Spin-polarized calculations and hyperfine parameters for hydrogen or muonium in GaAs

Chris G. Van de Walle

Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304

L. Pavesi

Università degli Studi di Trento, Dipartimento di Fisica, 38050 Povo (Trento) Italy

We present first-principles spin-density-functional calculations for neutral hydrogen or muonium in GaAs. The effect of spin polarization on the total energy of the system is evaluated, and found to be rather small, thereby confirming results obtained with a spin-averaged approach [L. Pavesi, P. Giannozzi, and F. K. Reinhart, Phys. Rev. B **42**, 1864 (1990)]. Hyperfine parameters are calculated for various geometries, allowing identification of specific configurations with experimental features observed in μSR (muon-spin-rotation) experiments.

I. INTRODUCTION

Hydrogen in semiconductors has been a subject of intense investigation in recent years, both because of the academic interest in this "prototypal" impurity, and because of its potential technological impact. The observation that hydrogen can passivate shallow impurities has been an important driving force. In III-V compounds, hydrogen passivation of shallow impurities has been observed to be sufficiently stable to allow device applications.[1] This emphasizes the importance of a thorough understanding of the behavior of hydrogen in III-V materials, the first step of which consists of investigations of hydrogen as an isolated interstitial impurity. Such studies for H in GaAs were recently reported by Pavesi, Giannozzi, and Reinhart[2]. However, those calculations were performed in a spin-averaged approximation. For systems with an unpaired electron (such as interstitial H in the neutral charge state) the procedure should consist of separating spin-up and spin-down electrons in the calculation, so that the unpaired electron has a specific spin state. The spin-averaged approach effectively puts half the electron in a spin-up state and half in a spin-down state, and makes no distinction between spin states. This approximation can affect the calculated total energy, and also makes it impossible to calculate quantities such as hyperfine parameters, which explicitly depend on the spin density (the difference between the charge densities of spin-up and spin-down electrons).

In this paper we report spin-polarized calculations for neutral H in GaAs, based on spin-density-functional theory and *ab initio* pseudopotentials. By comparison with spin-averaged calculations, we can evaluate the effect of spin polarization on the total energy. Our results will indicate that this effect is rather small (less than 0.15 eV). This justifies the use of the spin-averaged approach for investigating structural properties and identifying (meta)stable sites and relaxations. Spin-polarized calculations also yield explicit information about spin densities, which can be used to calculate hyperfine parameters. A procedure to extract such information from

pseudopotential calculations was recently developed by one of us.[3,4] These results can be compared to experimental quantities, allowing an unambiguous identification of the microscopic structure. For H in GaAs, experimental hyperfine parameters were obtained using muon-spin rotation (μSR). Muonium is a pseudoisotope of hydrogen, and consists of an electron bound to a positive muon (μ^+). The mass of μ^+ is $\frac{1}{9}$ of that of the proton; the dynamical behavior of muonium may therefore differ from that of hydrogen. From a static point of view, however, hydrogen and muonium are equivalent, since both the proton and muon are point particles with identical charge. The experimental techniques of muon-spin rotation and muon level-crossing resonance, which have provided a wealth of information about muonium in solid-state materials, are described in Ref. 5. Two distinct types of paramagnetic centers have been observed; they are labeled Mu ("normal muonium") and Mu* ("anomalous muonium"). The muon-electron hyperfine coupling is purely isotropic for normal muonium.[6] Anomalous muonium exhibits very different properties. Its isotropic hyperfine coupling is much smaller than for normal muonium and a significant anisotropic coupling is found, showing a $\langle 111 \rangle$ symmetric hyperfine interaction (C_{3v} symmetry).[7] We will show that our calculated hyperfine parameters for muonium in a bond-center position closely agree with the anomalous muonium signal, while normal muonium can be identified with a muon in the neighborhood of a tetrahedral interstitial site.

II. THEORETICAL TECHNIQUES

The calculations are based on spin-density-functional theory,[8] in a supercell geometry, and using a plane-wave basis set. Except for the hydrogen atom, for which we use the bare Coulomb potential, we represent the atoms in our calculations by *ab initio* pseudopotentials. Norm-conserving pseudopotentials were generated according to the Hamann-Schlüter-Chiang scheme.[9] These pseudopotentials were slightly different from the ones used in the

total-energy calculations of Ref. 2. However, we have verified that our calculational approach for the hyperfine parameters yields results which are not sensitive to the choice of pseudopotential.[4] A theoretical equilibrium lattice parameter of 5.61 Å was used.

Spin-polarized calculations provide explicit information about spin-up and spin-down wave functions. The paramagnetic defect centers discussed here have either an isotropic hyperfine interaction, or one with axial symmetry. The Hamiltonian for the hyperfine interaction is typically expressed in terms of the parameters a and b,

$$a = \frac{8\pi}{3} \frac{\mu_0}{4\pi} g_e \mu^e g_I \mu^I \rho_{\text{spin}}(\mathbf{R}) \, , \tag{1}$$

$$b = \frac{\mu_0}{4\pi} g_e \mu^e g_I \mu^I \int d^3 \mathbf{r} \rho_{\text{spin}}(\mathbf{r}) \frac{3\cos^2\tau - 1}{2r^3} \, , \tag{2}$$

where $\mu_0 = 4\pi 10^{-7} \text{ T}^2 \text{m}^3 \text{J}^{-1}$ is the permeability of vacuum, g_e is the electron g factor, μ^e is the Bohr magneton, g_I and μ^I are the gyromagnetic ratio and nuclear magneton of the nucleus at coordinate $\mathbf{R}$, $\mathbf{r}$ is the coordinate of the electron, r is the distance between the electron and the nucleus, and τ is the angle between $\mathbf{r}$ and the symmetry axis. Values for g_I and μ^I for specific nuclei are found in tables (see, e.g., Ref. 10). a and b have units of energy; they are usually expressed as a frequency (in MHz), using $E = h\nu$. ρ_{spin} is the spin density, which corresponds to the difference between the charge densities of the spin-up and the spin-down electrons, i.e., $\rho_{\text{spin}} = \rho_\uparrow - \rho_\downarrow$.

The parameter a [Eq. (1)] represents the isotropic hyperfine interaction (Fermi contact interaction); it depends on the spin density at the nucleus itself, where only the s-like wave functions contribute. The parameter b [Eq. (2)] represents the anisotropic hyperfine interaction, which reflects the p-like part of the wave function.

Extracting hyperfine parameters from pseudopotential calculations requires an appropriate formalism. The spin density entering into Eqs. (1) and (2) is an all-electron density, whereas our pseudopotential calculations only yield pseudo-wave-functions for the valence electrons. The neglect of core polarization is usually not serious (see Ref. 11). More important is the fact that in pseudopotential calculations the valence wave functions coincide with the true wave functions only outside a certain "core radius," and deviate inside. Equations (1) and (2) show that the value of hyperfine parameters is largely determined by contributions from inside the core radius. We therefore need a procedure to reconstruct the full (all-electron) wave functions from the pseudo-wave-functions. Since the potential in the core region is essentially atomlike and not much affected by the crystalline environment, one expects the shape of the wave functions in the core region to be very similar to atomic wave functions. The matching conditions to the wave functions outside the core region will determine the amplitudes of the wave functions inside the core, and hence the hyperfine parameters. This insight was utilized in Ref. 3 to obtain hyperfine parameters by a scaling procedure: hyperfine parameters were calculated from pseudo-wave-functions in the solid, and then divided by corresponding quantities in the pseudo-atom. This ratio can then be multiplied by the appropri-

ate hyperfine parameter in the all-electron atom to yield the full hyperfine parameter for the defect. More recently, we[4] have been able to show that this procedure can be put on a firm theoretical footing by combining concepts from pseudopotential theory with augmented-wave methods. The complete theoretical framework is given in Ref. 4.

We have tested convergence as a function of supercell size and as a function of plane-wave cutoff. For the purposes of calculating hyperfine parameters, two aspects of convergence should be investigated: (1) convergence of the energy minimization procedure that yields the stable structure of the defect, and (2) convergence of the formalism that produces the hyperfine parameters. To address (1), the supercells should be large enough to allow for relaxation of a sufficient number of atomic shells around the defect, and to ensure sufficient separation of the defects; in addition, the plane-wave cutoff should be large enough to obtain reliable energy differences between different configurations. Convergence tests addressing these specific points were reported in Ref. 2; it was concluded that supercells containing 32 host atoms (i.e., 16 As and 16 Ga atoms), and an energy cutoff of 12 Ry were sufficient to obtain accurate information about the structure.

Aspect (2) of convergence can be investigated by fixing the atoms in a particular position, and calculating the corresponding hyperfine parameters as a function of supercell size and of plane-wave cutoff. Regarding supercell size, there are reasons to expect that cells sufficient to obtain accurate structural information will also suffice to extract hyperfine parameters: (a) Deep-level defects have relatively well localized states. (b) The hyperfine parameters are determined by the wave function in the immediate neighborhood of the defect (e.g., the anisotropic hyperfine parameter contains an r^{-3} dependence), and are therefore insensitive to the wave function far from the defect. (c) Since spin-up and spin-down components are subtracted to obtain the spin density, some cancellation of errors is expected. The spin density is actually strongly localized in the immediate vicinity of the defect, as we will see below. Nonetheless, it is always safer to explicitly check convergence. In the present case, we found that the hyperfine parameters changed by less than 5% between the 16- and 32-atom calculations.

Convergence with respect to plane-wave cutoff is typically investigated by increasing the size of the basis set in a small supercell. Such tests indicate that an energy cutoff of 12 Ry is sufficient to obtain accurate hyperfine parameters. While this may seem rather low for a defect containing hydrogen, with its very localized potential, one should keep in mind that our procedure for extracting hyperfine parameters[4] uses $ratios$ of quantities calculated for the defect compared to quantities calculated for a (pseudo)atom. The latter calculation should be performed using the same plane-wave cutoff as for the defect in the solid. This procedure largely eliminates systematic errors due to incomplete convergence. Our results for convergence both as a function of basis-set size and of supercell size are consistent with those previously reported for H in Si.[3]
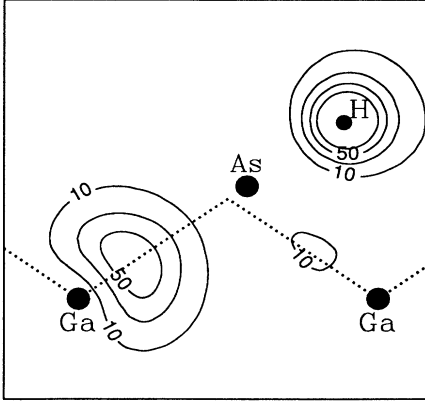
FIG. 1. Contour plot of the spin density in the (110) plane through the atoms for neutral H at the antibonding (AB) position near an As atom in GaAs, obtained from first-principles spin-density-functional calculations. The relaxed positions of the atoms are indicated. Dotted lines connect the unrelaxed positions of the host atoms. The contour interval is 20, in units of electrons per unit cell (for a supercell containing 1 H, 16 As, and 16 Ga atoms).

III. EFFECT OF SPIN POLARIZATION ON TOTAL ENERGIES

The coordinates of the atoms for the various structures were taken from Ref. 2. Those authors identified the following stable and metastable structures for H^0 in GaAs: the global minimum is for H in an antibonding (AB) configuration near an As atom. The neighboring As atom relaxes toward the H atom by a distance of 0.31 Å,
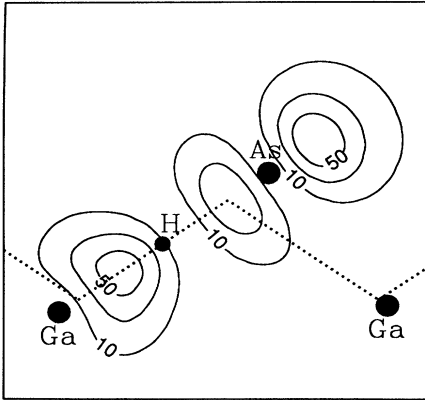

FIG. 2. Contour plot of the spin density in the (110) plane through the atoms for neutral H at the bond-center position, obtained from first-principles spin-density-functional calculations. The relaxed positions of the host atoms are indicated. Dotted lines connect the unrelaxed positions of the host atoms. The contour interval is 20, in units of electrons per unit cell (for a supercell containing 1 H, 16 As, and 16 Ga atoms). The spin density is highly anisotropic, located mainly in p-like states on the host atoms on either side of the hydrogen atom.

TABLE I. Theoretical values of the isotropic (a) and anisotropic (b) hyperfine parameters for muonium at the antibonding site near an As atom in GaAs. Values are given for the muon at the center of the defect, for the first [75]As neighbor, for the first [69]Ga neighbor (there are three of those), and for the third [69]Ga neighbor, which is located along the H-As axis.

	η_s^2	a (MHz)	η_p^2	b (MHz)
Muon	0.238	1011		3
As_{1nn}	0.017	200	-0.060	-18
Ga_{1nn}	0.026	252	0.003	~ 0
Ga_{3nn}	0.142	1396	0.345	67

and the As-H distance is 1.56 Å. The atomic positions are schematically illustrated in Fig. 1 (spin densities will be discussed in Sec. IV). The bond-center (BC) position, in which both Ga and As neighbors show significant relaxation, is a local minimum (about 0.2 eV higher than the global minimum); in this configuration, the As atom relaxes outward by 0.66 Å, and the Ga atom by 0.31 Å. The atomic positions are schematically illustrated in Fig. 2.

The calculations in Ref. 2 were carried out without inclusion of spin polarization, i.e., no distinction was made between spin-up and spin-down states. This is appropriate in case all bands are occupied by two electrons (which would occur for the H^+ and H^- charge states), but only approximately correct if the defect contains an unpaired electron. Here we examine the effect on the total energy due to the inclusion of spin polarization. For that purpose, we compare the difference in the calculated total energy between a calculation in the spin-averaged scheme (analogous to Ref. 2), and a fully spin-polarized one. We expect a lowering in the total energy, since the effect of spin polarization is to introduce an exchange splitting in the energy level of the unpaired electron. Assuming that the average position of all bands remains the same, the lowering of the state with the unpaired electron should lower the total energy.

We found the effect to be largest when H is located at a tetrahedral interstitial (T_d) site. For H at the T_d site surrounded by As atoms (T_d^{As}), the energy lowering due to spin polarization is 0.15 eV. For H located at the bond-center position, the energy lowering due to spin polarization is only 0.05 eV. When H is located at the antibond-

TABLE II. Theoretical values of the isotropic hyperfine parameters for muonium at the T_d^{As} site in GaAs. Values are given for the muon at the center of the defect, as well as for the first ([75]As) and second ([69]Ga) neighbors. The experimental value for normal muonium in GaAs is $a = 2884$ MHz (Ref. 6).

	η_s^2	a (MHz)
Muon	0.59	2497
As_{1nn}	0.009	106
Ga_{2nn}	0.005	46

ing site close to an As atom (the global minimum), the energy due to spin polarization is 0.07 eV. We conclude that the correction due to spin polarization is always rather small, and becomes smaller as the spin density on the proton decreases (i.e., as H becomes more strongly bonded to the host atoms). These conclusions are consistent with previous findings for hydrogen in silicon,[12] where the maximum correction due to spin polarization occurred for H at the T_d site, with a magnitude of only 0.1 eV. The qualitative conclusions reached in Ref. 2 regarding relative stability of various sites therefore remain unchanged when spin-polarization effects are included.

IV. HYPERFINE PARAMETERS

The calculated spin density for the AB and BC configurations is shown in Figs. 1 and 2. It is a common practice to express the measured value of the hyperfine parameters with respect to an atomic reference.[13] Calling the references A_s^{free} and A_p^{free}, we can define the ratios $\eta_s^2 = a / A_s^{free}$ and $\eta_p^2 = b / A_p^{free}$. The calculated hyperfine parameters are reported in Tables I–IV. We list the values corresponding to muonium to allow easy comparison with the experimental μSR results. Values for hydrogen can be obtained simply by scaling by the ratio of proton-to-muon magnetic moment.

From Table I we find that the global minimum configuration, at the AB site, gives rise to hyperfine parameters which do not correspond to any of the observed hyperfine signals. Indeed, the theoretical parameters differ significantly from the experimental ones for anomalous muonium (see Table IV), as well as those for normal muonium (see Tables II and III). Normal muonium in GaAs has an isotropic hyperfine interaction; this puts severe restrictions on the type of atomic configurations that can give rise to this feature. Both the BC and AB configurations are highly anisotropic. One possibility for normal muonium might be a rapid tunneling between equivalent AB-type positions; the relaxation of the host atoms in such a situation would probably be smaller than in the "static" AB configuration studied here. Another possibility is that normal muonium is located at or near the T_d site. In practice, it may actually be difficult to distinguish between these two possibilities. For the purposes of this study, we have placed the muon at the (two types of) T_d site; the calculated hyperfine parameters are listed in Tables II and III. The experimental value measured for normal muonium in GaAs is $a = 2884$ MHz (Ref. 6); it is close to the theoretical values both for the

TABLE III. Theoretical values of the isotropic hyperfine parameters for muonium at the T_d^{Ga} site in GaAs. Values are given for the muon at the center of the defect, as well as for the first (^{69}Ga) and second (^{75}As) neighbors. The experimental value for normal muonium in GaAs is $a = 2884$ MHz (Ref. 6).

	η_s^2	a (MHz)
Muon	0.62	2646
Ga$_{1nn}$	0.009	92
As$_{2nn}$	0.005	58

T_d^{As} and the T_d^{Ga} sites.

For the bond center (Table IV), the agreement with experiment for anomalous muonium[7,14] is generally good, except for the isotropic hyperfine parameter on the As atom. This could be interpreted as an indication that the assumed atomic relaxations are not entirely correct. The value of this parameter becomes closer to experiment if the As atom is brought closer to the muon (i.e., the As relaxes less far outward); however, this occurs at the expense of the agreement in the other parameters (including the anisotropic parameter on the As). It is therefore more likely that the deviation in this particular parameter simply reflects the error bar in the calculation, which is not surprising in light of the very small value of the spin density on this atom ($\eta_s^2 = 0.006$).

For the case of the bond-center site we had an opportunity to check the influence of the choice of pseudopotential on the calculated results. One set of pseudopotentials was taken directly from the tables of Bachelet, Hamann, and Schlüter,[15] the other was generated according to the Hamann-Schlüter-Chiang scheme,[9] but using somewhat larger core radii. The resulting hyperfine parameters agreed to better than 10%, confirming the general validity of the calculational approach.

The only previous theoretical study of hyperfine parameters for muonium in GaAs, by Maric et al.,[16] using a Hartree-Fock cluster approach, focused on the bond-center configuration, and found $a = 20$ MHz for the muon (compared to an experimental value of 131 MHz). The agreement with experiment cannot be called quantitative; Hartree-Fock–type calculations seem to have difficulty producing accurate hyperfine parameters (see the discussion in Ref. 4). b was only estimated in Ref. 16, at a value between 50 and 60 MHz (compared to 43.6 MHz experimentally).

TABLE IV. Theoretical and experimental (Refs. 7 and 14) values of the isotropic (a) and anisotropic (b) hyperfine parameters for muonium at the bond-center site in GaAs. Values are given for the muon at the center of the defect, as well as for the first (^{69}Ga and ^{75}As) neighbors.

| | η_s^2 | a (MHz) | | η_p^2 | b (MHz) | |
	Theoretical	Theoretical	Experiment	Theoretical	Theoretical	Experiment
Muon	0.025	106	131.4		33	43.6
Ga$_{1nn}$	0.103	1014	929.3	0.287	56	61.4
As$_{1nn}$	0.006	74	273.3	0.327	99	144.9

V. SUMMARY

We have performed spin-polarized density-functional calculations for various configurations of (neutral) hydrogen or muonium in GaAs. We find that inclusion of spin polarization in the calculation of the paramagnetic defect has only a small effect (less than 0.15 eV) on the energy of the system. We have also used the spin-polarized wave functions to calculate hyperfine parameters, using a recently developed formalism.[4] The experimentally observed anomalous muonium signal can be unambiguously identified with the bond-center configuration. The experimental normal muonium signal is in rather good agreement with the isotropic hyperfine parameter for muonium at a T_d site, even though the T_d sites are less stable than the AB sites, to which the muon is expected to relax

under static conditions.[2] We speculate that under the dynamic conditions characteristic of the muonium experiment, the lattice relaxation required for a stable AB-type position does not take place, confining the muon to the T_d site itself, or to a small region around it, maybe tunneling among equivalent AB-type positions.

[1] J. Chevallier, B. Clerjaud, and B. Pajot, in *Hydrogen in Semiconductors, Semiconductors and Semimetals,* edited by J. I. Pankove and N. M. Johnson (Academic, San Diego, 1991), Vol. 34, Chap. 13, p. 447.

[2] L. Pavesi, P. Giannozzi, and F. K. Reinhart, Phys. Rev. B **42**, 1864 (1990); L. Pavesi and P. Giannozzi, *ibid.* **46**, 4621 (1992).

[3] C. G. Van de Walle, Phys. Rev. Lett. **64**, 669 (1990).

[4] C. G. Van de Walle and P. E. Blöchl, preceding paper, Phys. Rev. B **47**, 4244 (1992).

[5] R. F. Kiefl and T. L. Estle, in (Ref. 1), Chap. 15, p. 547.

[6] R. F. Kiefl, J. W. Schneider, H. Keller, W. Kündig, W. Odermatt, B. D. Patterson, K. W. Blazey, T. L. Estle, and S. L. Rudaz, Phys. Rev. B **32**, 530 (1985).

[7] R. F. Kiefl, M. Celio, T. L. Estle, G. M. Luke, S. R. Kreitzman, J. H. Brewer, D. R. Noakes, E. J. Ansaldo, and K. Nishiyama, Phys. Rev. Lett. **58**, 1780 (1987).

[8] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965); L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971); U. von Barth and L. Hedin, *ibid.* **5**, 1629 (1972); exchange and correlation potentials are based on the data from D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980), as parametrized by J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[9] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[10] *CRC Handbook of Chemistry and Physics,* 69th ed., edited by R. C. Weast (CRC, Boca Raton, FL, 1988), p. E-80; the gyromagnetic ratio is obtained by dividing the magnetic moment by the spin.

[11] H. Overhof, M. Scheffler, and C. M. Weinert, Phys. Rev. B **43**, 12494 (1991).

[12] C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. B **39**, 10791 (1989).

[13] J. R. Morton and K. F. Preston, J. Magn. Reson. **30**, 577 (1978).

[14] R. F. Kiefl, J. H. Brewer, S. R. Kreitzmann, G. M. Luke, T. M. Riseman, T. L. Estle, M. Celio, and E. J. Ansaldo, in *Proceedings of the 15th International Conference on Defects in Semiconductors, Budapest, Hungary, 1988,* edited by G. Ferenczi (Trans Tech, Aedermannsdorf, Switzerland, 1989), p. 967.

[15] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **24**, 4199 (1982).

[16] Dj. M. Maric, S. Vogel, P. F. Meier, and S. K. Estreicher, Phys. Rev. B **40**, 8545 (1989).