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## LETTER TO THE EDITOR

# Cluster calculations of muonium states in semiconductors

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**Abstract.** The electronic structure of interstitial hydrogen in diamond, silicon and germanium is investigated by means of cluster calculations on the level of the unrestricted Hartree–Fock self-consistent field approximation. A stable configuration for H is found at a bond-centred site and its hyperfine properties are compared to experiments on paramagnetic muonium states.

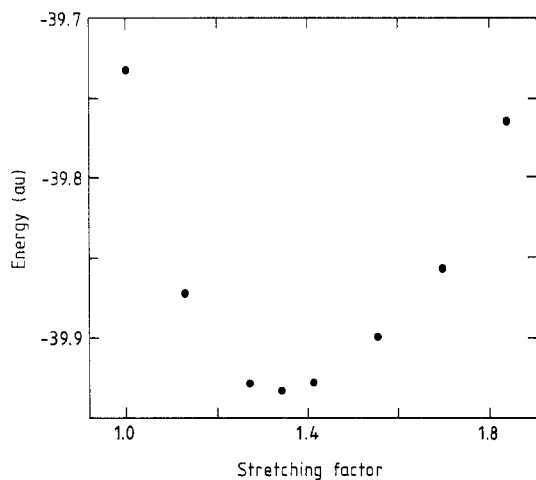
Isolated atomic hydrogen could not be observed by electron spin resonance in any semiconductors until very recently [1]. Yet a large amount of data has been obtained [2, 3] from muon-spin rotation ( $\mu$ SR) experiments on muonium (Mu), an unstable isotope of hydrogen, where the proton is replaced by a positive muon. Two quite distinct paramagnetic muonium states are identified by  $\mu$ SR in the elemental semiconductors diamond, silicon and germanium as well as in other substances: *normal muonium* with an isotropic hyperfine interaction and *anomalous muonium* with a trigonally symmetric one.

Numerous theoretical efforts aiming at an explanation of the sites, the electronic structure and the hyperfine properties of these states have been published [2–12]. A comprehensive investigation on hydrogen in different charge states in diamond and silicon clusters was performed using semiempirical methods by Mainwood and Stoneham [4], which showed a very shallow minimum for neutral H at the interstitial tetrahedral (T) site. From Hartree–Fock cluster calculations Sahoo and co-workers [5] deduced that the T site is stable in diamond and assigned the normal muonium to this site. A careful study of the influence of cluster size and choice of basis functions was made by Estreicher [12].

For anomalous muonium a bond-centred (BC) model was proposed by Symons and Cox [7] based on qualitative arguments. Quantitative calculations, which proved the BC site to be the lowest energy site in diamond and Si (if lattice relaxation is taken into account), were presented in [10–12]. In a clue experiment [13] in which the  $^{29}\text{Si}$  hyperfine structure was resolved it was established that anomalous muonium in Si is located at the BC site.

In this Letter we report on *ab initio* unrestricted Hartree–Fock calculations to study muonium centres in various clusters of diamond, silicon and germanium using pseudopotentials [14] to treat the core electrons in Si and Ge. Different program

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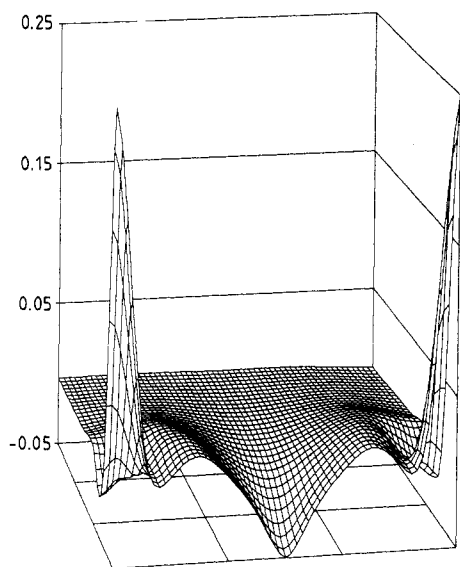
**Figure 1.** Energy of the  $\text{Ge}_8\text{H}_{18}\text{Mu}$  cluster with the muon at the BS site against stretching factor of the Ge–Ge bond length.

**Table 1.** Calculated electronic and hyperfine properties of the clusters with Mu at the bond-centred sites. Distance  $d$  in Å from Mu to the relaxed X site, change in energy  $\Delta E$  in Hartree upon relaxation, Fermi contact density at the muon  $f$  normalised to the atomic hydrogen value, magnetic moments  $m$  in  $\mu_B$  at the neighbouring host atoms, calculated contact frequencies  $\nu_c$  and dipolar frequencies  $\nu_{\text{dip}}$  in MHz, and experimental values  $\nu_c^{\text{exp}}$  and  $\nu_{\text{dip}}^{\text{exp}}$ .

Cluster	$d$	$\Delta E$	$f$	$m$	$\nu_c$	$\nu_{\text{dip}}$	$\nu_c^{\text{exp}}$	$\nu_{\text{dip}}^{\text{exp}}$
$\text{C}_8\text{H}_{18}\text{Mu}$	1.098	0.469	-0.23	0.74	-1030	130	-205	187
$\text{Si}_8\text{H}_{18}\text{Mu}$	1.576	0.206	-0.15	0.79	-670	47	-67	25
$\text{Ge}_8\text{H}_{18}\text{Mu}$	1.645	0.201	-0.19	0.77	-848	42	-96	35

packages [15, 16] have been used. Exploratory calculations showed that results obtained with minimal basis sets are not reliable. Thus all calculations were performed with at least double-zeta basis functions and some selected results were checked by including polarisation functions as well.

In order to study the BC model,  $\text{X}_8\text{H}_{18}\text{Mu}$  clusters with  $\text{X} = \text{C}, \text{Si}$  or  $\text{Ge}$  were investigated. First the bond lengths of the saturating H atoms were determined without the Mu and with the X atoms fixed at their corresponding crystallographic sites. Minima of the total energy were obtained for the following values: 1.082 Å (C), 1.469 Å (Si), and 1.559 Å (Ge). The importance of a correct saturation of small clusters has been discussed by Estreicher [12], whose results for C and Si we reproduced. Next, unrestricted Hartree–Fock calculations were performed on clusters with Mu in the middle of the two innermost host atoms, the position of which was symmetrically varied along their bond direction. The change in the energy as a function of the stretching factor is shown in figure 1 for  $\text{Ge}_8\text{H}_{18}\text{Mu}$ . The maximal reduction in energy by  $\Delta E = 0.20$  Hartree is found for a relaxation of 34.3%, i.e. for a distance of  $d = 1.645$  Å between the muon and its two nearest Ge atoms. The results for all of the three clusters investigated are summarised in table 1. To estimate the adequacy of the basis set a calculation with double-zeta plus polarisation functions was performed for the diamond cluster. It gave



**Figure 2.** Spin density calculated for  $\text{Si}_8\text{H}_{18}\text{Mu}$  in a plane through the Si–Mu–Si bond. The minimum is at the muon ( $-0.046$  au) and the maxima ( $0.248$ ) are at the two neighbouring Si atoms.

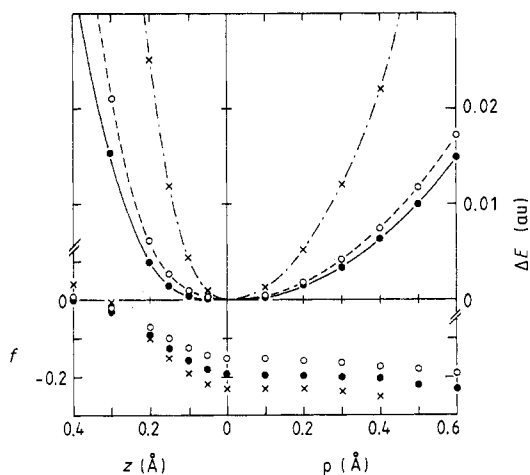
**Table 2.** Calculated atomic spin populations:  $p(\text{Mu})$  at the muon,  $p(\text{X}^{\text{nn}})$  at the nearest neighbouring host atoms,  $p(\text{X}^{\text{nnn}})$  at the next nearest neighbours,  $r(\text{X}^{\text{nn}})$  and  $r(\text{X}^{\text{nnn}})$  the corresponding ratio of the populations on p orbitals to those on s orbitals.

Cluster	$p(\text{Mu})$	$p(\text{X}^{\text{nn}})$	$r(\text{X}^{\text{nn}})$	$p(\text{X}^{\text{nnn}})$	$r(\text{X}^{\text{nnn}})$
$\text{C}_8\text{H}_{18}\text{Mu}$	-0.165	0.742	7.5	-0.109	4.0
$\text{Si}_8\text{H}_{18}\text{Mu}$	-0.194	0.790	8.3	-0.100	3.3
$\text{Ge}_8\text{H}_{18}\text{Mu}$	-0.200	0.765	8.7	-0.088	3.2

a minimal energy for a relaxation of 42.5% as compared to 41.8% for the double-zeta basis. A comparison between an all-electron calculation and one with the use of pseudopotentials for Si showed no appreciable difference.

The electronic structure of muonium at the BC site confirms the suggestions of Cox and Symons [7]. The highest occupied molecular orbital has a node at the muon. This leads to a very small spin density. In figure 2 the calculated spin density in a plane through the Si–Mu–Si bond is shown for  $\text{Si}_8\text{H}_{18}\text{Mu}$ . The density is large at the two nearest-neighbour host atoms, but small and of opposite sign at the muon. The Fermi contact density  $f$  at the muon (normalised to the value for atomic hydrogen) is also given in table 1. The values obtained for the relaxation, the change in energy and the contact density for the diamond and silicon clusters are in good agreement with those reported in [10–12].

The atomic spin populations are summarised in table 2. The value calculated for the two next-nearest Si atoms is 0.79. This is considerably larger than the experimental value of 0.21 [13] that has been deduced indirectly from the superhyperfine interaction at  $^{29}\text{Si}$ . The corresponding ratio of the populations on the p orbitals to those on the s orbitals, however, is 8.3 and compares well with the experimental value of 9.0.



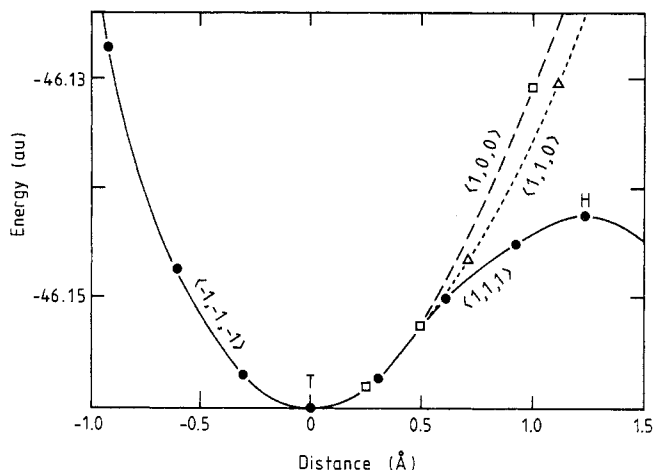
**Figure 3.** Energy surfaces for  $X_8H_{18}Mu$  with variation of the Mu site along the bond ( $z$  direction) and perpendicular to it ( $\rho$ ):  $\times$ , X = C;  $\circ$ , X = Si;  $\bullet$ , X = Ge. In the lower part the contact spin densities  $f$  at the muon (normalised to the free atomic value) are presented.

Writing the spin Hamiltonian of the interaction between the muon spin  $I$  and the electronic spins  $S$  in the form

$$H = h\nu_c I \cdot S + h\nu_{\text{dip}} [3(n \cdot I)(n \cdot S) - I \cdot S]$$

where  $n$  denotes the anisotropy axis and, under the crude assumption that the dipolar frequency  $\nu_{\text{dip}}$  can be calculated by contracting the spin densities to magnetic moments  $m$  localised at the neighbouring atoms, we obtain values for  $m$ , the contact frequencies  $\nu_c$  and  $\nu_{\text{dip}}$  that are presented in table 1. The corresponding experimental values  $\nu_c^{\text{exp}}$  and  $\nu_{\text{dip}}^{\text{exp}}$  were extracted from the data [3] by assigning negative signs to the frequencies for the components of the hyperfine tensor, except for the parallel component in diamond [17].

Considering the levels of the approximations, the values for  $\nu_{\text{dip}}$  are in remarkable agreement with experiments, while those for the contact term all have the right sign but in general are too high. This discrepancy is explained by the fact that the positive muon with its small mass will show a zero-point motion with an appreciable spread of its wavefunction. To estimate the influence of this effect the energy surfaces for Mu in  $X_8H_{16}Mu$  were calculated with all atomic sites fixed according to the fully relaxed positions except for the muon site, which was varied parallel and perpendicular to the bond direction. The results are summarised in figure 3. It may be seen that the potentials are deep enough to localise the muon at the BC site. The spread of the wavefunction in an harmonic approximation is estimated to be about 0.12 Å (0.18) for C, 0.18 (0.23) for Si, and 0.20 (0.25) for Ge along (perpendicular to) the bond. Upon variation of the muon position around the BC site, the spin densities at the neighbouring host atoms do not change significantly. The contact densities, which are shown in the lower part of figure 3, however, change rapidly for different muon positions along the band and even become positive for larger  $z$  values. This leads to a reduction of the static  $\nu_c$  values that will be less pronounced in diamond when compared with Si and Ge. A quantitative analysis of this effect requires an improved treatment of the contact density, as well as taking into account the anharmonicities of the potentials.



**Figure 4.** Energy profiles for muonium in the cluster  $\text{Ge}_{10}\text{H}_{16}\text{Mu}$  which is centred around the T site.

As regards the normal muonium state, previous Hartree–Fock calculations on clusters centred around the tetrahedral interstitial site have been reported for diamond [5, 6] and for Si [9, 11]. With the help of the pseudopotentials for Ge [14] we calculated the energy surface for Mu in a  $\text{Ge}_{10}\text{H}_{16}$  cluster using various basis sets. In figure 4 results are shown which have been obtained with double-zeta basis functions for Ge and H and with a larger basis set (8s, 2p and with a varied scaling factor) on the Mu. The latter set was chosen following the arguments in [8]. In agreement with the results for the other semiconductors we also find in Ge an energy minimum at the T site and a relative maximum at the H site. The barrier height for Ge is 0.018 Hartree. This value depends sensitively on the basis set (for a minimal basis set it is higher by a factor of 2.2). A symmetric relaxation of the four nearest atoms to the T site leads to a small reduction of the energy that is practically independent on the muonium position. In view of the small cluster sizes it is not possible to compare the relative energies of the state with Mu at the T site with that at the relaxed BC site mentioned above. In the potential well shown in figure 4 the muon is very weakly bound and tunnelling to the other equivalent sites is likely to occur. The calculated spin densities at the muon, however, are only slightly lower than in the free atom case and it is not possible to explain the experimental values of the hyperfine frequencies for normal muonium. Further investigation to elucidate this puzzling problem are in progress.

In conclusion, we calculated the properties of an interstitial hydrogen impurity in semiconductor clusters. Previous results for the relaxation and the contact densities for H at the bond-centre site in diamond and silicon were confirmed and additional information on the electronic structure was obtained. Our investigations also included germanium. The spin densities and potentials calculated explain, at least partially, the measurements on anomalous muonium in the elemental semiconductors. An improved calculation of the effect of the zero-point motion has to take the potential into account in a self-consistent manner and should also be performed for a larger cluster where the relaxation of the next-nearest neighbours can be investigated.

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