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## CLUSTER CALCULATIONS OF BOND-CENTERED HYDROGEN IN SEMICONDUCTORS

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**Abstract:** Cluster calculations at the unrestricted Hartree-Fock level show a stable configuration for neutral interstitial hydrogen at the bond-centered site in diamond, silicon, and germanium. The calculated electronic structure of this defect center is discussed and its hyperfine properties are compared to experiments on paramagnetic muonium states.

### 1. Introduction

Data on isolated atomic hydrogen in semiconductors are very scarce [1] but a large amount of information about muonium, an unstable isotope of hydrogen, has been provided by muon-spin rotation ( $\mu$ SR) experiments (for reviews see [2,3]). Two distinct paramagnetic muonium states have been observed in the elemental semiconductors diamond, silicon and germanium as well as in several other substances. Normal muonium has an isotropic hyperfine interaction, and anomalous muonium a trigonally symmetric one. In a recent experiment [4] in which the  $^{29}\text{Si}$  hyperfine structure was resolved, it was established that anomalous muonium is located at the bond-centered (BC) site.

By means of *ab-initio* unrestricted Hartree-Fock calculations we have investigated the electronic structure of hydrogen located at the BC site in the clusters  $\text{X}_8\text{H}_{18}$ , where X stands for C, Si or Ge and where hydrogen atoms are used to saturate the surface dangling bonds. The influence of core electrons was accounted for by pseudopotentials. All calculations were performed with at least double-zeta basis functions.

### 2. Description of the Method

The host crystals are represented by clusters where the host-saturator bond lengths were first determined with the host atoms fixed at their corresponding crystallographic sites. Minima of the total energy were obtained for the following X-H bond lengths: 1.082 Å (C), 1.469 Å (Si) in agreement with the results of Estreicher [5], and 1.559 Å for Ge. A hydrogen atom was placed in the center of the cluster in between the two innermost host atoms, the positions of which were then symmetrically varied along the bond direction. The calculated relaxation of the bond is given in Table 1. The results for C and Si agree with those obtained previously [5,6,7].

### 3. Results

The obtained electronic structure of hydrogen at the BC site confirms the suggestions of Cox and Symons [8]. The highest occupied molecular orbital has a node at the hydrogen. The density at the two nearest neighboring host atoms is large and of opposite sign to the

small value at H. The Fermi contact density  $f$  at H (normalized to the value of atomic H) and the atomic spin populations on the two nearest host atoms are also shown in Table 1. From these quantities we deduce hyperfine parameters which can be compared to the  $\mu$ SR data. The spin populations on the host atoms give rise to a dipolar hyperfine frequency  $\nu_{dip}$  while  $f$  leads to the muon contact hyperfine frequency  $\nu_c$ . The results for  $\nu_{dip}$  are in remarkable agreement with experiments [2,3] while those for the contact term are in general too large. This discrepancy can be explained by the fact that the muon wavefunction will have an appreciable spread which requires an averaging of the contact density. Corresponding investigations which require a detailed calculation of the muon energy hypersurface are in progress.

Cluster	rel	$f$	$p(X^{nn})$	$\nu_c$	$\nu_{dip}$	$\nu_c^{exp}$	$\nu_{dip}^{exp}$
$C_8H_{18}Mu$	42.0%	-0.23	0.742	-1030	130	-205	187
$Si_8H_{18}Mu$	34.1%	-0.15	0.790	-670	47	-67	25
$Ge_8H_{18}Mu$	34.3%	-0.19	0.765	-848	42	-96	35

Table 1: Calculated electronic and hyperfine properties of interstitial H (or Mu) at the bond-centered site: Relaxation ( $rel$ ) of the bond, Fermi contact density at the muon  $f$  normalized to the atomic hydrogen value, calculated atomic spin population  $p(X^{nn})$  at the nearest neighbouring host atoms, calculated contact  $\nu_c$  and dipolar  $\nu_{dip}$  hyperfine frequencies in MHz, and experimental values  $\nu_c^{exp}$  and  $\nu_{dip}^{exp}$ .

Another quantity of interest is the ratio of the spin populations of the atomic p-orbitals to those on s-orbitals for which we obtain the values 7.5 (4.0) for C, 8.3 (3.3) for Si, and 8.7 (3.2) for Ge for the nearest (next-nearest) host atoms. The large values at the nearest neighbor atoms indicate a strong distortion of the bonding due to the interstitial muon while those for the next-nearest neighbors correspond to a usual sp-hybridization. The value of 8.3 for Si compares well with the experimental result [4] of 9.0.

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