PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
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Computational Studies of Hydrogen-Related Complexes in Semiconductors [and Discussion]

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Computational studies of hydrogen-related complexes in semiconductors

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The two main computational techniques to calculate the microscopic electronic structure of localized defects in solids are reviewed. Cluster calculations using the Hartree–Fock method as well as density-functional methods have been widely used to determine the equilibrium structure of hydrogen and hydrogen-related complexes in semiconductors. Results for the structure of both acceptor-hydrogen and donor-hydrogen pairs in silicon obtained by various methods and at different levels of approximations are discussed. Comparisons are made among the calculated vibrational frequencies of hydrogen in these passivation complexes. The spin density distribution for bond-centred hydrogen or muonium in diamond is investigated. Owing to the light masses of the proton and the muon it is necessary to average the computed hyperfine parameters over the finite extension of the ground-state wave function.

1. Introduction

Hydrogen is present during every step of the processing of silicon and other semiconductor devices. It passivates the shallow acceptors and donors, thus can be used to treat impurities and to improve the electrical and optical properties of semiconductors. On the other hand, it can also be an unintentional contaminant which diffuses into the electronic devices and alters the electrically active dopant profile in the near-surface region. For these technological reasons, it is of great importance to understand the microscopic structures of hydrogen in silicon and in acceptor- and donor-doped silicon. Therefore it is not surprising that considerable effort has been devoted to this field. Recent reviews are given by Pearton *et al.* (1992), Myers *et al.* (1992) and in various chapters of Pankove & Johnson (1991).

Numerous experimental techniques, such as ion-channelling and infrared absorption measurements, have been deployed to determine the atom relaxations and the H vibrational spectroscopy. Moreover, a large amount of information has been obtained using the positive muon as a pseudo-isotope of the proton. In particular, muon spin rotation (μSR) has been frequently used to pin-point the muon or proton position in the lattice. Theoretically, many methods have been applied with various degrees of success, among them are semi-empirical procedures, Hartree–Fock cluster calculations, and the density functional method in the localized orbital basis as well as in the plane wave basis.

The reasons for the quantitative, and occasionally qualitative differences among the results of different theoretical studies can be complex. In this paper, we

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carry out extensive investigations of the microscopic structures of H in silicon and acceptor- and donor-doped silicon by using various theoretical schemes, and derive a more comprehensive picture of the advantages and shortcomings of each method by comparing the results with those of experimental measurements.

The paper is organized as follows. In § 2 the theoretical schemes used in this work are outlined. The computational applications of these methods on systems of H in acceptor and donor-doped silicon are discussed in §§ 3 and 4 respectively. In § 5 the results for the H centre in pure Si are presented and compared with those from μSR experiments. § 6 is reserved for the conclusion.

2. Computational techniques

The calculation of the microscopic structure of hydrogen-related complexes in semiconductors poses two general problems. The first is an adequate treatment of an impurity in a crystal, a system in which the symmetry of the Bravais lattice is destroyed. This lack of symmetry makes it impossible to use powerful tools of theoretical solid-state physics. The second problem is the treatment of the many-electron system.

To cope with the absence of translational symmetry one uses either molecular clusters or supercells by assuming that the disturbance introduced by the impurity is localized. In the cluster approach the impurity problem is modelled by a molecule containing the defect and neighbouring host atoms. The size of these clusters, i.e. the number N of atoms taken into account, should on the one hand be as large as possible to simulate the actual situation of an impurity in an infinite crystal lattice, on the other, N should be kept as small as possible to make a first-principle treatment of the quantum-mechanical many-electron problem still feasible. In addition, hydrogen atoms are used to saturate the dangling bonds of the host atoms on the surface of the cluster. Therefore, a sufficiently large N has to be chosen to avoid the influence of surface effects.

In the supercell approach one constructs periodically repeated supercells which are replicas of the impurity complex (such as B–H) and its neighbouring host atoms (Si). In this way, some of the original lattice symmetry is restored. To keep the effect of the artificially introduced interactions between impurities in different supercells minimal, the size of the supercell should be as large as possible. This requirement again has to be balanced against the feasibilty in both the sophistication of the theoretical method and the computing time.

The quantum-mechanical many-electron problem essentially can be treated in two different ways. In the Hartree–Fock (HF) approach, the exchange interaction between electrons is accounted for exactly, whereas correlation effects are neglected completely. The latter can subsequently be considered by perturbation theory, such as Møller–Plesset corrections or configuration interaction expansions. In the density-functional method (DFM) the electron ground-state density $n(\boldsymbol{r})$ is the determining quantity since there exists an exact variational principle for $n(\boldsymbol{r})$. In practice, however, the density $n(\boldsymbol{r})$ is expanded into a set of fictitious one-electron wave-functions $\phi_j(\boldsymbol{r})$. In cluster calculations, a set of appropriate wave-functions localized at the atomic sites are used. In the supercell approach, the density $n(\boldsymbol{r})$ is expanded into a set of plane-wave states. The notable approximation used in the DFM is the local density approximation (LDA) for the exchange-correlation potential. Even though it is commonly accepted, LDA is

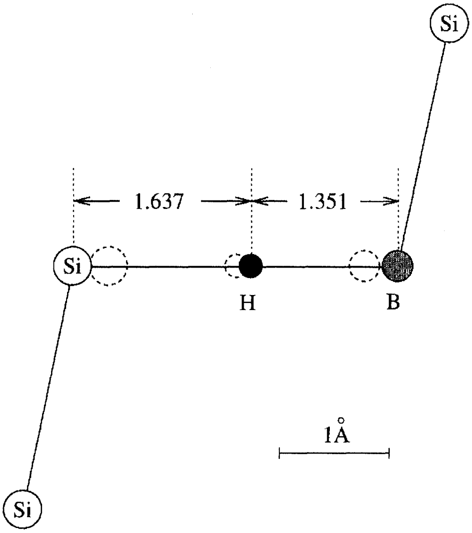

Figure 1. Calculated geometry of the lowest energy configuration of the B–H complex in silicon. The distances are given in Åand the dashed circles indicate the location of the undisturbed substitutional sites.

known to yield inaccurate details in eletronic structures, e.g. a lower value of semiconducting band gap. Various gradient corrections which go beyond the LDA have been proposed.

In our computational studies of hydrogen-related complexes in semiconductors we have used both HF and DFM approaches. For HF and DFM cluster calculations with localized basis sets several generally accessible program packages are available. We also have developed a program package which performs the total-energy calculation in the plane-wave basis. In the program, the Kleinman–Bylander decoupling form of the norm-conserving pseudo-potential developed by Troullier and Martins is adopted. Integrations over the first Brillouin-zone are replaced by summations over special $\boldsymbol{k}$-points generated with the extended Monkhorst–Pack scheme by Froyen. Furthermore, the LDA for the exchange-correlation potential is used.

3. Hydrogen–acceptor pairs in silicon

The system which has been most extensively studied is the passivation of substitutional B in Si by hydrogen. In the now accepted model for this complex, the H is located near the bond-centred (BC) site between the B and one of its neighbouring Si atoms, as has originally been suggested by Pankove *et al.* (1983) and confirmed in cluster calculations first by DeLeo & Fowler (1985). However, we note that in one of the channelling experiments (Bech Nielson *et al.* 1988) where deuterium is diffused into boron-doped silicon, it is found that deuterium is displaced from the B–Si bond axis by 0.2 Å. In figure 1 the computed equilibrium sites from a DFM calculation with plane wave basis sets (Zhou *et al.* 1995) are shown.

An inspection of table 1, in which the results of most of the calculations are summarized, shows that the distance between H and Si from calculations based

Table 1. *Equilibrium geometry of the* Si–H–B *complex*

(ΔB (ΔSi) is the displacement of B (Si) from its unrelaxed position calculated by various authors. All distances are in Å. The results of the calculations (*a*), (*b*), (*c*) and (*d*) are based on Hartree–Fock-type methods, those of (*e*), (*f*) and (*g*) are based on density-functional methods. (*a*) DeLeo & Fowler 1985; (*b*) Amore Bonapasta *et al.* 1987; (*c*) Estreicher *et al.* 1989; (*d*) Maric & Meier 1991; (*e*) Chang & Chadi 1988; (*f*) Denteneer *et al.* 1989; (*g*) Zhou *et al.* 1995.)

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)	(*g*)
H–Si	1.56	1.46	1.44	1.49	1.63	1.65	1.64
H–B	1.51	1.59	1.66	1.53		1.36	1.35
ΔSi	0.16	0.22	0.26	0.16		0.24	0.33
ΔB	0.55	0.48	0.49	0.47	0.47	0.42	0.31

on the density functional theory is in general larger than that from HF–type calculations, with a shorter H–B distance in consequence. Experimentally, the B displacement from its unrelaxed position (ΔB) has been determined in an ion-channelling experiment (Marwick *et al.* 1988) to be 0.28 ± 0.03 Å. The only quantitative agreement with this experimental data has been achieved by a recent DFM calculation using a 64-atom supercell. In addition, a value of 1.6 ± 0.3 Å for the H–B distance has been derived from a nuclear magnetic resonance (NMR) experiment in hydrogenated amorphous Si (Boyce & Ready 1991).

To investigate the systematic difference between the results of HF and DFM in further detail, we have recently performed cluster calculations in which correlation effects have been included as corrections to the HF results. Within the Møller–Plesset perturbation theory of second order (MP2), an increase of the Si–H distance by 2.5% has been found, whereas the H–B distance shortens by 6% and ΔB is reduced by 9%. Thus partially accounting for correlations within the HF approach brings a closer agreement to the DFM results for comparable sizes of clusters and supercells. In this respect it should be stressed that the DFM results by Zhou *et al.* (1995) were obtained with a 64-atom supercell and a high cut-off energy of 22 Ryd for the plane-wave expansion.

Another effective tool commonly used is the infrared absorption experiment, which searches for hydrogen vibrational modes and corresponding frequencies. For the Si–H–B complex, it has been observed that the frequency for the stretching mode (i.e. hydrogen vibration along the Si–H bond) is 1903 cm^{-1} (Stavola *et al.* 1988), which has been well reproduced by both HF and DFM calculations.

The passivation of a substitutional acceptor by hydrogen or muonium also induces electric field gradients (EFG) at the nuclear sites. Valuable experimental information on the microscopic structure of these complexes could thus be obtained from measurements of the induced nuclear quadrupole splitting for nuclei with spin $J > \frac{1}{2}$. Cox *et al.* (1990) proposed to use the muon level crossing resonance (μLCR) technique to study these effects.

The muon polarization in an external magnetic field B applied parallel to the initial polarization is in general preserved. At those values B_r, however, where the muon Zeeman energy equals the quadrupolar splitting of the acceptor nucleus, the weak dipolar interaction between the muon and the nucleus may induce transitions between the energy levels which lead to a resonant loss of muon polarization.

A quantitative description of the corresponding spin dynamics is obtained by considering the spin Hamiltonian

$$H = -\hbar\gamma_\mu I^z B - \hbar\gamma_J J^z B + \hbar\omega_Q(\boldsymbol{n}\cdot\boldsymbol{J})^2 + \hbar\omega_D\left(\boldsymbol{I}\cdot\boldsymbol{J} - 3(\boldsymbol{n}\cdot\boldsymbol{I})(\boldsymbol{n}\cdot\boldsymbol{J})\right). \quad (3.1)$$

The first two terms describe the Zeeman interactions of the muon (with spin I) and the nucleus (with spin J) with an external field B along the z direction, respectively, giving rise to the Zeeman frequencies $\omega_\mu = \gamma_\mu B$ and $\omega_J = \gamma_J B$. The third term determines the quadrupolar energy of J due to an electric field gradient directed along the unit vector $\boldsymbol{n}$. The fourth term, finally, contains the mutual interaction between I and J, the dipolar interaction. For $\boldsymbol{n}$ parallel to the axis of the magnetic field, an analytical solution of the spin dynamics described by (3.1) is possible (Meier 1987). For a spin $J = 3/2$, a resonance occurs at the field value

$$B_\mathrm{r} = 2(\omega_Q + \omega_D)/(\gamma_\mu - \gamma_J) \quad (3.2)$$

and the muon polarization behaves in the vicinity of B_r according to

$$p(B) = \tfrac{3}{4} + \tfrac{1}{4}(B - B_\mathrm{r})^2/[(B - B_\mathrm{r})^2 + b^2] \quad (3.3)$$

with the abbreviation

$$b^2 = 3\omega_D^2/(\gamma_\mu - \gamma_J)^2. \quad (3.4)$$

A first principle calculation of field gradients and quadrupolar frequencies ω_D is not possible if pseudo-potentials are used to freeze the core electron states. Maric *et al.* (1991) have used HF methods to determine the equilibrium structure of hydrogen-acceptor pairs in silicon. Polarized double-zeta basis sets were used for the valence orbitals and pseudo-potentials for the core orbitals. All-electron wave-functions were then used to calculate the EFG at the acceptor site. For B (Al) a value of $V_{zz} = -0.38$ a.u. (-1.01 a.u.) was obtained. The field dependence of the muon polarization function was then calculated for various orientations of the crystal axes with respect to the field axis. Due to the natural abundancies of both ^{11}B (spin 3/2) and ^{10}B (spin 3) which lead to different resonance fields B_r, very distinct field dependencies are expected. Furthermore, the sensitivity of the spectra on exact alignment and the superposition from paramagnetic bond-centred muonium has been studied (Füchslin & Meier 1994). Attempts to detect such spectra experimentally have so far, however, proved inconclusive (see Cox, this volume).

In contrast to the situation in the paramagnetic bond-centred muonium state which will be discussed in § 5, the HF results for the diamagnetic passivation complexes are not significantly modified by taking correlation effects into account. Results obtained by second order Møller–Plesset perturbation theory indicate that the values of the EFG change by about 10–20%. In addition, the finite spread of the muon wave function due to the light mass of the muon has also been taken into account in recent calculations. These gave only minor reductions on the order of 2%.

It should be remarked also that the field gradients at the site of the bond-centred H have been calculated. This is done with the hope that by passivating a boron doped Si sample by deuterium instead of hydrogen, a NMR/NQR experiment could be feasible.

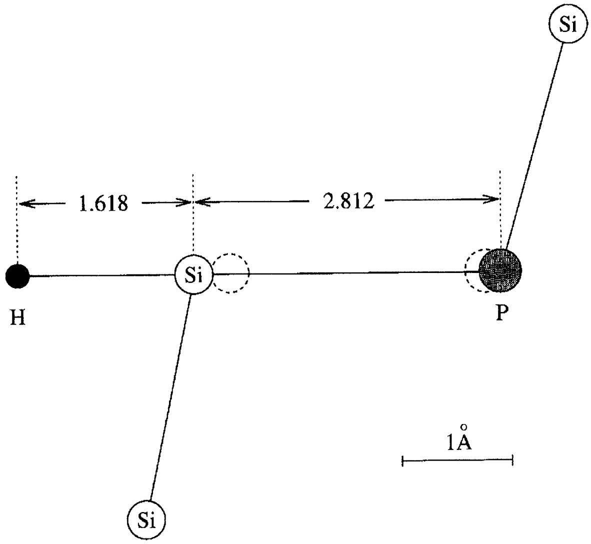

Figure 2. Calculated geometry of the lowest energy configuration of the P–H complex in silicon. The distances are given in Å and the dashed circles indicate the location of the undisturbed substitutional sites.

4. Hydrogen–donor pairs in silicon

In the lowest energy configuration for the hydrogen-donor pair in silicon, the H is at an antibonding site of a silicon atom which is next to the donor impurity (Johnson *et al.* 1986). Essentially all microscopic calculations reproduced this result. The values for the displacements of the atoms, however, differ somewhat. As an example, figure 2 shows the atom positions of the H–Si–P complex obtained from a recent DFM calculation (Zhou *et al.* 1995).

The measured axial vibrational frequencies of H are 1555 cm^{-1} in the H–P complex, and 1561 cm^{-1} in the H–As complex, respectively (Bergman *et al.* 1988). The values for the wagging modes (perpendicular to the bond) are 809 cm^{-1} and 810 cm^{-1}. Hartree–Fock-like methods in general predict strong bonding between Si and H with distances of the order of 1.4 Å and frequencies higher than 2100 cm^{-1} for the axial mode. In contrast, the DFM based calculations show a weaker bonding with distances around 1.6–1.7 Å. The corresponding stretching and wagging frequencies are lower than the experimental ones.

A recent DFM calculation (Zhou *et al.* 1995) has shown that the size of the supercell plays a crucial role. Using supercells with 8, 16, 32 and 64 atoms, the calculated stretching frequency varies appreciably, with respective values of 1406, 1463, 1487 and 1536 cm^{-1}. This demonstrates that – at least for the case of the P–H complex in Si – results obtained from calculations using small supercells may be affected by the artificially introduced interactions between the impurities.

Further indications on the accuracy of various approximations frequently used in *ab initio* calculations have been observed for the H–As complex (Suter *et al.* 1995). For a $\text{Si}_{13}\text{AsHH}_{24}$ cluster the equilibrium geometry was determined using a density-functional method with localized basis sets. Subsequently, the potential energy surface (PES) for the passivating hydrogen atom was calculated. The vibrational frequencies for hydrogen were then determined from the curvature of the PES at the equilibrium site ($1775\,\mathrm{cm}^{-1}$) as well as from a numerical solution of the Schrödinger equation corresponding to the full PES ($1762\,\mathrm{cm}^{-1}$). Furthermore, the influence of gradient corrections to the local density approximation has been investigated.

In principle, the technique of μLCR, as discussed in the previous section, could also be used to investigate the microscopic electronic structure of donor-hydrogen complexes, say the As–H pair. The position of the hydrogen or muonium at the antibonding site of a Si atom, however, implies a large separation of about 4.5 Å between H (muonium) and As which leads to a small value of the corresponding dipolar coupling frequency ω_{D}. The predicted μLCR spectrum then shows very narrow and shallow resonances near B_{r}, the detection of which would be a great challenge to experimentalists.

5. Paramagnetic bond-centred hydrogen

In a variety of semiconductors two distinct paramagnetic muonium centres have been observed (see Cox, this volume): normal muonium, $\mathrm{Mu}_{\mathrm{T}}^{0}$, with an isotropic hyperfine interaction and $\mathrm{Mu}_{\mathrm{BC}}^{0}$, 'anomalous muonium' or 'Mu*' with an axial symmetric hyperfine interaction about the ⟨111⟩ directions. The microscopic structure of the latter centre remained unexplained for quite some time until Cox & Symons (1986) proposed the model in which the muon is located at the centre of a stretched bond between host atoms. In a first approximation, the unpaired electron occupies an antibonding orbital with a node at the bond centre (BC), leading to a vanishing contact spin density at the muon (at least in elemental semiconductors).

The validity of this model was confirmed by experiments as well as by *ab initio* calculations which found this BC site to be the stable equilibrium site with relaxations of the neighbouring atoms by 33% (40%) in the case of silicon (diamond). The quantitative understanding of the contact spin density, ν_{c}, however, remained a problem for a long time. While calculations with the restricted Hartree–Fock method gave a zero contact density by symmetry, the value obtained with unrestricted HF calculations for Si was $\nu_{\mathrm{c}} = -730\,\mathrm{MHz}$, an order of magnitude off the experimental value of $-67\,\mathrm{MHz}$. This demonstrated that electron correlation effects are indispensable for a correct description of this centre. Van de Walle (1990) determined the hyperfine constants of $\mathrm{Mu}_{\mathrm{BC}}^{0}$ in Si in a DFM calculation and obtained $\nu_{\mathrm{c}} = -27\,\mathrm{MHz}$.

An extended investigation of the influence of correlation effects on the spin density distribution of $\mathrm{Mu}_{\mathrm{BC}}^{0}$ in diamond was performed by Paschedag *et al.* (1993, 1994). Calculations for a $\mathrm{C_8HH_{18}}$ cluster have been carried out both with a HF method followed by a configuration interaction (CI) expansion as well as with a DFM using the local density approximation. The computational procedure in the first method included a restricted open-shell HF calculation to obtain a reference set of molecular orbitals and a subsequent CI expansion which included single and double excitations. The DFM approach used Gaussian type atomic orbitals. Figure 3 shows the potential energy surface for $\mathrm{Mu}_{\mathrm{BC}}^{0}$ as calculated with these different methods. It is seen that the potential energies exhibit differences in the order of 30%, depending on the method used.

Also plotted in figure 3 are the squared wave-functions, $|\,\psi(r)\,|^2$, calculated for hydrogen and for muonium in the CI-potential. Since the spread of the muon

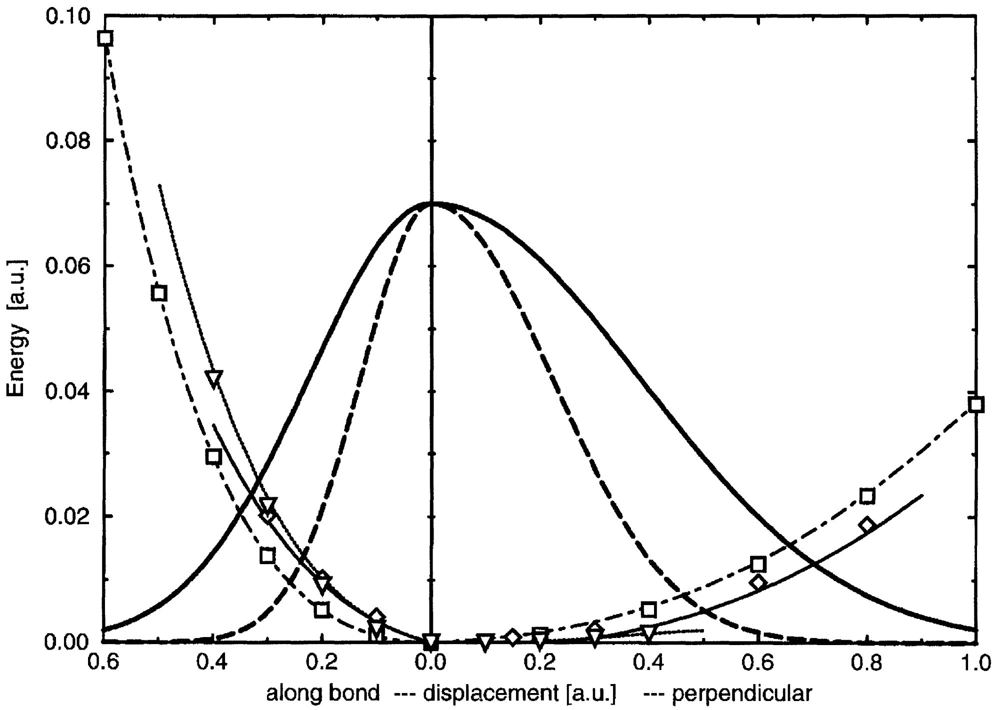

Figure 3. Potential energy of $\mathrm{H}^0_{\mathrm{BC}}$ in diamond along (left) and perpendicular (right) to the bond as calculated using different techniques. □, Hartree–Fock; ◇, CI; ▽, Gaussian type DFM. The solid (long dashed) line represents the scaled squared wave functions of the muon (proton).

wave-function is appreciable, the value for the contact spin density ν_{c} at the BC site is not the quantity which is actually measured, rather one has to average the calculated ν_{c} over the extension of $|\psi(r)|^2$ in order to make comparison with experimental results.

The variation of some of the calculated hyperfine parameters along two sections of the potential energy surface is shown in figure 4. It is seen that the change of the contact density at the muon is substantial. By averaging these values appropriate to the corresponding extension of the ground-state wave function one obtains, e.g. a reduction of 33% in $|\nu_{\mathrm{c}}|$ for muonium in the case of the CI calculation. The reduction is 15% for the hydrogen. This corresponds to a residual isotope shift (corrected for different magnetic moments) $R = \nu_{\mathrm{c}}^{\mathrm{Mu}}\mu_{\mathrm{H}}/\nu_{\mathrm{c}}^{\mathrm{H}}\mu_{\mu}$ of 0.80. The measured hyperfine parameters in ^{13}C enriched diamond (Schneider *et al.* 1993) and the calculated values are given in table 2.

These results demonstrate that besides the crucial influence of correlation effects on the spin density, the light mass of the proton – and in particular that of the muon – also has to be considered in order to achieve quantitatively correct results for the hyperfine parameters of bond-centred muonium.

Recently, both DFM and CI calculations have also been performed for BC muonium with an eight atom Si cluster. For the CI calculation the core electrons of six Si atoms were treated in a pseudo-potential approach while atomic orbitals for all electrons were used on the two Si atoms next to the BC site. Again, the variation of the calculated hyperfine parameters, notably the contact density at the

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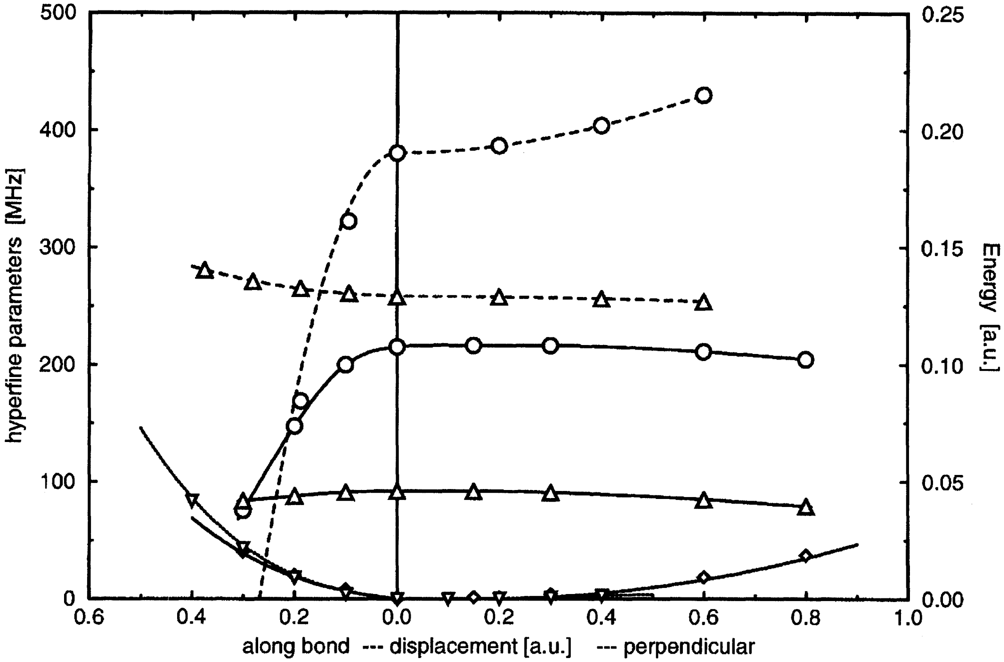

Figure 4. Absolute values of the isotropic hyperfine parameter ν_c of the muon (○) and nearest neighbour carbon atoms (△) against displacements of the muon along (left) and perpendicular (right) to the centre C–C bond. Values are given for CI (solid line) and Gaussian type DFM calculations (dashed line). Also shown are again the potential surfaces for CI (◇) and DFM (∇).

muon, as a function of position required an appropriate average over the extent of the ground-state wave function. In addition, the influence of gradient corrections to the local density approximation of the DFM has been investigated. In Si, the hyperfine parameters have also been measured for the proton (Gorelkinskii & Nevinnyi 1987). The experimental residual isotope shift R is 0.93.

6. Conclusions

Two main computational techniques to calculate the microscopic electronic structure of localized defects in solids have been discussed: the Hartree–Fock method and the density-functional approach. Both have been applied to determine the equilibrium sites of acceptors and donors passivated by hydrogen or muonium in silicon. The vibrational frequencies of H in these passivation complexes have been calculated. Increasing computer power today allows one to perform first-principle calculations of the electronic structure which go beyond the HF approximation while large supercells can be treated in the DFM. For closed shell systems, such as the passivation complexes, these improved calculations lead in some cases to better agreement with experimental data. For a quantitative understanding of the spin density in open shell systems, e.g. the bond-centred hydrogen or muonium in diamond or silicon, it is indispensable to account for correlation effects. Although valuable information on hydrogen in semiconductors can be obtained by using positive muons, the interpretation of the data often has to take into consideration the light mass of the muon which implies a considerable

Table 2. *Measured and calculated hyperfine parameters for* $\mathrm{Mu}^0_{\mathrm{BC}}$ *in diamond*

(Hyperfine parameters at the muon, at the nearest neighbour (nn) ^{13}C and at the next nearest neighbour (nnn) ^{13}C. The values in MHz are expressed in terms of a contact frequency ν_{c} and a dipolar term ν_{dip}. The experimental values are from Schneider *et al.* (1993), the theoretical values are from Paschedag *et al.* (1993).)

	experiment		theory	
	ν_{c}	ν_{dip}	ν_{c}	ν_{dip}
μ^+	−205.5	186.5	−145	194
nn ^{13}C	126	46	90	51
nnn ^{13}C	1	...	−11	...

extension of its ground-state wave function. In addition, the dynamical properties (diffusion, tunnelling) are quite different for the muon and the proton. An understanding of these effects requires more calculational efforts.

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Discussion

T. A. Claxton (*Department of Chemistry, University of Leicester, U.K.*). In boron doped silicon the bond-centred hydrogen is closer to boron in Professor Meier's density functional theory calculations but closer to silicon in his Hartree–Fock calculations. Which calculation is in agreement with experiment?

The question is prompted by calculations we have done on the stability of MuCO relative to the fragment Mu and CO. Whereas density functional theory calculations predict MuCO is stable, Hartree–Fock calculations, including various levels of electron correlation, predict MuCO is unstable. All calculations used the same triple zeta basis set with polarization functions.

P. F. Meier. There is no direct experimental information about the hydrogen–boron distance.

W. Jackson (*Palo Alto, CA, U.S.A.*). Is it computationally practical to include the H wavefunction as a variational parameter as well as the electronic wavefunction in the direction minimization method? Such a calculation would correctly account for zero point motion as well as quantum diffusion.

A. J. Fisher (*Department of Physics, Durham University, U.K.*). This is a difficult problem because of the extremely strong correlations between the muon and the bonding electrons. However, one can take advantage of the fact that the muons are effectively isolated (so muon exchange is neglibible), and of the large mass of the muons relative to the electrons. The temperature-dependent quantum effects on the muon motion can then be included by a path-integral approach, while retaining an explicit treatment of the electron wavefunction.