for hydrogen or muonium. The first successful computational studies involving the BC site in silicon and diamond were reported by Estle *et al.* and by Estreicher.[11] This was accomplished using a Hartree-Fock PRDDO (partial retention of diatomic differential overlap) method by permitting the silicon near neighbors to relax outward by a substantial amount in response to the hydrogen (or muonium) impurity. It was concluded there that the BC site was stable and that the *T* site was metastable. Since this first calculation, four other calculations have supported the BC site as the stable position for hydrogen in silicon; these are a MNDO cluster calculation,[12] an MINDO/3 (modified intermediate neglect of differential overlap) cluster calculation,[13] a local-density, pseudopotential, Green's-function calculation,[14] and a Hartree-Fock cluster calculation.[15] As in the original PRDDO study,[11] all find substantial outward relaxations of the silicon near neighbors.

It is important to note that in all but the MNDO (Ref. 12) and Hartree-Fock (Ref. 15) calculations the hydrogen is found to be stable at the geometrical center of the bond, equidistant from both silicon neighbors. These two report qualitatively different results, with the hydrogen bonded to only one silicon atom, and the other silicon more distant. The MNDO cluster, however, had a bias which might have artificially encouraged the bonding to a single silicon atom.

In this study, we expand on this earlier MNDO treatment using primarily a cluster environment which is symmetric about the geometrical center of a bond. We describe the clusters used and the MNDO electronic-structure method in the following section.

## III. COMPUTATIONAL METHOD

The hydrogen impurity and its environment are simulated in this treatment by finite fragments of the solid; this is a cluster approach. We use two different clusters to simulate the BC environment. The first cluster, $X\mathrm{Si}_5\mathrm{H}_{12}$ (abbreviated to Si-5 cluster), is centered at a host-atom site. The hydrogens serve to tie up the silicon dangling bonds at the surface of the cluster; *X* represents the hydrogen impurity. This is the cluster used in the MNDO treatment mentioned above.[12] A related cluster, $X\mathrm{Si}_4\mathrm{H}_{12}$, produces a substitutional environment and has been used as a framework for the treatment of many other defect systems.[25]

The primary cluster used in this study, $X\mathrm{Si}_8\mathrm{H}_{18}$ (Si-8 cluster), includes two near-neighbor silicon atoms about the BC site and six silicon atoms about those. With silicons at rigid-lattice positions and no impurity present, this cluster is symmetric about the BC site. Here, 18 hydrogen atoms serve to terminate the cluster.

The electronic structures of these molecular clusters are calculated using the semiempirical MNDO method.[26] Accordingly, the 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 approximations and results for many molecules have been reported in the literature.

Resulting from these electronic-structure calculations are single-particle energies and wave-function coefficients appropriate to given atomic positions. The interpretation of the single-particle–energy differences as excitation energies must be handled with caution, as summarized in Ref. 25. More important, however, are the total energies as functions of atomic positions which are produced by this semiempirical method. These total energies are used to establish the stable geometry, migration and reorientation energies, and vibrational frequencies.

In its simplest application the host atoms are kept at their rigid-lattice sites and the total energy is monitored as a function of the impurity position. A somewhat more elaborate procedure involves the simultaneous relaxation of the impurity atom(s) and the neighboring silicon atoms. In order to more realistically simulate the change in total energy due to displacements of the clusters' outer silicon atoms (four silicon atoms in Si-5 and six silicon atoms in Si-8), we connect these silicons to springs with parametrized spring constants for parallel (along bond) and perpendicular (perpendicular to bond) displacements. This has been described in Ref. 25 and referred to as a "hybrid" approach, since one part of the total energy derives explicitly from the electronic-structure calculation, and the other (spring) part is added to simulate the interaction between silicon atoms in the cluster and more distant silicon atoms not present in the cluster. In the case of Si-8 the inner two silicon atoms relax against each other (or each against an interstitial hydrogen, when present) and against the outer shell of six silicon atoms. In both cases the hydrogen terminators follow the outer silicon atoms with the corresponding bond angles and lengths preserved (taken in this treatment to be 109.47° and 1.48 Å, respectively). When the cluster calculations contain this additional spring energy, we will refer to the clusters as Si-5(hyb) or Si-8(hyb).

Although an extended discussion of cluster termination was reported in Ref. 25, we augment that with a brief description of how those conclusions, appropriate to substitutionally centered clusters, relate to the BC cluster treated here. First, with regard to terminator-silicon distance, the natural Si-H distance is appropriate for use in $X\mathrm{Si}_8\mathrm{H}_{18}$ for the same reason as it is for $X\mathrm{Si}_{16}\mathrm{H}_{36}$. In both cases there are two shells of silicon atoms between the impurity and the terminators. The use of the crystalline-silicon Si-Si distance for termination has been advocated in Ref. 25 only to improve electronic structures where (i) there is no silicon relaxation, and (ii) where there is only one shell of silicon atoms separating the substitutional impurity from the hydrogen terminators.

A second point relates to the use of a BC cluster with a frozen outer shell of silicon atoms (and terminators). It was reported in Ref. 25 that the well-known spontaneous off-center displacements of substitutional nitrogen and oxygen were quenched (or partially quenched), contrary to experiment, when using the $X\mathrm{Si}_{16}\mathrm{H}_{36}$ cluster in this frozen-shell mode. These, however, are particularly extreme cases since, in a cage of frozen outer silicon atoms, the critical asymmetric displacements of the near-neighbor silicon atoms produce exceptionally large and rather artificial increases in silicon near-neighbor to next-near-neighbor distances. These extreme bond-stretching displacements would not occur if the next-near-neighbor shell of silicon atoms were to relax. For the BC cluster treated here, the motion of the two near-neighbor silicon atoms along the bond are directed toward the *center* of the triangle formed by the cage of outer silicon atoms; hence, they are not so confined by a frozen cage of outer silicon atoms and terminators.

## IV. COMPUTATIONAL RESULTS AND DISCUSSION

We first describe the fully relaxed configurations found using the clusters Si-5(hyb) and Si-8(hyb), where the hydrogen interstitial and the silicon atoms are free to move. As previously reported for the Si-5(hyb) cluster, the hydrogen impurity was found to be stable at the BC site, with the adjacent silicon atoms relaxed outward so that the new silicon-silicon distance is 3.18 Å (compared with 2.35 Å in crystalline silicon).[12] This is consistent with the Hartree-Fock PRDDO calculations of Estle *et al.* and Estreicher.[11] The stable site originally identified using the MNDO method with rigid-lattice silicon atoms (the *M* site) is energetically unfavorable when the silicon atoms are allowed to relax. We found from these MNDO computations that the hydrogen is stable at a distance of 1.47 Å from one silicon atom and 1.72 Å from the other. This suggested a model for the bond-centered hydrogen which is qualitatively different from those produced by the other recent treatments, where the hydrogen was found to be stable at a site equidistant from the neighboring silicon atoms. However, even within the framework of the MNDO cluster approximation these results do not decisively establish a stable asymmetric BC configuration, since this particular cluster is biased toward one of the two near-neighbor silicon atoms.

We now consider the results from our Si-8(hyb) cluster calculations. This cluster is symmetric about the BC site in the absence of the hydrogen impurity and with silicon atoms at the rigid-lattice sites. In Fig. 1 we show the locations of the hydrogen impurity and silicon host atoms found from this calculation for the stable configuration. Some relevant distances are given in Table I. Also presented in Table I are the corresponding distances when the system is in its positive charge state. Notice that when the interstitial is positive, the hydrogen is located at the geometrical center of the silicon-silicon bond; however, when the neutralizing electron is added, the hydrogen and silicon atoms spontaneously displace to sites of lower symmetry along the bond.

The most decisive statement which can be made on the basis of these computational results is that a BC

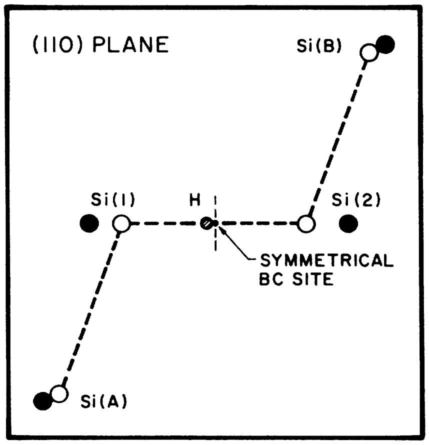

FIG. 1. Relaxed hydrogen and silicon positions. These atomic positions, shown in a (110) plane, correspond to the host-atom positions (open circles) and low-energy arrangement (solid and hatched circles) found using the MNDO method with our Si-8(hyb) cluster for the neutral species (see text).

TABLE I. Important interatomic distances calculated for the neutral and positive-charge states of $HSi_8H_{18}$. For both cases, the hydrogen and silicons are relaxed using our Si-8(hyb) cluster.

| | Neutral H (Å) | Positive H (Å) |
|---|---|---|
| Si(1)-H | 1.48 | 1.59 |
| Si(2)-H | 1.77 | 1.59 |
| Si(1)-Si(2) | 3.25 | 3.18 |
| Si(1)-Si(*A*) | 2.39 | 2.40 |
| Si(2)-Si(*B*) | 2.38 | 2.40 |

configuration is the stable geometry for interstitial hydrogen in silicon. This supports the Si-5(hyb) result,[12] the stable geometry reported by Estle *et al.* and by Estreicher,[11] and the recent $\mu$SR hyperfine study of Mu* by Kiefl *et al.*[9] A more subtle computational result is that these MNDO calculations, even with an otherwise symmetric cluster, produce a neutral hydrogen impurity site which is closer to one silicon atom than the other. With the silicon atoms frozen as in Fig. 1, the total energy is shown in Fig. 2 as a function of hydrogen position. This double well disappears when one electron is removed to create the positive charge state. Therefore, based on statics these results are qualitatively different from those reported by other investigators since we find the hydrogen impurity to be bonded to one of the silicon neighbors and relatively independent of the other. We will return to this point.

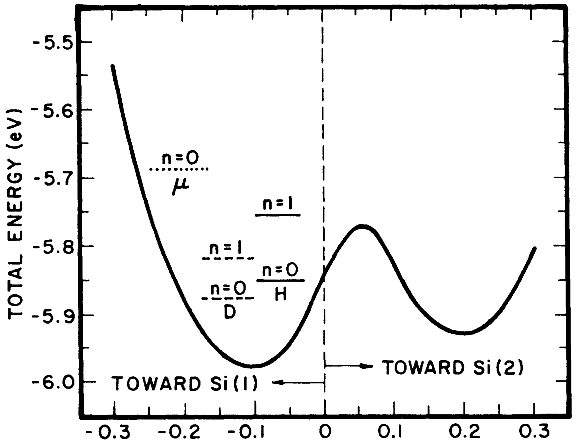

FIG. 2. Total energy vs hydrogen displacement along the bond. Here, the silicon atoms are frozen as in Fig. 1, while the neutral hydrogen atom is displaced. Zero hydrogen displacement corresponds to the hydrogen located at the geometrical center of the bond as defined by silicon atoms at their rigid-lattice positions. Computed vibrational energies for hydrogen, deuterium, and muonium appropriate to this potential-energy function are shown. (Note: The levels are located on the left-hand side of the diagram for convenience only; they are not intended to convey a specific wave-function localization.)

For completeness, we show in Fig. 3 the corresponding single-particle electronic structures. In Fig. 3(a) we show the single-particle states appropriate to the unrelaxed simulation of the host ($Si_8H_{18}$);[27] allowing these silicons to relax in our cluster produces little change in Fig. 3(a). In Fig. 3(b) we have inserted the neutral hydrogen and allowed the system to relax. (Although, strictly speaking, the gap states here should not be labeled by *g* and *u*, we retain this notation for convenience.) The wave-function–expansion coefficients are given in Table II for the last occupied state (unpaired electron) and the first unoccupied state above it. Notice that little amplitude is found on the hydrogen impurity, even when it is off the symmetric BC site. This is consistent with the $\mu$SR observations, although a quantitative comparison would re-

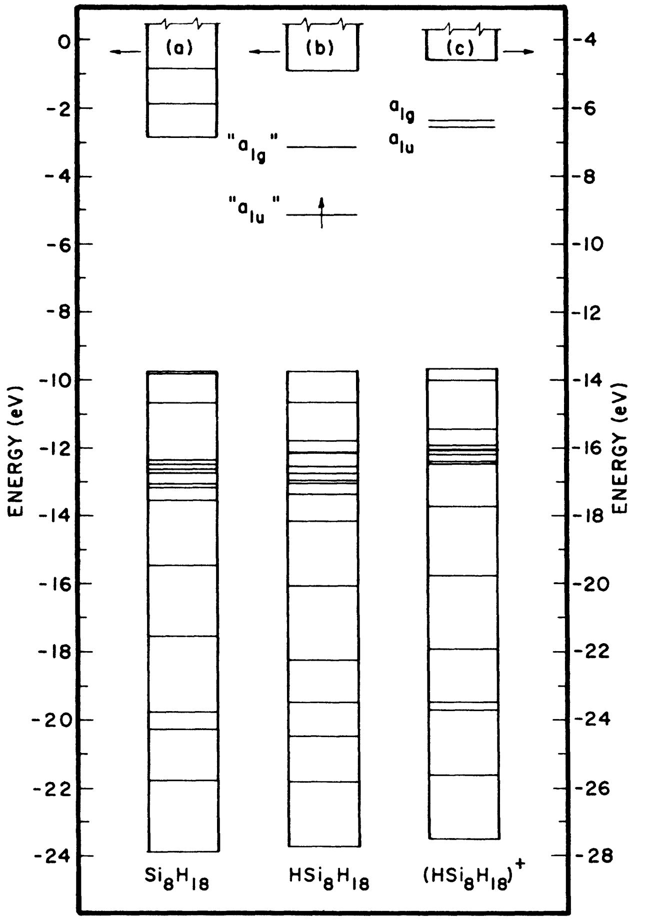

FIG. 3. Single-particle electronic structures. Single-particle electronic structures are shown for (a) cluster $Si_8H_{18}$ with silicon atoms at rigid-lattice sites, (b) cluster $HSi_8H_{18}$ with all atoms relaxed, and (c) cluster $HSi_8H_{18}$ in the positive charge state with all atoms relaxed. In our model system the lower block of states corresponds to the valence band and the upper block to the conduction band. Band gaps tend to be exaggerated in these calculations (see Ref. 27). Panels (b) and (c) correspond to our Si-8(hyb) cluster (see text). Note that although *g* and *u* are not good symmetry labels for the asymmetric (neutral) case [panel (b)], we retain the notation for convenience.

TABLE II. Wave-function–expansion coefficients for the states $a_{1u}$ and $a_{1g}$, appropriate to the cluster $HSi_8H_{18}$. For both neutral and positive charge states, the hydrogen atom and silicon atoms are relaxed using our Si-8(hyb) cluster. A *positive p*-state amplitude corresponds to an orientation along the Si(1)-Si(2) axis with the positive lobe pointing to the right in Fig. 1. Note that although $g$ and $u$ are not good symmetry labels for the asymmetric (neutral) case, we retain the notation for convenience.

| | Neutral H | | Positive H | |
|---|---|---|---|---|
| | $a_{1u}$ | $a_{1g}$ | $a_{1u}$ | $a_{1g}$ |
| H $s$ | 0.030 | 0.118 | 0.000 | 0.107 |
| Si(1) $s$ | 0.103 | −0.412 | 0.285 | −0.286 |
| Si(1) $p$ | 0.110 | 0.059 | 0.165 | 0.047 |
| Si(2) $s$ | −0.378 | −0.110 | −0.285 | −0.286 |
| Si(2) $p$ | 0.150 | −0.092 | 0.165 | −0.047 |

quire the inclusion of zero-point vibrational effects. We do not attempt this here. The two near-neighbor silicon atoms account for about 19% of the unpaired spin, which is roughly half the value estimated from experiment;[9] our result also appears to overestimate the $s$ amplitude, although contact with experiment here is clouded by the presence of the nearby hydrogen. Such an underestimation of the unpaired spin is not uncommon.[25] We also note that most of the unpaired spin is on the silicon that is located opposite the hydrogen displacement direction [Si(2)]. This asymmetry at first does not appear to be consistent with experiment; however, motional effects are critical here. We return to this point later.

The single-particle electronic structure is shown for the positive charge state of fully relaxed interstitial hydrogen in Fig. 3(c). The wave-function–expansion coefficients are also given in Table II.

We now describe a simple model for the electronic structure of interstitial hydrogen located at a BC site. We begin by considering the hydrogen impurity located at the symmetric BC site. For convenience, we examine these features in the single-particle electronic structures for the relaxed positive charge state,[27] shown in Fig. 3(c). The state at the bottom of the valence band is primarily bonding between the hydrogen $s$ state and the silicon $s$ states on either side. The highest state with a significant hydrogen amplitude is in the conduction band and is anti-bonding between the hydrogen $s$ state and the silicon $p$ states on either side. Moving up from the bottom of the valence band, the $s$ state bonding character changes to antibonding. The state labeled $a_{1g}$ is weakly antibonding. It is therefore nearly degenerate with the state labeled $a_{1u}$, which, of course, has no amplitude on the hydrogen. The $a_{1g}$ state is slightly higher as a consequence of the weak antibonding character. The last (unpaired) electron would occupy the lower ($a_{1u}$) state, with the unoccupied ($a_{1g}$) state above it.

It is difficult to reveal and further explore basic features using our Si-8(hyb) simulations as a consequence of the many atomic coordinates and the asymmetrically displaced near-neighbor silicon atoms which are present. Therefore, we explore these features by a simple application of our Si-8 cluster, where we freeze the coordinates of the outer six silicon atoms, and move the inner ones in or out symmetrically. Hence, we have only one coordinate which characterizes host-atom positions.

We first consider this cluster with a hydrogen interstitial at the symmetrical BC site and silicon near neighbors each relaxed outward by 0.4 Å. We show by circles on the left-hand side of Fig. 4 the single-particle energies in the band gap. We do this for the single positive charge state so that the levels of interest, $a_{1g}$ and $a_{1u}$, are both unoccupied.[27] For the neutral defect, the last electron would go into the lower $a_{1u}$ state. The $a_{1g}$ state is near and above the $a_{1u}$ state. Therefore, these states are similar to the corresponding Si-8(hyb) states shown in Fig. 3(c) and are consistent with the simple model just described.

At this juncture we can see the possibility of a spontaneous off-center displacement of the hydrogen along the bond. Such an asymmetric displacement would couple the unoccupied $a_{1g}$ state to the occupied $a_{1u}$ state so that the occupied state would be driven down with displacement. If these states are sufficiently close together and the coupling is sufficiently strong (relative to the quadratic restoring forces), then the total energy would decrease with the displacement reflecting the downward motion of the odd state, but only when it is occupied (neutral charge state). This would be an example of a "pseudo-Jahn-Teller" (PJT) effect, which is well documented in the literature.[28]

This is consistent with our Si-8(hyb) calculations; however, we again appeal to our Si-8 cluster for simplicity and monitor the total energy as a function of hydrogen position off the geometrical center of the bond. The total energies resulting from these computations are shown for the neutral charge state in Fig. 5. The most conspicuous feature is that the hydrogen will spontaneously displace to a site of lower symmetry at a critical silicon separation

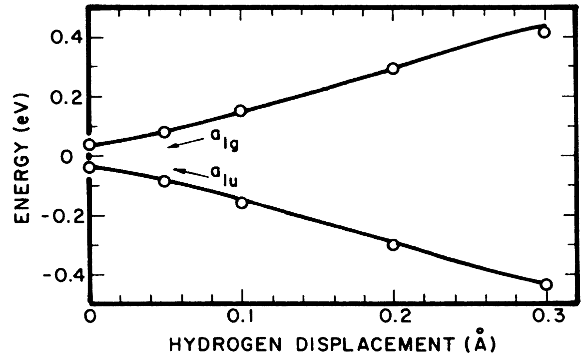

FIG. 4. Single-particle energy levels in the gap vs hydrogen displacement along the bond. The circles represent MNDO single-particle energies appropriate to the positive charge state of the cluster $HSi_8H_{18}$, where the near-neighbor silicon atoms are each displaced outwards by 0.4 Å (our Si-8 cluster). The solid lines represent a simple two-level linear pseudo-Jahn-Teller fit to these single-particle energies (see text).

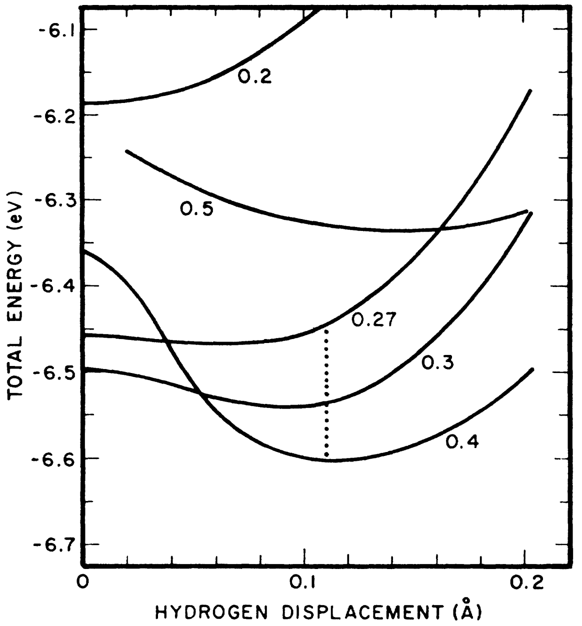

FIG. 5. Total energies vs hydrogen displacement along the bond. These total energies, appropriate to the neutral cluster $HSi_8H_{18}$ (Si-8), are shown for various outward silicon displacements (e.g., 0.4 on the figure corresponds to outward silicon displacements of 0.4 Å each).

of about 2.9 Å (i.e., with each silicon moved outward by 0.27 Å); this is not unexpected. The lowest system energy corresponds to outward silicon displacements of 0.4 Å and an *off-center hydrogen*. A related system, the linear triatomic molecule, was studied by Opik and Pryce as an example of what became known as a PJT effect.[28] There it was demonstrated that the central atom would spontaneously displace to a site of lower symmetry when the outer atoms were sufficiently far apart. This perturbative description has been used to understand such displacements for many defect systems in solids.

A feature common to all pseudo-Jahn-Teller systems is that the presence, character, or absence of such a displacement depends on the charge state [i.e., the occupancy of the critical valence state(s)]. This feature is found here in the simple Si-8 simulation, where the positive hydrogen is found to be stable on center, just as it is in the Si-8(hyb) simulation described earlier. This suggests that a PJT description might be appropriate here.

The argument for such a description is more convincing when one also examines the single-particle energies and wave-function coefficients for the two nearly degenerate states which are coupled by the off-center hydrogen displacement. We show the single-particle states appropriate to the levels in the gap in Fig. 4 and the wave-function coefficients in Fig. 6 (again, using our Si-8 cluster for the positive charge state[27] where the silicon atoms are displaced outward by 0.4 Å each).

The two states appropriate to the symmetric location of the hydrogen are approximated by the following combination of (unnormalized) $s$ orbitals:[29]

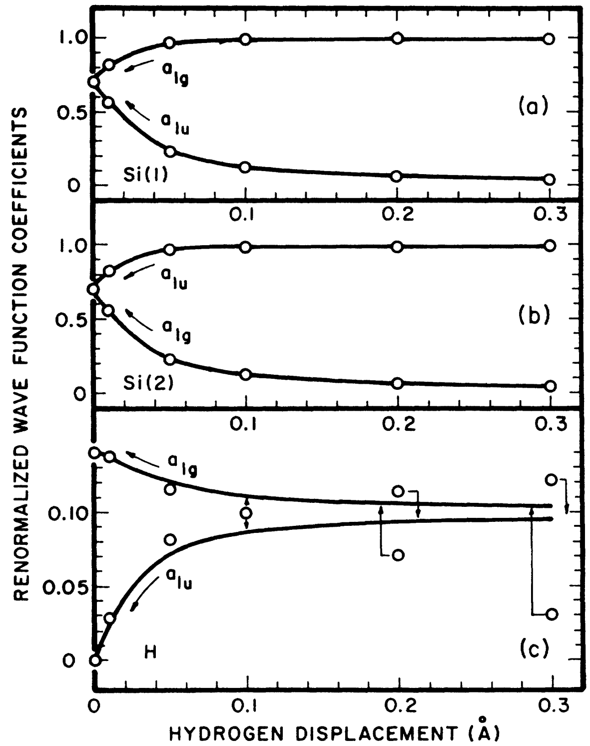

FIG. 6. Silicon and hydrogen wave-function coefficients from the Si-8 MNDO calculations (circles) and the simple two-level pseudo-Jahn-Teller fit (lines). See the text and the caption to Fig. 4.

$$\phi(a_{1g})=a+c-\varepsilon b$$

and

$$\phi(a_{1u})=a-c\ ,$$

where $a$ and $c$ refer to Si(1) and Si(2), respectively, and $b$ refers to the hydrogen. In the linear-coupling approximation for displacement $Q$, the matrix of the Hamiltonian between these states is given by

$$\begin{vmatrix} D/2 & -2\varepsilon VQ \\ -2\varepsilon VQ & -D/2 \end{vmatrix} .$$

$D$ is the spacing between levels appropriate to $Q=0$; it is found from the left-hand side of Fig. 4 to be 0.077 eV. $\varepsilon$ is the fractional amount of H amplitude in the even state for $Q=0$; it is found from the left-hand side of Fig. 6(c) to be 0.14, where 0.20 is appropriate to the unnormalized expression above [i.e., $0.14=0.20/(2+0.20^2)^{1/2}$]. $V$ is the hydrogen-$s$-state–silicon-$s$-state coupling constant. A value of $V=-3.6$ eV/Å produces the best fit to Fig. 4. The agreement between the PJT model and the more rigorous MNDO calculations is quite good, as shown in Fig. 6.

This fit simply confirms that our MNDO results can be understood in terms of a simple PJT picture. Even if this static asymmetry is present, it may or may not be apparent in an experiment as a consequence of motional effects. In particular, if the barrier between the two equivalent off-center BC sites is small, then motional effects may cloud the identification of distinguishable silicon neighbors. However, since there are precedents for such off-center configurations, we feel that it deserves further examination. One might be tempted, for example, to develop an analogy between the hydrogen interstitial and the $E_4'$ center in silicon dioxide,[2] where a hydrogen atom, located between two silicon atoms at an oxygen vacancy site, favors one of the two silicon atoms and forms a rather conventional Si—H bond with it. The adjacent silicon then contains a dangling bond; it is the site of the system's unpaired spin. One problem with this analogy is that silicon dioxide has an intrinsic asymmetry. Perhaps more important, however, is that the silicon-silicon distance appropriate to an oxygen vacancy in silicon dioxide is considerably larger than the crystalline-silicon near-neighbor distance. We note that such a hydrogen off-center displacement has been proposed for hydrogen in amorphous silicon;[30] however, there it is argued that the effect is natural since silicon near neighbors can be found with various separations, particularly separations considerably greater than 2.35 Å.

We now consider the motion of the hydrogen impurity. In particular, we estimate the barrier to migration between equivalent BC minima along neighboring bonds and equivalent BC minima along the same bond (which we call "inversion," for convenience). We consider this latter barrier first, and return to the problem of migration shortly.

We have already shown the total energy for the Si-8(hyb) cluster with respect to hydrogen displacement along the bond in Fig. 2, where the silicon atoms are frozen as in Fig. 1. This simplest possible estimate suggests a barrier for inversion of about 0.2 eV. At best, this one-coordinate method produces a measure of the upper limit on the barrier height.

Alternative methods for estimating a barrier height include setting the silicon coordinates at intermediate positions when calculating the saddle-point energy, or allowing the silicon atoms to fully relax for every hydrogen position. In this latter method, the silicon atoms respond to the instantaneous positions of the hydrogen impurity. We have calculated the barrier appropriate to this fully adiabatic energy surface, and we find, however, that the barrier is clouded in our calculation by what is perhaps an expected effect: When the hydrogen atom is moved along the bond, the silicon atoms follow the hydrogen, the energy increasing beyond the midway hydrogen position until it drops abruptly as the silicon atom "snaps" back. In other words, even when the hydrogen is fixed on center, asymmetric silicon displacements will still lower the total energy. Hence, there is no well-defined saddle point for reorientation that can be readily extracted. We have reported such abrupt rebonding before in a treatment of substitutional nitrogen in silicon.[25] This effect is well known in electric-circuit theory and is called "drag loop." We observe a similar effect when we consider hydrogen migration between adjacent bonds. This general effect should be explored further, but we will not pursue it here. Instead we consider another alternative measure of the barrier which seems particularly appropriate in this case.

We use the fact that hydrogen, being substantially lighter than silicon, will for the most part follow the silicon motion adiabatically. Therefore, we argue that the appropriate *barrier is the energy required in moving the silicon atoms so that the hydrogen can spontaneously reorient.* Here, we view the inversion in terms of what has been described in the literature as the "opening of a door," which, in our case, permits the hydrogen to displace.[31] Alternatively stated, the impurity motion is occasionally permitted by the appropriate motion of the host atoms.

We again appeal to our simple Si-8 treatment. Recall that the hydrogen is stable on center until the silicon atoms are displaced outward by 0.27 Å each. Conversely, when the silicon atoms are moved from the equilibrium displacements of 0.4 Å each to 0.27 Å each, an off-center hydrogen will spontaneously displace to the center of the bond. This symmetrical configuration is the saddle point for inversion. Therefore, the vertical dotted line in Fig. 5 represents such an estimate of the inversion energy; hence, we estimate a barrier for inversion of $\lesssim 0.1-0.2$ eV. We note in passing that this figure also reveals the corresponding adiabatic estimate, where the silicons are permitted to relax for each hydrogen position. By this measure, the inversion energy is the difference between the absolute minimum energy and the minimum energy appropriate to an on-center hydrogen atom and symmetrically located silicon atoms. This latter minimum occurs when the silicon atoms are displaced outward by approximately 0.3 Å; hence, the adiabatic barrier is estimated from the figure to be $\lesssim 0.1$ eV.

By all of these estimates this barrier for inversion that we predict is quite small. Therefore, the motional effects are likely to be significant. From the lower portion of the left-hand (deeper) well of Fig. 2, we estimate a hydrogen vibrational frequency of 2500 $\text{cm}^{-1}$, corresponding to a spring constant of 23 eV/$\text{Å}^2$. This would be consistent with a rather constrained Si-H system since a typical Si—H covalent bond produces a hydrogen vibrational frequency in the range 2100–2300 $\text{cm}^{-1}$.

Due to the extreme anharmonic nature of this potential-energy surface, we do not use this force constant. Instead, we solve the one-dimensional problem exactly using the potential-energy function of Fig. 2. The vibrational energies for hydrogen, deuterium, and muonium are included in the figure. Note that for hydrogen the zero-point energy is close to the barrier for inversion along the bond; for muonium it is much higher than the barrier. The photon frequencies for infrared excitation (estimated from the $n=0$ to 1 transitions) are 800 $\text{cm}^{-1}$ for hydrogen and 470 $\text{cm}^{-1}$ for deuterium; the corresponding ratio (isotope shift) is 1.7.

Based on these computational results, we now consider whether or not the symmetric and asymmetric models of interstitial BC hydrogen can be distinguished experimentally. Unfortunately, the hydrogen frequency which we calculate is close to that estimated by Deak *et al.*,[13] where the hydrogen atom is symmetrically located between the two neighboring silicons; such a low hydrogen frequency is characteristic of a symmetrical, three-center (Si-H-Si) system. As a consequence, the hydrogen frequency alone may not distinguish these two models. On the other hand, the asymmetric model might be distinguished in an infrared experiment by the anharmonic hydrogen-deuterium isotope shift that we predict, and by other more subtle features that are associated with defect systems having small barriers.[32]

We now ask the question: Would this asymmetry for hydrogen in a BC site be revealed by a measurement of the silicon hyperfine? Unfortunately, we must conclude that a motionally averaged hyperfine would be detected for muonium, hydrogen, and deuterium; hence, any inequivalence of the silicon atoms would not be revealed. We base this conclusion on the large tunneling splitting which we find (800 $\mathrm{cm}^{-1}$ for hydrogen). This corresponds to a tunneling rate of $2.4\times10^{13}$ Hz, which is orders of magnitude greater than the hyperfine frequency of roughly 100 MHz (say, from *A* of Ref. 9). In order to distinguish the inequivalent silicon atoms of our asymmetric model, one would need a *heavy*-hydrogen pseudoisotope, where the tunneling splitting would be small.

Before terminating the discussion of the asymmetric displacement, we comment briefly on the fact that this result is produced by some computational studies and not others. As described earlier, three other computational studies have reported that on-center (symmetric) hydrogen is the low-energy configuration;[11,13,14] one other study reports results similar to those found in our treatment.[15] Each method incorporates a set of simplifying approximations into an otherwise intractable many-body problem. The manifestations of these approximations with regard to the symmetric-versus-asymmetric positions of the BC hydrogen are not apparent. In fact, it would be quite difficult to isolate and correlate specific computational approximations with this instability to asymmetric displacement. This is not surprising since a PJT instability can be quite sensitive to small quantitative computational differences. We can only say that the asymmetric result is produced with our MNDO cluster method when used in three modes: the two described, and a third approach where the outer shell of silicon atoms plus terminators ($\mathrm{Si_6H_{18}}$) moves *rigidly* with the near-neighbor silicons. Therefore, we suggest the off-center model as a possibility, and beyond that we must appeal to experiment.

We return to the problem of barriers and proceed as before to estimate a migration barrier to an adjacent bond. We consider our Si-8 cluster and permit the hydrogen to fully relax in a (110) plane (such as shown in the inset of Fig. 7) for various outward silicon displacements. The relaxed hydrogen coordinates (in terms of angles and distances) and total energies are shown in Fig. 7. Here we see that as the silicons are moved in toward their rigid-lattice positions the hydrogen is ultimately pushed off the bond. When the silicons finally reach their rigid-lattice values, the hydrogen is 41° off the bond axis, approaching the 54.7° which would be the precise saddle point for reorientation (with silicon atoms at rigid-lattice site).[33] This 41° is within a few degrees of the corresponding value obtained from our Si-5 and Si-5(hyb) calculations.[12] Although this is not quite the saddle point for migration, we do not attempt to refine it. The energy increases by 0.8 eV in reaching this point from the equilibrium position, as seen in Fig. 7(b). Hence, we conclude that the barrier for migration is $\lesssim 1.0$ eV.

## V. SUMMARY

Our MNDO cluster calculations support the bond-centered position as a stable site for interstitial hydrogen or muonium in silicon. This conclusion is based on results using a variety of clusters. In our computations we find evidence in a static picture for a hydrogen which is bonded to one of the neighboring silicons and not to the other (asymmetric model). This is in contradiction to other, recent computations which produce a hydrogen stable at the precise center of the bond.[11,13,14] However, our calculated barrier for inversion along the bond is only

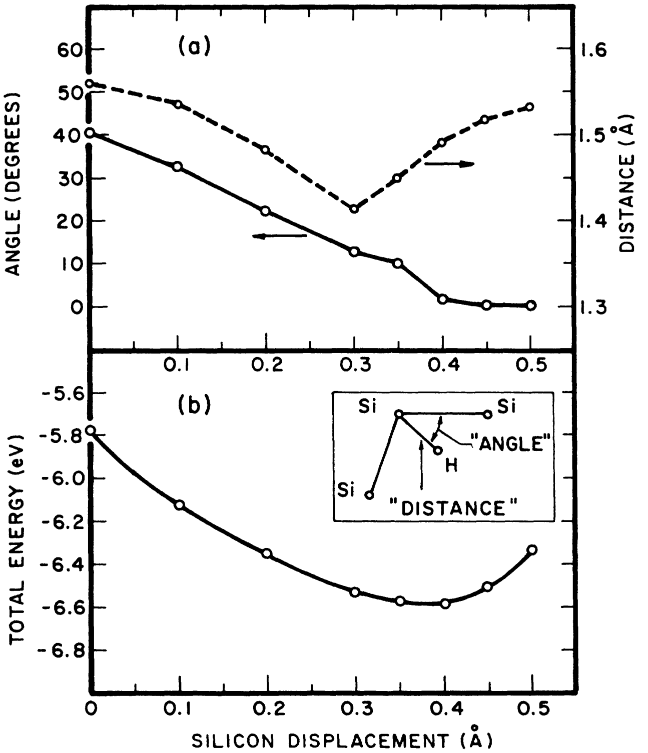

FIG. 7. Hydrogen location and cluster total energy vs silicon displacement. Using our Si-8 cluster, the hydrogen is permitted to relax in a (110) plane for various outward silicon displacements (0.0–0.5 Å each). In panel (a) the locations of the relaxed hydrogen atom are shown in terms of the angles and distances defined in the inset. The corresponding total energies are shown in panel (b).

$\lesssim 0.1-0.2$ eV; hence, motional effects are significant. As a consequence of motional averaging, the silicon hyperfine would not be expected to reveal the inequivalence of the silicon atoms in the asymmetric model. If hydrogen and deuterium were observed in an infrared experiment, then the presence of a barrier to inversion may be apparent in the isotope shift, which we predict to be quite anharmonic for the asymmetric model. We further calculate a barrier for migration between equivalent BC sites in a (110) plane of $\lesssim 1.0$ eV.

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