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# Equilibrium sites and electronic structure of interstitial hydrogen in Si

Stefan Estreicher
*Department of Physics, Texas Tech University, Lubbock, Texas 79409*

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The equilibrium sites and electronic structure of interstitial hydrogen or muonium in Si clusters are calculated using the approximate *ab initio* method of partial retention of diatomic differential overlap and *ab initio* Hartree-Fock with minimum, expanded and polarized basis sets. The clusters range in size from $Si_2H_6$ to $Si_{44}H_{42}$. The interstitial sites considered include the tetrahedral, hexagonal, antibonding and bond-centered sites, as well as more exotic locations such as the $C$, the $M$, and the "umbrella" sites (which is similar to an antibonding site, but in a distorted environment). Lattice relaxations and distortions are included up to second-nearest neighbors. Basis-set effects are discussed. The most stable site is the relaxed bond-centered site, which is the location of anomalous muonium. The associated energy level is deep in the gap. In contrast to diamond, bond-centered hydrogen in Si vibrates primarily along the bond. The tetrahedral interstitial site is the only other minimum of the energy. It is not deep enough to localize a proton which probably diffuses along $\langle 111 \rangle$ directions. The energy level associated with interstitial H at the tetrahedral site is below the top of the valence band.

## I. INTRODUCTION

Hydrogen plays multiple roles in crystalline silicon. It saturates dangling bonds[1-6] at surfaces, vacancies, and grain boundaries, and passivates a number of electrically active impurities.[7-14] However, isolated paramagnetic hydrogen centers have not been detected[15] by EPR in Si, possibly because the concentration of paramagnetic hydrogen is too low. Hydrogen-induced defects have been seen[3,16] by infrared absorption, photoluminescence, and deep-level transient spectroscopy. Further, two paramagnetic forms of muonium,[17,18] a light isotope of hydrogen, have been observed by the muon spin-rotation ($\mu$SR) technique. They are labeled "normal" and "anomalous" muonium (Mu and Mu*) and coexist in diamond, Si, Ge, GaP, and GaAs. Mu always shows an isotropic hyperfine interaction. This indicates that it is either localized at the tetrahedral interstitial site, or is delocalized symmetrically around this site, or diffuses rapidly through the lattice. The spin density at the muon in Si is about 45% of the free-atom value. This shows a considerable delocalization of the impurity wave function, which otherwise has *s* character. There is experimental evidence that Mu diffuses rapidly in Si and Ge, even at low temperatures.[19-21] On the other hand, Mu* has trigonal symmetry and is localized, as is indicated by the strong anisotropy of its hyperfine tensor in all hosts in which it is observed. In Si, its components[18] parallel and perpendicular to the symmetry axis are 16.8 and 92.6 MHz respectively. The average contact density is only 1.5% of the free-atom value. Mu* is more stable than Mu, at least in diamond, as shown by the Mu-to-Mu* transition observed at high temperatures.[22] In the case of Si, a similar transition is observed, but only in electron-irradiated samples.[23] It is possible that defects induced by irradiation localize Mu, which then converts to Mu*.

Many theoretical efforts have been aimed at predicting the equilibrium sites of hydrogen in Si. Extended Hückel theory[5] predicts that the tetrahedral interstitial ($T$) site is stable if no vacancies are present. In these calculations, the barrier between two adjacent $T$ sites, via the hexagonal ($H$) site, was estimated to be in the range 0.8 to 1.6 eV, and the energy level associated with the impurity at the $T$ site is 0.4 eV below the top of the valence band. A self-consistent Green's function calculation[24] of the spin density at a hydrogen assumed to be at the $T$ site in Si predicts about 41% of the free-atom value, which is very close to the experimental result for Mu. However, another self-consistent pseudopotential calculation[25] predicted that the equilibrium site for interstitial H in Si is not the $T$ site but the antibonding (AB) site, about 1.6 Å from a host atom, along a $\langle 111 \rangle$ axis, "behind" a covalent bond. The AB site would be almost 2 eV below the $T$ site. It has been suggested[26] that interstitial deuterium is at the AB site in Si, although molecular $D_2$ rather than atomic D could have been observed.[2] A recent empirical tight-binding calculation also favored the AB site.[11] The method of complete neglect of differential overlap (CNDO), a semiempirical approximation to minimal-basis-set *ab initio* Hartree-Fock (HF) calculations, predicts[27] that the potential energy surface has a very shallow minimum at the $T$ site, about 0.05 eV below the $H$ site. However, MNDO calculations[28] (modified neglect of differential overlap) indicate that the equilibrium location of interstitial H is at a site of lower symmetry, labeled $M$, located midway between two adjacent $C$ sites. The $C$ site in turn is in the middle of the rhombus formed by the $T$ site, two of its nearest neighbors (NN's), and the adjacent second NN (see figures in Refs. 28 or 29). A site close to $C$ is favored by another recent MNDO calculation.[30] A different site was proposed by Cox and Symons[31] using chemical arguments: the "umbrella" site, which is close to the AB site, but in a distorted environment. Finally, minimal-basis-set *ab initio* HF calculations[32] using a small Si cluster predicted the *T* site to be the lowest in energy, with a barrier between adjacent *T* sites of about 0.4 eV.

Although different sites are predicted by different methods, only one minimum of the total energy is found in each case. The discrepancy between theoretical results illustrates the uncertainties related with the choice for the values of the semiempirical parameters and/or to problems associated with the description of the surface of the clusters. Some of these problems have recently been analyzed[33] using various Si clusters terminated with H saturators. An approximate *ab initio* method and *ab initio* HF calculations were used to calculate a number of properties of the clusters and of an interstitial impurity as a function of cluster size and surface. If a small cluster is used and if the dangling bonds are insufficiently saturated, the impurity tends to be attracted to the surface. This may result in various low-symmetry "equilibrium" sites, which disappear when larger clusters are used.[33] The effects of parametrization are more difficult to estimate, but they may be significant.[34] Standard values for semiempirical parameters are obtained, e.g., from atomic ionization potentials, or equilibrium bond lengths and angles. It is not clear how to adjust these numbers when dealing with interstitials or when large lattice relaxations or distortions are present.

Concerning anomalous muonium Mu* a number of models have been proposed, including a hexagonal interstitial model[18,35] and a Jahn-Teller distorted substitutional muonium with a net charge of $+2e$ in group-IV semiconductors.[36–38] If the NN's to the *H* site are not allowed to relax, the impurity is at a saddle point of the potential energy surface and its wave function resembles the free atom rather than Mu*. When large lattice relaxations are included, the wave function ultimately becomes antibonding with a node at the site of the impurity. However, the atomic displacements required for this situation to occur are unrealistically large and are accompanied by a considerable increase in the total energy. This rules out the *H* site as a candidate for Mu* in Si. A qualitatively similar result is obtained in the case of diamond. The vacancy-associated model has a number of weaknesses.[37] For example, other charge states or other symmetries should be realized and are not observed, and the model cannot explain the Mu-to-Mu* transition.[22,23] Finally, a bond-centered model based on qualitative chemical arguments was proposed by Symons,[39] and Cox and Symons.[31] The bond-centered (BC) site later proved to be the lowest-energy site for neutral interstitial H in diamond[40–42] and silicon[41] if large lattice distortions are included. In diamond, without lattice relaxation, the BC site is a saddle point of the energy, 13.5 eV above the *T* site. But an expansion of the covalent bond by 42% lowers the energy by almost 16 eV. A qualitatively similar result was obtained in Si, but the published results are incomplete.[41] At this point, it appears that the BC site is the most stable interstitial site for neutral H in diamond and Si, and is the location of Mu*. Recently, level-crossing spectroscopy[43] experiments demonstrated unambiguously that in GaAs, Mu* is a neutral interstitial located at or close to the center of the Ga—As bond.

In this paper, calculations of the equilibrium sites and electronic structure of an isolated interstitial hydrogen impurity in silicon are reported. The host crystal is represented by a variety of clusters. The dangling bonds are saturated with hydrogen atoms located along the relevant ⟨111⟩ axes, 1.41 Å from the Si atoms.[33] The clusters are centered at the *T* ($Si_{10}H_{16}$ and $Si_{30}H_{40}$), *H* ($Si_{14}H_{20}$) and BC sites ($Si_2H_6$, $Si_8H_{18}$, and $Si_{44}H_{42}$). The theoretical techniques used are the approximate *ab initio* HF method of partial retention of diatomic differential overlap[44–47] (PRDDO) and *ab initio* HF. PRDDO contains no adjustable parameters, reproduces consistently and accurately results of *ab initio* minimal-basis-set calculations[29,41,42,44–46] at a fraction of the cost, and is able to handle large clusters. For example, self-consistency with $Si_{30}H_{40}$ and an interstitial H at a site without symmetry, is achieved in some 15 min. of CPU time on a Cray X-MP. The same calculation at the *ab initio* HF level would be very expensive, even with a minimal basis set. PRDDO is used to find the small clusters which reproduce large cluster results, thus providing quality inputs for higher-level calculations. It is also used to study lattice relaxations and distortions effects in larger clusters. The equilibrium geometries predicted by PRDDO are in general reliable.[44–46] In this paper, equilibrium geometries were obtained with $Si_{44}H_{42}$ (five complete host atom shells around the BC site) and with $Si_{30}H_{40}$ (four shells around the *T* site). First and second NN's were allowed to relax for various sites of the impurity. None of the displaced atoms are directly connected to surface atoms in these clusters. Whenever possible, *ab initio* HF calculations were performed to analyze basis-set effects. Minimal-basis-set results usually overestimate potential energy barriers[29,33,42] and must be complemented by calculations containing more basis functions. In a minimal-basis-set calculation, only one Slater-type orbital (STO) per occupied orbital is included. In order to save computing time, *ab initio* HF techniques use fixed linear combinations of Gaussians for each STO, thus providing analytical results for one-electron and many two-electron integrals. Expanded basis sets contain several linearly independent STO's per occupied orbital and polarized basis sets include unoccupied orbitals. The basis sets used[48] here for the *ab initio* HF calculations are STO-3*G* (minimal basis set, three Gaussians fitted to each STO), 3-21*G* (expanded basis set with three Gaussians fitted to each core STO and a set of two Gaussians plus another independent Gaussian per valence orbital), and 3-21*G** (3-21*G* with 2*s* and 2*p* functions on the impurity,[49] 2*s* functions on the saturators, and a set of *d* orbitals[50] on each Si atom).

In Sec. II, the results for bond-centered H are reported. In Sec. III, other interstitial sites are considered: *T*, *H*, AB, *C*, and *M* sites, as well as the umbrella site. The *T-H-T* and BC-*T* barriers are calculated. For each equilibrium site, the position of the impurity energy level is calculated. The results are summarized in Sec. IV.

## II. BOND-CENTERED HYDROGEN

In diamond, a covalent C—C bond stretches by about 42% to accomodate a bond-centered H interstitial.[40–42] This relaxation lowers the energy by some 15.9 eV. Small symmetry-conserving second NN's relaxations lower the energy by an additional 0.7 eV. The relaxed BC site is more stable than the $T$ site by some 2.7 eV. Finally, the BC-$T$ potential barrier[42] is less than 2.4 eV. If a linear interpolation is used, the maximum is located at $x = 0.66$ between the BC ($x = 0$) and the $T$ ($x = 1$) sites.

In Si, the Si—Si covalent bond also becomes a bridged Si—H—Si bond. This relaxation and the resulting decrease in total energy were computed for various clusters and with various basis sets. The results are summarized in Table I. The qualitative effect of a 40% expansion of a covalent bond in the diamond lattice is illustrated in Fig. 1. The result is simply a rotation of the first-to-second-NN bonds, which essentially preserves bond lengths. Two symmetry-conserving displacements of the second NN's were considered at the PRDDO level with $Si_{44}H_{42}$. The stretch of the first-to-second-NN bond length (by $\epsilon$%) and the displacement of the six second NN's (by $z$%) parallel to the symmetry axis. The equilibrium configuration corresponds to $\epsilon = 2.5$ and $z = 3.0$, both displacing the second NN's away from the BC site. The length of the bridged bond is then optimized again and increases from $\lambda = 34.9$ to 36.0%. This lowers the energy by an additional 0.59 eV. As discussed below, the length of the Si—H bridged bond in crystalline Si is shorter than it is in the radical $H_3Si$—$H$—$SiH_3$. The fact that second-NN displacements result in an expansion of this bond is therefore consistent with intuition. Symmetry-lowering displacements of the second NN have not been considered. Since the second-to-third-NN bond lengths and angles in the relaxed configuration are very close to their equilibrium values, relaxations or distortions of third (or further) NN's are expected to be very small, and the defect is quite localized. At the *ab initio* HF level, the first NN relaxations are slightly shorter than with PRDDO, typically $\lambda = 33$ to 34% instead of 35 to 36% (see Table I). In any case, at equilibrium, the H interstitial is 1.57 to 1.59 Å away from the nearest Si.

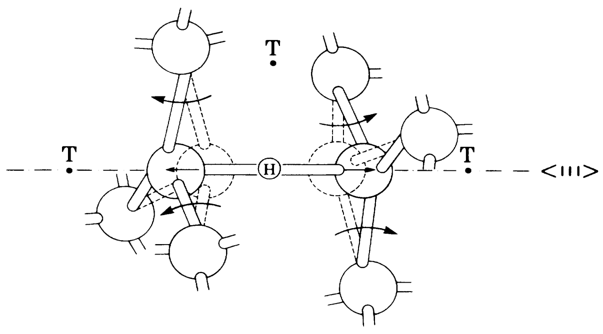

FIG. 1. Schematic representation of a 40% expansion of a covalent bond in the diamond lattice to accomodate a bond-centered interstitial hydrogen. The dotted atoms show the unrelaxed positions. Only the first NN's to the BC site are displaced. The first-to-second-NN bonds rotate, but their length does not vary significantly in this process. Three tetrahedral interstitial sites ($T$) are shown.

It is common for interatomic distances in bridged bonds to be longer than in the equivalent single bonds. For example, in the radical $H_3C$—H—$CH_3$, the bridged C—H bond length is 1.33 Å with PRDDO. However, in diamond,[42] the same bond length is only 1.09 Å, because the rigidity of the lattice prevents larger expansions. Thus, the C—H distance for bond-centered hydrogen in diamond is equal to the C—H distance in $CH_4$. As a result, because of the strong nuclear repulsion, the curvature of the potential energy for displacements of the impurity along the bond is about five times larger than for displacement perpendicular to it. Therefore, the impurity vibrates primarily in the plane perpendicular to the bond. In the case of silicon, the (bridged) Si—H bond length in the radical $H_3Si$—H—$SiH_3$ is 1.72 Å with PRDDO, and the same bond length in crystalline silicon is 1.58 Å. In $SiH_4$, it is only 1.43 Å with PRDDO. Now, the bridged bond is much closer to its natural bond length and the impurity is further away from the nearest Si atom than it would be in $SiH_4$. The potential energy for displacements of the impurity along the bond is more U-shaped than parabolic, with a flat profile for small displacements (typically ±0.1 Å) followed by a steep increase. On the average, the curvature of the po-

TABLE I. Equilibrium relaxation of the Si—Si bond to accomodate a bond-centered hydrogen (or muonium) interstitial. The expansion is measured by $\lambda$ and $d$ is the resulting distance between the interstitial and the nearest Si. $\Delta E$ stands for $E(\lambda=0) - E(\lambda)$. The basis sets for *ab initio* results (STO-3$G$, 3-21$G$ and 3-21$G^*$) are discussed in Sec. I. For $Si_{30}H_{40}$ and $Si_{44}H_{42}$, the energy relative to the (unrelaxed) $T$ site, $E - E_T^0$, is also given. With a 3-21$G^*$ basis set, satisfactory convergence in the $E(\lambda=0)$ calculations could not be obtained within a reasonable amount of CPU time.

| Cluster | Method | $\lambda$ (%) | $d$ (Å) | $\Delta E$ (eV) | $E - E_T^0$ (eV) |
|---|---|---|---|---|---|
| $Si_8H_{18}$ | PRDDO | 34.9 | 1.586 | −9.43 | no $T$ site |
| | STO-3$G$ | 33.1 | 1.565 | −7.49 | no $T$ site |
| | 3-21$G$ | 33.6 | 1.571 | −5.44 | no $T$ site |
| | 3-21$G^*$ | 34.0 | 1.576 | | no $T$ site |
| $Si_{30}H_{40}$ | PRDDO | 35.9 | 1.598 | −9.53 | −0.87 |
| $Si_{44}H_{42}$ | PRDDO | 34.8 | 1.585 | −9.39 | −0.89 |

tential energy is some 20% smaller along the bond than in directions perpendicular to it. Thus, in Si, bond-centered H vibrates primarily along the bond, at a frequency about $\frac{1}{3}$ of that of a single Si—H bond.[51] This qualitative difference between diamond and silicon could explain the observed difference in the Mu* hyperfine tensor between diamond and Si or Ge: The ratio of the component of the hyperfine tensor of Mu* parallel to the symmetry axis to the component perpendicular to it is negative in diamond and positive in Si and Ge,[52] which reflects that $|A_s| < 2|A_p|$ in C and $|A_s| > 2|A_p|$ in Si.

At the BC site, the contact spin density relative to the free-atom value is $-0.21$ with PRDDO (irrespective of cluster size), $-0.18$ with STO-3*G*, $-0.15$ with 3-21*G* and $-0.14$ with 3-21*G**. The negative coupling for the isotropic part of the hyperfine tensor arises from spin polarization of bonding electrons. All the *ab initio* HF calculations were performed with $Si_8H_{18}$. The calculated contact densities are not to be compared directly to the average hyperfine interaction of Mu* in Si, since the zero-point motion of the muon is large. As it vibrates along the bond, the contact density becomes more positive, and the average hyperfine interaction is much closer to zero.[18] A realistic calculation should include displacements of the impurity along the bond and in directions perpendicular to it. Since the entire region around the impurity is characterized by spin densities with small absolute values, the results may depend on the procedure used and the densities must be calculated very accurately. Therefore, no prediction will be attempted here. However, the qualitative agreement with Mu* is obvious. The spin density on the two NN's to the BC site is positive, and the singly occupied molecular orbital is antibonding ($\sigma^*$).[31,39] Hydrogen is not unique as a bond-centered interstitial: The best known examples are oxygen[53] and boron,[54] which are at (or close to) a bond-centered site.

The barrier between the BC ($x=0$) and $T$ ($x=1$) sites was estimated with PRDDO and $Si_{30}H_{40}$ by linear interpolation of the coordinates of all the atoms between the two equilibrium configurations. The maximum is 2.0 eV above the $T$ site and occurs at $x=0.50$. The actual barrier is lower, since minimal basis set calculations overestimate barrier heights[29,33,40-42] and since the geometry was not optimized at intermediate steps.

The "valence band" energy eigenvalues for bond-centered $H$ in $Si_8H_{18}$ calculated with PRDDO and *ab initio* HF, and in $Si_{44}H_{42}$ calculated with PRDDO are shown in Fig. 2. The energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied one (LUMO) is very large and should not be confused with the fundamental band gap in silicon. Although the HOMO usually is associated with the top of the valence band (not counting the impurity energy level of course), the LUMO has nothing to do with the bottom of the conduction band. HF theory does not optimize the unoccupied orbitals which therefore have artificially high energies. To calculate the real HF band gap, one must remove an electron from the

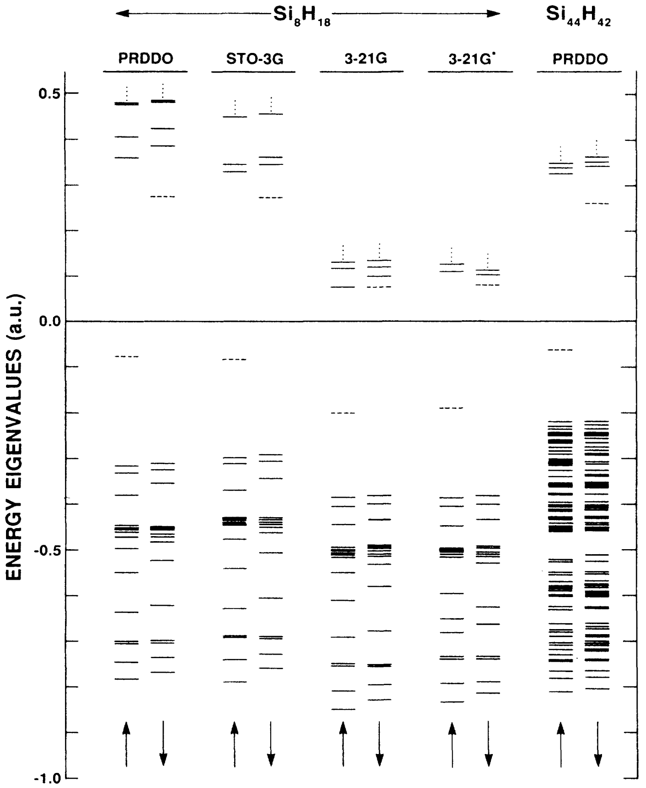

FIG. 2. "Valence band" calculated for spin up and down electrons with PRDDO and *ab initio* HF for various clusters and basis sets. The interstitial H is at the relaxed BC site. The energy level associated with the impurity are shown with dashed lines (see text). Note that if expanded and polarized basis sets are used, the entire spectrum is shifted downward and the energies of unoccupied orbitals are closer to each other.

TABLE II. Energy for an interstitial H or Mu at the hexagonal ($H$), antibonding (AB), $C$ and $M$ sites with respect to the $T$ site, calculated with $Si_{10}H_{16}$ and various basis sets and with PRDDO and various clusters. All energies are in eV. No lattice relaxation is included. The basis sets for *ab initio* HF calculations are discussed in Sec. I.

| Cluster | Method | $E_H - E_T$ | $E_C - E_T$ | $E_M - E_T$ | $E_{AB} - E_T$ |
|---|---|---|---|---|---|
| $Si_{10}H_{16}$ | PRDDO | 0.89 | 3.60 | 1.50 | 1.17 |
| | STO-3*G* | 0.68 | 3.23 | 1.21 | 0.91 |
| | 3-21*G* | 0.59 | 2.30 | 1.12 | 0.78 |
| $Si_{30}H_{40}$ | PRDDO | 0.85 | 3.19 | 1.31 | 0.97 |
| $Si_{44}H_{42}$ | PRDDO | 0.88 | 3.05 | 1.25 | 0.88 |

HOMO and place it in the LUMO. As can be seen in Fig. 2, the absolute positions of the HOMO and of the LUMO vary with cluster size and basis set. However, the position of the impurity energy level relative to them varies very little. For any basis set and cluster size (up to $Si_{44}H_{42}$) it is far away from any occupied or unoccupied energy eigenvalue, i.e., deep in the gap.

## III. OTHER INTERSTITIAL SITES

At the PRDDO level, only the $T$ site is a minimum of the total energy in an unrelaxed lattice. The second-lowest stationary point is a saddle point at the $H$ site. This result is confirmed by *ab initio* HF calculations with $Si_{10}H_{16}$. Neither the AB, the $C$, nor the $M$ sites are minima of the total energy. The energies for interstitial H at the $H$, $C$, $M$, and AB sites relative to that at the $T$ site are given in Table II for various clusters and basis sets. The energy has also been calculated for many other positions of the interstitial, e.g., between the $T$ and the $C$ or $M$ sites and for several points around these sites, in an attempt to find regions of low energy susceptible to become minima if lattice relaxations are included. The calculations were done with $Si_{30}H_{40}$ and PRDDO and no minimum other than the $T$ site was found. For example, if the interstitial is at the $M$ site, a displacement along one of the $\langle 100 \rangle$ directions lowers the energy and a search for maximum energy gradients leads the impurity back to the $T$ site. The impurity energy level at the $T$ site is in the valence band, as predicted by other groups,[2,5,55] The level is $-1.2$ eV with PRDDO, $-1.6$ eV with STO-3$G$ and $-0.7$ eV with 3-21$G$ with respect to the top of the valence band. When the interstitial H is at the $T$ site, the total energy is 1.7 eV above that of the same cluster with the hydrogen atom at infinity.

Note that larger basis set calculations result in lower $T$-$H$-$T$ potential barrier. The best estimate (upper bound) for this barrier is 0.59 eV (with a 3-21$G$ basis set). *Ab initio* calculations with polarized basis sets are likely to predict an even lower barrier, and a proton will not be localized at the $T$ site. Lattice relaxations do not modify this situation: At the $T$ site, the first NN's relax radially outward by 1.0% and the second NN's by 1.2%, and this lowers the energy by only 0.08 eV. At the hexagonal site, the six NN's relax outward by 1.5% to lower the energy by 0.09 eV. These numbers are much smaller than the ones obtained in the case of interstitial H in diamond,[29,56] probably because the cavity around the $T$ site in Si is significantly larger than it is in diamond. The contact density for a H localized at or close to the $T$ site in Si is about 3% larger than that of the free atom, irrespective of basis set or cluster size. The calculated contact density for neutral interstitial hydrogen at the $T$ site in diamond[29] is about 20% larger than that of the free atom. Although PRDDO and *ab initio* HF theory are not designed to predict densities with experimental accuracy (the energetics are much more reliable), it is disappointing that the calculated enhancement factor $f = |\Psi|^2 / |\Psi_{\text{vac}}|^2$ is much larger than the measured value. Although $f$ is independent of basis set (at least up to 3-21$G$) and cluster size (up to $Si_{44}H_{42}$), it depends[29] on the impurity orbital exponent. It is possible that much larger clusters and/or correlation corrections are needed in order to obtain a more accurate value. Density-functional calculations in the optimized geometries would provide much more reliable contact densities.

The "umbrella site" was proposed by Cox and Symons[31] to explain the low contact density observed for Mu in group-IV semiconductors. Because the muon-spin-rotation ($\mu$SR) signal is isotropic, rapid tunneling of the muon between equivalent umbrella sites was proposed. In the umbrella position, the muon is close to the AB site, but the corresponding Si—Si bond is allowed to expand. The increase in energy due to this relaxation is compensated by the tendency of the host atoms to form a covalent bond with H. The net result could be a lowering of the total energy and of the contact density at the impurity. The umbrella site calculations were done in the following way: First, the impurity was placed at the AB site ($E = E_T + 1.17$ eV). Then, the nearest Si—Si bond was relaxed to minimize the energy: a 6.5% increase of the bond length lowers the energy, but only by 0.05 eV, while the contact density is lowered by 15% with respect to that at the $T$ site. Then the position of the impurity along the $\langle 111 \rangle$ direction was energy optimized. This sent it back to the $T$ site.

Thus, although the $T$ site emerges as the only minimum of the total energy in an unrelaxed lattice, it is clear that interstitial hydrogen or muonium is not localized. It probably hops from $T$ to $T$ site along $\langle 111 \rangle$ directions and is delocalized around the $T$ site as well. A dynamic process involving umbrella-type locations cannot be ruled out.

## IV. SUMMARY AND DISCUSSION

Properties of neutral interstitial hydrogen in Si have been calculated using PRDDO and *ab initio* HF with minimal, expanded and polarized basis sets, whenever computationally feasible. The PRDDO results are in good quantitative agreement with the ones obtained using minimal basis set *ab initio* HF. Expanded and polarized basis set calculations predict lower potential energy barriers, but do not result in qualitative differences. The results are cluster-size independent,[33,42] at least in the range $Si_8H_{18}$ to $Si_{44}H_{42}$.

The potential energy surface for neutral interstitial hydrogen in Si has two minima, and H is metastable in silicon, as it is in diamond.[42] The most stable site is the relaxed BC site. The Si—Si bond expands by about 34% (Table I) to accomodate an interstitial hydrogen. This results in a Si—H bond length of 1.58 Å in the bridged Si—H—Si bond. This is larger than the corresponding bond length in $SiH_4$ (1.43 Å) but shorter than in the $H_3Si$—H—$SiH_3$ radical (1.72 Å). In silicon, the bond-centered hydrogen vibrates primarily along the bond. In diamond, it vibrates almost exclusively in the plane perpendicular to the bond. At the BC site, hydrogen has all the properties observed for anomalous muonium.[17,18] The average contact density is small and negative, the defect is stable and very anisotropic with trigonal symmetry. The energy level associated with bond-centered H in Si is deep in the gap.

The other minimum of the potential energy surface is a shallow minimum at the *T* site. Lattice relaxations around this site are negligible. The second lowest stationary point of the energy is at the *H* site, which is less than 0.59 eV above the *T* site. Since larger basis-set calculations will predict an even lower barrier height, interstitial H is likely to diffuse along *T-H-T* directions. None of the other sites investigated correspond to minima of the energy (e.g., *C*, *M*, and AB sites: Table II), and more complicated mechanisms involving lattice distortions (such as the umbrella site[31]) do not change this situation. The impurity energy level for hydrogen at the *T* site is below the top of the valence band (hyperdeep[57]).

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