Structural Identification of Hydrogen and Muonium Centers in Silicon: First-Principles Calculations of Hyperfine Parameters

Chris G. Van de Walle

Philips Laboratories, North American Philips Corporation, Briarcliff Manor, New York 10510

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First-principles calculations are used to evaluate the hyperfine and superhyperfine parameters for hydrogen and muonium at various sites in the Si lattice. Good agreement is found with muon-spin-rotation experiments, leading to an unambiguous identification of "anomalous muonium" with the bond-center site. The results establish the power and reliability of pseudopotential-spin-density-functional theory for calculating signatures of defects.

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Experimental techniques such as electron paramagnetic resonance (EPR) or muon spin rotation (μSR)[1] probe the interaction between electronic wave functions and nuclear spins. When applied to defects in semiconductors, they provide a clear signature of the defect; based on the observed symmetry and the strength of various interactions, models for the structure can be developed. A conclusive structural identification of the defect can be obtained if reliable theoretical calculations of the hyperfine parameters for various configurations are available. Comparison of theory and experiment then determines whether a proposed structure is consistent with experimental observations. In this paper I show that first-principles spin-unrestricted electronic structure calculations, based on pseudopotential-density-functional theory, yield values in good agreement with experiment. I focus on hydrogen and muonium in silicon, recently the subject of various experimental[2,3] and theoretical[4-9] investigations, and provide an unambiguous determination of the structure of the controversial anomalous muonium center. Values of superhyperfine parameters for various ^{29}Si neighbors are also predicted.

Understanding the behavior of hydrogen in semiconductors is important from both a fundamental and a technological point of view.[9] Because of the experimental difficulty in obtaining EPR signals from isolated hydrogen atoms, most of the information has been obtained using the μSR and muon level-crossing resonance techniques.[1,2] Muonium is a pseudoisotope of hydrogen; it consists of an electron bound to a positive muon (μ^+). The mass of μ^+ is $\frac{1}{9}$ that of the proton, and its lifetime is 2.2 μs. Two distinct types of paramagnetic centers have been observed for muonium in many semiconductors;[1] they are labeled Mu ("normal muonium") and Mu* ("anomalous muonium"). The muon-electron hyperfine coupling is isotropic for Mu; its value is reduced from the vacuum value, but the reduction is far less than in the case of a shallow impurity, indicating the deep, localized character of the defect. Because of its isotropic character, Mu has usually been associated with the tetrahedral interstitial (T) site. Anomalous muonium exhibits very different properties: Its isotropic hyperfine coupling is much smaller than for Mu, indicating that the paramagnetic electron spends much of its time away from the muon. The muon hyperfine interaction is highly anisotropic and axially symmetric about the $\langle 111 \rangle$ axis. The contact interaction is small and negative on the muon, and the spin density is strongly p-like on two equivalent Si neighbors, consistent with large lattice relaxation and a substantial increase in the Si-Si separation. The so-called $AA9$ center, associated with hydrogen (H) in Si, has been shown to have very similar characteristics.[3]

The structure of the anomalous muonium center is still controversial. A number of theoretical studies[4-6,8,9] have shown the bond-center site is a likely candidate. In addition, the so-called vacancy-associated model has been proposed, mainly on the basis of hyperfine parameters obtained from cluster calculations.[7] I show here that accurate *ab initio* calculations of the hyperfine and superhyperfine parameters for muonium in silicon yield values in such close agreement with experiment[2] that they allow a clear identification of Mu* as a bond-center impurity. This illustrates how first-principles density-functional calculations, which yield information about total energies (stable sites) as well as electronic structure (hyperfine parameters), can be a powerful tool in the structural identification of defects in semiconductors.

For most purposes, the theoretical results for hydrogen and muonium are equivalent, since both the proton and muon are point particles with identical charge. Only when dynamics are important does the difference in mass and lifetime lead to differences in behavior. The similarity of the experimental hyperfine results for muonium[2] and hydrogen[3] indicates that such effects are minor for the problem at hand. We have carried out first-principles total-energy calculations[8,9] for hydrogen in Si in the neutral charge state (appropriate for paramagnetic centers). The bond-center (BC) position is the global minimum of the energy surface; large relaxations of the neighboring Si atoms (over 0.45 Å for the nearest neighbors) are required to accommodate the impurity. The

energy at the T site is ~ 0.3 eV higher than at the BC site; T is not a local minimum, but the energy surface in that region is quite flat. Negligible relaxation of the surrounding lattice takes place here. Because of the large lattice relaxation required for the global-minimum BC site, a significant fraction of muonium atoms may stay in the interstitial channels.[10] If Mu tunnels between equivalent sites in the neighborhood of T, the effective isotropy of the center is preserved. The sites that emerge from the theoretical total-energy surface are therefore consistent with the normal and anomalous muonium results obtained from μSR. An unambiguous determination of the defect structure, however, is possible if the hyperfine parameters for the various locations can also be calculated from first principles.

The interaction between an electron and a nuclear spin in general includes an isotropic (contact interaction) and an anisotropic (dipole-dipole) part:[11]

$$\frac{2\mu_0}{3} g_e \mu^e g_I \mu^I \mathbf{S}^I \cdot \mathbf{S}^e \delta(\mathbf{R}) + \frac{1}{4\pi} \mu_0 g_e \mu^e g_I \mu^I \frac{1}{r^3} [3(\mathbf{S}^I \cdot \hat{\mathbf{r}})(\mathbf{S}^e \cdot \hat{\mathbf{r}}) - \mathbf{S}^I \cdot \mathbf{S}^e] . \quad (1)$$

$\mathbf{S}^I$ and $\mathbf{S}^e$ are the nuclear- and electronic-spin operators, and $\mathbf{R}$ is the coordinate of the nucleus with magnetic moment μ^I and g factor g_I. Integrating this expression over the electronic wave function produces the Hamiltonian for the hyperfine interaction. The paramagnetic muonium states observed to date in semiconductors have either an isotropic hyperfine interaction, or one with axial symmetry, which allows the Hamiltonian to be written as

$$\mathcal{H} = (a-b)\mathbf{S}^e \cdot \mathbf{S}^I + 3bS_z^e S_z^I , \quad (2)$$

$$a = \frac{2\mu_0}{3} g_e \mu^e g_I \mu^I |\psi(\mathbf{R})|^2 , \quad (3)$$

$$b = \frac{\mu_0}{8\pi} g_e \mu^e g_I \mu^I \int d^3r \, |\psi(\mathbf{s})|^2 \frac{3\cos^2\tau - 1}{r^3} . \quad (4)$$

$\mathbf{s}$ is the coordinate of the electron, τ is the angle between $\mathbf{s}$ and the symmetry axis, and r is the distance between the electron and the nucleus. The parameter a represents the isotropic interaction, and b the axially symmetric anisotropic interaction; they have units of energy, but are often expressed as a frequency (in MHz), using $E = h\nu$. The notation $|\psi(\mathbf{s})|^2$ is used here to represent a spin density, which corresponds to the difference between the charge densities of the spin-up and the spin-down electrons. Equation (1) describes the interaction of the muonium (or hydrogen) electron with any nucleus that has a nonvanishing magnetic moment. If this nucleus is the muon (or proton) itself, the Hamiltonian describes the regular hyperfine or Fermi contact interaction. In free space, this leads to a value of the hyperfine constant a [Eq. (3)] of 4463 MHz for muonium, or 1420 MHz for H (see Ref. 1).

The calculations were carried out within spin-density-functional theory,[12] using an *ab initio* norm-conserving pseudopotential[13] for Si, and the Coulomb potential for the muon. A supercell geometry was used, in which the impurity is surrounded by a sufficiently large number of Si atoms, and this whole structure is periodically repeated. It is essential to check whether the supercells are large enough to include all relevant details of the spin-density distribution, and ensure sufficient separation of impurities in neighboring supercells. For that purpose, calculations were performed for supercells containing 8, 16, and 32 atoms. The basis set in the calculations consists of plane waves up to an energy cutoff $(E_1;E_2)$.[14] Tests were carried out to ensure that the results are converged with respect to size of the basis set and special point[15] set used in the Brillouin-zone integrations.

Since we use the full Coulomb potential (and not a pseudopotential) for the muon, a very high energy cutoff would be required to accurately represent the details of the wave function near the proton. For the purpose of calculating the total energy of the system, such complete convergence is unnecessary as long as only *differences* in the total energy are considered.[9] Similarly, absolute convergence of the wave functions and spin densities is not required, provided they are compared with appropriate quantities calculated with the same convergence parameters. In this case, the appropriate reference is the spin density at the muon for muonium in free space. By performing a calculation with only one atom in a large supercell, we obtain the value of the spin density $|\psi(0)|^2_{\text{vac}}$ at exactly the same energy cutoff as used in the calculation for the solid. We then find that the ratio $|\psi(0)|^2_{\text{solid}}/|\psi(0)|^2_{\text{vac}}$ converges very fast as a function of energy cutoff, as evidenced by Table I. Convergence tests for other sites and for anisotropic hyperfine parameters produced very similar results. Subsequently, all theoretical results will be for 32-atom supercells at a cutoff of (7.5;15) Ry.

Table I shows results for the reduction of the isotropic hyperfine parameter for muonium at the T site in Si. The electronic structure for muonium at T corresponds to that of an s-like state centered on the impurity. μSR experiments (see Ref. 1) yield a reduction of the spin

TABLE I. Values of $|\psi(0)|^2_T/|\psi(0)|^2_{\text{vac}}$ for muonium at the tetrahedral interstitial site in Si, as a function of supercell size and energy cutoff (in Ry). The experimental value (Ref. 1) is 0.45.

	(6;12)	(7.5;15)	(15;30)
8 atoms	0.557	0.564	0.559
16 atoms	0.521	0.530	
32 atoms	0.493	0.515	

density in normal muonium (compared to the free atom) by 0.45 in Si. The converged calculated value for $|\psi(0)|^2_T/|\psi(0)|^2_{\rm vac}$ is within 10% of the experimental result. Katayama-Yoshida and Shindo,[16] who were among the first to apply *ab initio* techniques to the calculation of defect signatures, obtained a reduction of the spin density by a factor 0.405 in normal muonium, based on a Green's-function LCAO method. From calculations for a variety of sites in the interstitial region we find that the spin density is maximum at T itself, and slowly decreases when moving away from T. When the muon is moved by 0.27 Å in eigher the [111] or the [001] direction, the spin density is reduced by $\sim 12\%$. This indicates that motional averaging slightly lowers our theoretically predicted value, bringing it in closer agreement with experiment.

Results for muonium at BC are displayed in Table II. The impurity was placed symmetrically between two Si atoms, and first- and second-neighbor relaxations were included.[9] The calculated spin density (and isotropic hyperfine parameter) for the muon at BC is small and negative. The electronic structure of this defect can, to a first approximation, be understood as arising from only three states:[4] the semiconductor bonding and antibonding states, and the muonium $1s$ orbital. The symmetric muonium orbital only couples to the bonding state, leading to a lowering of this state (which still contains two electrons), and the occurrence of a state at higher energy. The original antibonding state has a node midway between the Si atoms, and is therefore now labeled as a nonbonding state of the defect complex. In the neutral charge state, this state contains one electron. This defect level has indeed been identified in the first-principles calculations. Since the muon sits at a node of the wave function of the unpaired electron, the spin density is very small. A negative spin density results from a polarization-transfer effect due to the unpaired electron some distance from muon, showing the importance of taking into account all valence states in a spin-unrestricted calculation, and not just the unpaired electron state. The sign of the spin density agrees with experiment,[2,3] but its magnitude is underestimated. In view of the small value of this parameter (more than an order of magnitude smaller than at T), the agreement can still be considered reasonable.

The dependence of the hyperfine constants on the atomic positions is also examined. Motion of muonium parallel or perpendicular to the bond, as well as small displacements of the Si atoms, leads to only small variations in the hyperfine parameters. The effect on the isotropic hyperfine constant is always a decrease in magnitude, indicating that the larger experimental value of $|a|$, as compared to our theoretical prediction, *cannot* be explained by vibrations or a static displacement of the muon from the exact BC site.

Besides the hyperfine constants for the muonium impurity itself, one should also investigate the so-called superhyperfine interaction for the neighboring ^{29}Si atoms. These values have been accurately measured[2] for the case of anomalous muonium. In the present calculations, the Si atom is represented with a pseudopotential; therefore the wave functions in the core region are different from the full wave functions. In principle it is possible, starting from the pseudo wave function, to reconstruct the full wave functions;[17] this rather complex procedure has been avoided here. Instead, I start from the assumption that the pseudo wave function itself carries most of the information regarding the changes induced by the impurity, provided it is compared with an appropriate reference quantity. This assumption is justified *a posteriori* by the good agreement of the results with experiment. The reference is once again determined from calculations on a single (pseudo) atom in a vacuum supercell. For the isotropic hyperfine parameter, the value of $|\psi(0)|^2_{\rm Si}/|\psi(0)|^2_{\rm vac}$ is calculated. For the anisotropic parameters, it is customary to compare b with $A_p^{\rm free}$, which is an average of r^{-3} determined for the valence p orbital.[18] The results are given in Table III. Both the reduction in the hyperfine parameters in going from first to second neighbors as well as the actual values themselves are in good agreement with experiment.

The present results for muonium at the bond center unequivocally establish this site as the location of anomalous muonium. The previously advocated vacancy-associated model[7] shows distinct disagreement with the experimental results,[2] which clearly establish that there are two equivalent Si neighbors along ⟨111⟩. The same cluster calculations[7] on which the vacancy-associated model was based produce hyperfine parameters for the bond center which deviate by more than an order of magnitude from the present results (which are in good agreement with experiment for Mu*).

TABLE II. Theoretical and experimental (Ref. 2) values of $\eta_s^2 = |\psi(0)|^2_{\rm BC}/|\psi(0)|^2_{\rm vac}$ and of the anisotropic hyperfine parameter b for muonium at the bond-center site in Si.

η_s^2		b (MHz)	
Theor.	Expt.	Theor.	Expt.
−0.006	−0.015	18.1	25.3

TABLE III. Theoretical and experimental (Refs. 2 and 19) values of $\eta_s^2 = a/A_s^{\rm free} = |\psi(0)|^2_{\rm Si}/|\psi(0)|^2_{\rm vac}$ and $\eta_p^2 = b/A_p^{\rm free}$ for the first and second ^{29}Si neighbors of muonium at the bond-center site in Si.

	η_s^2		η_p^2	
	Theor.	Expt.	Theor.	Expt.
First neighbors	0.020	0.021	0.214	0.186
Second neighbors	0.0055	0.0049	0.017	0.0083

Finally, I present predictions for the superhyperfine parameters of ^{29}Si neighbors of normal muonium. Because of the fast motion of normal muonium, these values have not been determined experimentally. The value of

$$\eta_s^2 = a/A_s^{\text{free}} = |\psi(0)|^2/|\psi(0)|^2_{\text{vac}}$$

for the first-nearest neighbor is 0.012, while that for the second-nearest neighbor is only slightly smaller, at 0.011. Using the value $A_s^{\text{free}} = -4594$ MHz from Ref. 18, we find $a = \eta_s^2 A_s^{\text{free}} = -55$ MHz for the first ^{29}Si neighbor. This value is close to an estimate made in Ref. 19, based on the assumption that the spin density not contributing to the muon hyperfine parameter is equally divided among the ten closest Si atoms.

In conclusion, I have shown that pseudopotential-spin-density-functional-supercell calculations can yield values for hyperfine and superhyperfine parameters that are in good agreement with experiment. The ability to reliably calculate signatures of defects, as well as accurate total-energy surfaces (including all relaxations), establishes this method as a powerful and versatile tool for the study of defects in semiconductors. The controversy regarding the structure of the anomalous muonium center has been resolved.

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