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First-principles calculations of hyperfine parameters

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Hyperfine parameters obtained from experimental techniques such as electron paramagnetic resonance contain a wealth of information about defects in semiconductors. Detailed structural information can only be extracted, however, if accurate calculations are available with which the experimental quantities can be compared. We show that reliable values for hyperfine parameters can be obtained from first-principles calculations based on spin-density-functional theory and pseudopotentials. We present a method that overcomes the complication that the wave functions in the core region are not directly available in a pseudopotential formalism. The power of the approach will be illustrated with examples for a number of different defect systems, including H in various semiconductors (Si, GaAs, and ZnSe), and the Zn interstitial in ZnSe.

I. INTRODUCTION

The study of defects in semiconductors has emerged as a very active area of condensed-matter physics, stimulated by the potential impact on technology. Both theory and experiment have produced important insights into the atomic and electronic structure of such defects. A large effort has been directed at the identification of the microscopic structure of point defects: Which are the atoms that make up the defect, what are the positions of these atoms in the lattice, and what is the relaxation of the host atoms in the neighborhood of the defect? Very few (if any) experimental techniques provide *direct* answers to these questions. Very often, a structural model is proposed, the consequences of which are then compared with the experimental data. This procedure often requires the ability to carry out reliable calculations for various properties of a given defect structure. Throughout this paper we use the word "defect" as a generic term indicating either native point defects (such as vacancies, self-interstitials, or antisites) or impurities.

Among experimental techniques, electron paramagnetic resonance (EPR) may be the one that offers the most detailed information about defect structure. This method, along with related techniques such as optically detected magnetic resonance (ODMR), probes the interaction of the electronic wave functions with the nuclear spins; the results are expressed in the form of *hyperfine parameters.* These values provide explicit information about the symmetry of the defect and the type of atoms which are involved. In principle, the hyperfine parameters even contain information about the positions of the various nuclei. However, this information can be extracted only by comparison with theoretical numbers obtained for various possible structures. A simple model consisting of a superposition of atoms has often been used for this purpose.[1] Such a model, however, clearly cannot adequately reflect the effects of bonding, hybridization, and spin polarization of the valence-band states. Some attempts at performing more sophisticated calculations, based on cluster calculations in the Hartree-Fock approximation, have not been very successful; the resulting hyperfine parameters deviate sometimes by orders of magnitude from experiment.[2] On the other hand, calculations based on density-functional theory have produced promising results. Most of this work was based on all-electron methods,[3] such as the linear-muffin-tin-orbital (LMTO) method[4,5] or the full-potential linearized augmented-plane-wave[6] (FLAPW) method. Unfortunately, these methods have been limited by the type and symmetry of structures that can be described accurately and by the size of systems that can be treated. The alternative pseudopotential method, which allows calculations on large supercells without any restriction on the symmetry, has therefore been used more widely in the theoretical investigation of point defects in semiconductors. Reliable and accurate calculations of hyperfine parameters based on pseudopotentials would open the door for an unambiguous identification of many defect structures, and are therefore highly desirable. In contrast to all-electron methods, however, the extraction of hyperfine parameters from a pseudopotential calculation is not straightforward.

In this paper we describe a method, based upon spin-density-functional theory and *ab initio* pseudopotentials, which produces reliable hyperfine parameters for a wide variety of defects in different semiconductors. A large number of applications will be presented to corroborate the validity and usefulness of the approach. An important advantage of the method is that the *same* computational approach also allows total-energy calculations which produce the stable or metastable structure of a defect. The theory thus allows (1) the prediction of a certain defect structure and (2) the identification of the defect by direct comparison of the calculated hyperfine parameters with experimental results.

Section II of this paper is devoted to the technical details of the approach. The pseudopotential method implies a modification of the wave function inside a core radius around each atom. Since this region contributes significantly to the hyperfine parameters, the latter cannot be directly obtained from the pseudo-wave-function. The solution to this problem is to reconstruct the all-electron wave function by combining free-atom wave functions with the pseudo-wave-functions obtained in the defect calculation.

Section III contains an overview of results obtained for various systems which have recently been studied experimentally. We will consider the case of hydrogen (or muonium) as an impurity in various semiconductors (Si, GaAs, and ZnSe), a topic of recent intense investigations.[7] The location of hydrogen in the lattice was the subject of controversy for some time. Experimental data were available, in this case, from the muon-spin-resonance (μSR) technique, which is closely analogous to EPR.[8,9] The calculation of hyperfine parameters for hydrogen in the bond-center position and comparison with the μSR data have conclusively resolved the issue.[10] Another illustration will be taken from the study of native point defects in ZnSe, where the Zn interstitial has been the first self-interstitial to be directly observed in a semiconductor.[11] Here, too, good agreement between theory and experiment confirms the identification of the defect and provides detailed information about the defect structure (relaxations, etc.), giving us confidence in the general reliability of the approach. Some of the results presented in Sec. III have previously been reported elsewhere.[10,12,13] The main conclusions are summarized in Sec. IV.

II. THEORETICAL METHODS

A. Formulas for hyperfine parameters

The interaction between an electron and a nuclear spin in general includes an isotropic (contact interaction) and an anisotropic (dipolar) part[14,15]

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

Here $\mu_0 = 4\pi 10^{-4}$ $\mathrm{T^2m^3J^{-1}}$ is the permeability of vacuum, g_e is the electron g factor, μ^e is the Bohr magneton, and g_I and μ^I are the gyromagnetic ratio and nuclear magneton of the nucleus at coordinate $\mathbf{R}$. $\mathbf{S}^I$ and $\mathbf{S}^e$ are the nuclear and electron spin operators, and r is the distance between the electron and the nucleus. When this expression is integrated over the electronic wavefunction, the Hamiltonian for the hyperfine interaction is obtained:

$$\mathcal{H} = \mathbf{S}^I\cdot\overset{\rightrightarrows}{A}\cdot\mathbf{S}^e \; , \tag{2}$$

where $\overset{\rightrightarrows}{A}$ is the so-called hyperfine tensor.

The paramagnetic defect centers observed to date in semiconductors usually have either an isotropic hyperfine interaction (for which $\overset{\rightrightarrows}{A}$ is simply proportional to the unit matrix) or one with axial symmetry. In the latter case, $\overset{\rightrightarrows}{A}$ is diagonal with elements $A_\parallel$ and $A_\perp$, and the interaction can be written as

$$\begin{aligned}\mathcal{H} &= A_\perp(S_x^I S_x^e + S_y^I S_y^e) + A_\parallel S_z^I S_z^e \\ &= (a-b)\mathbf{S}^e\cdot\mathbf{S}^I + 3bS_z^e S_z^I \; .\end{aligned} \tag{3}$$

The parameters a, b, and $A_\perp$ and $A_\parallel$ are related by

$$A_\perp = a - b \; , \tag{4}$$

$$A_\parallel = a + 2b \; . \tag{5}$$

a and b are given by

$$a = \frac{2\mu_0}{3} g_e\mu^e g_I\mu^I \rho_{\mathrm{spin}}(\mathbf{R}) = \frac{8\pi}{3}\,\frac{\mu_0}{4\pi} g_e\mu^e g_I\mu^I \rho_{\mathrm{spin}}(\mathbf{R}) \; , \tag{6}$$

$$b = \frac{\mu_0}{4\pi} g_e\mu^e g_I\mu^I \int d^3\mathbf{r}\,\rho_{\mathrm{spin}}(\mathbf{s})\frac{3\cos^2\tau - 1}{2r^3} \; , \tag{7}$$

where $\mathbf{s}$ is the coordinate of the electron and τ is the angle between $\mathbf{s}$ and the symmetry axis. Values for g_I and μ^I for specific nuclei are found in tables (see, e.g., Ref. 16). a and b have units of energy; often they are expressed as a frequency (in MHz), using $E = h\nu$, or as a wave number (in 10^{-4} $\mathrm{cm^{-1}}$), using $E = hc/\lambda$. To convert from units of MHz to units of 10^4 $\mathrm{cm^{-1}}$, simply divide by 3.

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., $\rho_{\mathrm{spin}} = \rho_\uparrow - \rho_\downarrow$. Equation (1) describes the interaction of the unpaired electron with any nucleus that has a nonvanishing magnetic moment. For an impurity in a semiconductor, the hyperfine parameters can relate to the nucleus of the impurity itself, but they can also relate to the nuclei of the surrounding host atoms. The latter are sometimes referred to as "superhyperfine parameters."

The parameter a [Eq. (6)] 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. As a simple illustration, in the free hydrogen atom, the spin density (i.e., wave function squared) at the nucleus has the value $1/\pi$; this leads to a hyperfine constant $a = 1420$ MHz. The parameter b [Eq. (7)] represents the anisotropic hyperfine interaction. Note that the factor $(3\cos^2\tau - 1)/2$ corresponds (within a normalization factor) to a d-like ($l = 2$) spherical harmonic, which we will denote as Y_d. The formula thus effectively projects out the d-like component of the spin density. This corresponds indeed to the common notion about the anisotropic hyperfine parameter, namely, that it captures the p-like component of the wave function: If we assume that the d-like component in the wave function is negligible (which is usually a good approximation for the defects under study), the wave function would consist of s and p components; schematically:

$\psi = \alpha\psi_s + \beta\psi_p$. The charge density for each spin component is the square of the wave function, and thus contains

$$|\alpha|^2|\psi_s|^2 + \alpha^*\beta\psi_s^*\psi_p + \alpha\beta^*\psi_s\psi_p^* + |\beta|^2|\psi_p|^2 .$$

The last term is the only one which contributes to an $l=2$ component in this expression, so it will be isolated when the d-like part of the spin density is projected out.

For practical purposes, we rewrite the formulas for a and b using the following notation and units (see Ref. 17): we set $g_I\mu^I = \gamma^I$, the gyromagnetic ratio of the nucleus, which we will express in units of MHz/T. All spin densities will be expressed in atomic units (a_{Bohr}^{-3}). Finally, a and b will be expressed in MHz. Using the values given above, we then obtain

$$a = 104.98\gamma^I \rho_{\mathrm{spin}}(\mathbf{R}) , \tag{8}$$

$$b = 12.531\gamma^I \int d^3\mathbf{r}\, \rho_{\mathrm{spin}}(\mathbf{s}) \frac{3\cos^2\tau - 1}{2r^3} . \tag{9}$$

B. Theoretical framework

In order to calculate the hyperfine parameters defined in Eqs. (6) and (7), we need values for the spin density $\rho_{\mathrm{spin}} = \rho_\uparrow - \rho_\downarrow$, which will be obtained from first-principles calculations. These calculations are based on spin-density-functional theory,[18] in which the spin-up and spin-down electrons produce different band structures and are subject to different potentials. These potentials and charge densities are coupled through the exchange and correlation term in the Schrödinger equation. No vector coupling is included here. Scalar relativistic effects are included through the pseudopotential.[19]

A supercell geometry is used, in which the defect is surrounded by a sufficiently large number of host atoms, and this whole structure is periodically repeated. It is essential to check convergence with respect to supercell size. The supercells need to be large enough to allow for relaxation of a sufficient number of shells around the atom. In addition, one should check whether the cells can include all relevant details of the spin-density distribution, and ensure sufficient separation of impurities in neighboring supercells. The tests reported in Sec. III focus on the latter issue, and are performed by carrying out calculations in increasingly larger supercells. The supercells in our studies usually contained 8, 16, and 32 atoms. Brillouin-zone integrations are performed based on the special-points methods.[20]

Within the pseudopotential formalism, the basis set consists either entirely of plane waves (up to a kinetic-energy cutoff E_{cut}) or of a mixture of plane waves and localized functions. The latter "mixed basis" approach[21] is essential for calculations of defects in ZnSe, where the Zn $3d$ states need to be included as valence states in order to obtain the correct structural properties,[22] but plane waves alone are unsuited as a basis set because of the localized nature of the d states.

The choice of supercell, basis set, and special points should be adapted to the nature of the defect at hand, and always subjected to tests. Further details about the calculational approach can be found in Refs. 23 and 24. We will also have occasion to illustrate the procedure when we describe various examples in Sec. III.

C. Pseudopotential theory of hyperfine parameters

Except for the hydrogen atom, for which we use the bare Coulomb potential, we represent the atoms in our calculation by *ab initio* pseudopotentials.[19] This has two consequences for the purposes of calculating the hyperfine parameters: (a) No information is available about core electrons and (b) the valence wave functions coincide with the true wave functions only outside a certain "core radius," and deviate inside. In particular, the true wave function contains oscillations (to ensure orthogonality to the core states), whereas the pseudo wave function is nodeless in the core region.

Point (a) implies that the core is frozen and effects due to core polarization are not included.[5,25] In Ref. 5 it was found, for chalcogen impurities in Si, that the contribution from core polarization to the contact hyperfine interaction was always less than 15% of the total value, and typically much smaller. In principle, these terms could be evaluated within our formalism by performing calculations on the all-electron atom placed in the appropriate potential. Given the small magnitude of these terms, though, we feel it is justified to neglect them here. Point (b) is more serious since the value of hyperfine parameters is largely determined by contributions from inside the core radius, i.e., in a region where we have no *explicit* information about the true wave function. The reason these contributions from the region near the nucleus dominate is obvious in the case of the isotropic hyperfine parameter, which is determined by the charge density at the nuclear site itself. In the case of the anisotropic hyperfine parameter [Eq. (7)], it is due to presence of the factor r^{-3} in the integrand, which heavily weighs contributions near the origin. In the context of *ab initio* norm-conserving pseudopotentials, there has been up to now no direct procedure for deriving the full wave function starting from the pseudo-wave-function (unlike the older, less accurate, empirical pseudopotentials, where orthogonalization to the core states sufficed).[26]

Such a procedure to reconstruct the all-electron (AE) wave function from the pseudo- (PS) wave-functions can be derived from a general framework developed by one of us.[27] This approach unifies and generalizes the concepts of the pseudopotential approach and the augmented-wave methods such as LAPW, LMTO, etc. We will give here a brief description of the underlying ideas to the extent that they will be needed for our purposes. Before we get into the mathematical expressions, let us describe the ideas in words.

The wave function obtained from a pseudopotential calculation is one ingredient to the correct AE wave function. The PS wave function coincides with the AE wave function outside the core region, but deviates near the nucleus. The shape of the wave function close to the nucleus is essentially atomlike, because the strong attractive potential of the atomic core dominates over the effect of the neighboring atoms. The potential in the core region is not affected much by the crystalline environment (up to a constant shift); by integrating outward, one obtains basically the same partial waves as in the atomic case. We may therefore assume that atomic partial waves are good solutions to the Schrödinger equation inside the core region. What actually changes when the atom is placed in the solid are the boundary conditions at the border of the core region. Indeed, the atomlike partial waves inside the core radius have to match onto the solid wave functions outside. Hence the weights of the partial waves in the expansion of the wave function in the core region change as one goes from the atom to the solid. In our approach these weights are determined in the solid from the overlap of the PS wave function with properly constructed projector functions that are localized in the core region. Knowledge of these weights allows us to reconstruct the AE wave function inside the core radius. The complete AE wave function is then obtained by taking the PS wave function in the solid, subtracting the contributions from the PS partial waves inside the core, and replacing them with the corresponding AE partial waves with the proper weights. This approach establishes a well-defined relationship between any PS wave function and the AE wave function. From the latter the hyperfine parameters can be extracted in a straightforward way.

This approach is particularly intuitive in the case of the isotropic hyperfine parameter (contact interaction), which is determined by the value of the spin density at the nucleus. Only the s component of the wave function has nonzero amplitude there, and therefore the contact interaction depends solely on the value of the s-like partial wave and its coefficient. Since the partial waves in the core region are atomlike, with a shape largely independent of the chemical environment, this coefficient is fixed by the requirement that the s-like partial wave in the core region must match onto its counterpart outside the core region (where the PS and AE wave functions coincide). This matching procedure, and the resulting coefficient, is therefore the same for PS wave functions and AE wave functions; the only difference lies in the shape (and value at the nucleus) of the PS versus the AE partial waves. If $\phi_s(0)$ is the value of the s-like AE partial wave at the nucleus, and $\tilde{\phi}_s(0)$ its PS counterpart, we thus expect that the true (AE) contact interaction will be related to the PS value by the factor $|\phi_s(0)|^2/|\tilde{\phi}_s(0)|^2$. This simple argument will be confirmed by the derivation presented below.

The one-to-one correspondence between the AE and PS wave functions described above allows one to express also more general quantities as a functional of the PS wave function instead of the AE wave function. The quantities that we want to calculate to extract the hyperfine parameters can be formulated as matrix elements, which in principle should contain the true AE wave function. The formalism will allow us to translate the expressions into what we call the PS representation.

1. General expressions for wave functions and matrix elements

In the spirit of the previous paragraph, we express the AE wave function $|\psi\rangle$ in the solid as a superposition of a PS wave function $|\tilde{\psi}\rangle$ and partial waves $|\phi\rangle$ of the AE potential as well as their PS counterparts $|\tilde{\phi}\rangle$:

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle o_i|\tilde{\psi}\rangle \ . \qquad (10)$$

The index i is a shorthand referring to a site and a particular angular momentum component; it may contain an additional label if more than one partial wave per site and angular momentum is used. Quantities relating to the PS wave functions are indicated by a tilde. The coefficients $\langle o_i|\tilde{\psi}\rangle$ are discussed below.

The PS wave function $|\tilde{\psi}\rangle$ in Eq. (10) can be obtained in a pseudopotential calculation for the solid containing a defect. The AE partial waves $|\phi_i\rangle$ are solutions of the radial Schrödinger equation for the spherically symmetric atomic potential, corresponding to the various atomic eigenstates. The PS partial waves $|\tilde{\phi}_i\rangle$ are smooth functions which are obtained similarly as solutions for the pseudoatom. Beyond a core radius r_c (which may be different for different angular momentum components), they become identical to the AE partial waves.

The coefficients $\langle o_i|\tilde{\psi}\rangle$ are determined from an overlap integral with a function $o(r)$ that "projects" the PS wave function onto individual PS partial waves. The projection takes place in the region close to the center of the atom, where the wave function is most free-atom-like (and least influenced by the environment). The definition of the functions $|o_i\rangle$ therefore involves a cutoff function f:

$$|o_i\rangle = \sum_j f|\tilde{\phi}_j\rangle \alpha_{ji} \ . \qquad (11)$$

The expansion coefficients α_{ij} are determined by the condition

$$\langle o_i|\tilde{\phi}_j\rangle = \sum_k \alpha_{ik}\langle \tilde{\phi}_k|f|\tilde{\phi}_j\rangle = \delta_{ij} \ , \qquad (12)$$

i.e., the coefficients α_{ij} correspond to the inverse of the matrix formed by $\langle \tilde{\phi}_i|f|\tilde{\phi}_j\rangle$. This choice ensures that for any wave function that can be expressed as a superposition of the PS partial waves $|\tilde{\phi}_i\rangle$, $\langle o_i|\tilde{\psi}\rangle$ recovers the expansion coefficients, so that

$$|\tilde{\psi}\rangle = \sum_i |\tilde{\phi}_i\rangle\langle o_i|\tilde{\psi}\rangle \quad \text{for } r < r_c \ . \qquad (13)$$

We can then express the matrix elements of a one-particle operator A as

$$\begin{aligned}\langle \psi_n|\mathrm{A}|\psi_m\rangle = {} & \langle \tilde{\psi}_n|\mathrm{A}|\tilde{\psi}_m\rangle \\ & + \sum_{ij}\langle \tilde{\psi}_n|o_i\rangle(\langle \phi_i|\mathrm{A}|\phi_j\rangle \\ & \qquad - \langle \tilde{\phi}_i|\mathrm{A}|\tilde{\phi}_j\rangle)\langle o_j|\tilde{\psi}_m\rangle \\ & + \Delta\mathrm{A}_{nm} \ . \end{aligned} \qquad (14)$$

It can be proved that the remainder $\Delta\mathrm{A}_{nm}$ vanishes exactly if Eq. (13) is satisfied.[27] If Eq. (13) does not hold strictly (e.g., because rather than a complete set only a finite number of partial waves are included), it can still be shown that $\Delta\mathrm{A}_{nm}$ is very small and can be neglected.[27]

Before we proceed and extract the hyperfine parameters along these lines, let us simplify the formalism. First, we make a definite choice for the cutoff function f: It shall vanish everywhere but within the core region of the atom, where it is unity. Second, we redefine our partial waves such that they vanish outside the core region, and they are properly normalized. With these definitions we can write $|o_i\rangle = |\tilde{\phi}_i\rangle$. Third, we restrict the number of partial waves to one per angular momentum and site.

2. *Derivation of an expression for the anisotropic hyperfine parameter*

We now apply this formalism to the calculation of the anisotropic hyperfine parameter. From Eq. (7) we see that the relevant operator is $(3\cos^2\tau - 1)/2r^3$, which we write as $Y_d(\mathbf{r})/r^3$, where Y_d is (to within a constant factor $\sqrt{5/4\pi}$) the spherical harmonic for $l=2$. We find, based on Eq. (14),

$$\left\langle \psi \left| \frac{Y_d(\mathbf{r})}{r^3} \right| \psi \right\rangle = \left\langle \tilde{\psi} \left| \frac{Y_d(\mathbf{r})}{r^3} \right| \tilde{\psi} \right\rangle + \sum_{ij} \langle \tilde{\psi} | \tilde{\phi}_i \rangle \left[\left\langle \phi_i \left| \frac{Y_d(\mathbf{r})}{r^3} \right| \phi_j \right\rangle - \left\langle \tilde{\phi}_i \left| \frac{Y_d(\mathbf{r})}{r^3} \right| \tilde{\phi}_j \right\rangle \right] \langle \tilde{\phi}_j | \tilde{\psi} \rangle \ . \tag{15}$$

The hyperfine parameters, of course, relate to the *spin density,* which is the difference between spin-up and spin-down densities. Since all formulas are linear in the charge density, the subtraction of spin components can be performed at any point in the calculation.

As discussed in Sec. II A, a situation of common interest is the one in which the d components of the wave function are negligible. Hence, we consider only s- and p-like contributions to the wave function. (Of course, this approximation is not applicable to transition metals, where the spin density is dominated by the d orbitals.) Under this assumption, the expression Eq. (15) simplifies considerably, because then only the p-type partial waves have nonzero matrix elements with the d-type operator for the anisotropic hyperfine constants:

$$\left\langle \psi \left| \frac{Y_d(\mathbf{r})}{r^3} \right| \psi \right\rangle = \left\langle \tilde{\psi} \left| \frac{Y_d(\mathbf{r})}{r^3} \right| \tilde{\psi} \right\rangle + \left[\frac{4\pi}{5} \right]^{1/2} \int_0^{r_c} r^2 dr \frac{1}{r^3} ([\phi_p(r)]^2 - [\tilde{\phi}_p(r)]^2) \sum_{p_i,p_j} \langle \tilde{\psi} | \tilde{\phi}_{p_i} \rangle C_{p_i,p_j,d_z} \langle \tilde{\phi}_{p_j} | \tilde{\psi} \rangle \ . \tag{16}$$

Here, C_{p_i,p_j,d_z} stands for the integral of the product of three spherical harmonics (the two p-type angular momenta of the partial waves and the d_z angular momentum component of the operator). The C_{p_i,p_j,d_z} coefficients can be expressed in terms of $3j$ symbols or Clebsch-Gordan coefficients; they need not be explicitly evaluated for our purposes, as we shall see. The notation $\phi(r)$ is used to describe the radial part of the partial wave, so that $\phi(\mathbf{r}) = \phi(r) Y_p(\mathbf{r})$.

In order to extract the expansion coefficients directly from the charge density, we make use of Eq. (13), which is valid (at least approximately) in the central region of the atom; to isolate this region, we again introduce the cutoff function $f(r)$. We find

$$\begin{aligned} \left\langle \tilde{\psi} \left| f(r) \frac{Y_d(\mathbf{r})}{r^3} \right| \tilde{\psi} \right\rangle &= \sum_{p_i,p_j} \langle \tilde{\psi} | \tilde{\phi}_{p_i} \rangle \left\langle \tilde{\phi}_{p_i} \left| f(r) \frac{Y_d(\mathbf{r})}{r^3} \right| \tilde{\phi}_{p_j} \right\rangle \langle \tilde{\phi}_{p_j} | \tilde{\psi} \rangle \\ &= \left[\frac{4\pi}{5} \right]^{1/2} \int r^2 dr \frac{f(r)}{r^3} [\tilde{\phi}_p(r)]^2 \sum_{p_i,p_j} \langle \tilde{\psi} | \tilde{\phi}_{p_i} \rangle C_{p_i,p_j,d_z} \langle \tilde{\phi}_{p_j} | \tilde{\psi} \rangle \ . \end{aligned} \tag{17}$$

Use of Eq. (17) allows us to eliminate the explicit dependence on the coefficients $\langle \tilde{\phi} | \tilde{\psi} \rangle$ in Eq. (16). Finally, we take Eq. (16), perform a summation over all states, and subtract spin components. The functions $|\tilde{\psi}\rangle$ correspond to one-electron eigenstates in the solid containing the defect; summing over all occupied eigenstates yields the charge density (for one spin component). After summing, the matrix elements can be written as integrations over charge densities; this eliminates the need to know individual wave functions. By subtracting spin-up and spin-down components, we obtain expressions as a function of spin densities:

$$\int d^3 r \, \rho_{\text{spin}}(\mathbf{r}) \frac{Y_d(\mathbf{r})}{r^3} = \int d^3 r \, \tilde{\rho}_{\text{spin}}(\mathbf{r}) \frac{Y_d(\mathbf{r})}{r^3} + \frac{\int d^3 r \, \tilde{\rho}_{\text{spin}}(\mathbf{r}) f(r) \frac{Y_d(\mathbf{r})}{r^3}}{\int r^2 dr \frac{f(r)}{r^3} [\tilde{\phi}_p(r)]^2} \left[\int_0^\infty r^2 dr \frac{1}{r^3} [\phi_p(r)]^2 - \int_0^\infty r^2 dr \frac{1}{r^3} [\tilde{\phi}_p(r)]^2 \right] . \tag{18}$$

This is the final expression that will be inserted into Eq. (7) to obtain the hyperfine parameters. $\tilde{\rho}_{\text{spin}}(\mathbf{r})$ is the spin density obtained from the pseudopotential calculation. Note that we have extended the two radial integrations to infinity using the fact that ϕ_p and $\tilde{\phi}_p$ coincide beyond the core region.[28]

We now translate this expression into physically more transparent terms. First we introduce, as is commonly done, the expectation values of $1/r^3$ with the atomic wave functions

$$\langle r^{-3}\rangle^{\mathrm{AE}}=\int_0^\infty r^2 dr \frac{1}{r^3}[\phi_p(r)]^2 , \tag{19}$$

and similarly for the pseudo-wave-function,

$$\langle r^{-3}\rangle^{\mathrm{PS}}=\int_0^\infty r^2 dr \frac{1}{r^3}[\tilde{\phi}_p(r)]^2 . \tag{20}$$

It is a common practice to express the measured anisotropic hyperfine parameter with respect to an atomic reference (see Refs. 17 and 29). Calling this reference A_p^{free}, we find, based upon Eqs. (7) and (19),

$$A_p^{\mathrm{free}}=\frac{2}{5}\frac{\mu_0}{4\pi}g_e\mu^e g_I\mu^I\langle r^{-3}\rangle^{\mathrm{AE}} , \tag{21}$$

or, with the units established in Eqs. (9),

$$A_p^{\mathrm{free}}=12.531\gamma^I\tfrac{2}{5}\langle r^{-3}\rangle^{\mathrm{AE}} . \tag{22}$$

The ratio of the hyperfine parameter b to A_p^{free} is denoted by η_p^2.

If we consider now, and this is confirmed by our calculations, that the dominant contribution to the hyperfine parameter comes from the region close to the nucleus, then the term in Eq. (18) that is proportional to

$$\int r^2 dr\, \phi_p^2/r^3=\langle r^{-3}\rangle^{\mathrm{AE}}$$

should give us a good first approximation to the final result. If we define

$$\kappa=\frac{\int d^3r\, \tilde{\rho}_{\mathrm{spin}}(\mathbf{r})f(r)\frac{Y_d(\mathbf{r})}{r^3}}{\frac{2}{5}\int r^2 dr\frac{f(r)}{r^3}[\tilde{\phi}_p(r)]^2} , \tag{23}$$

then κ is a first approximation to η_p^2, as can be seen by comparison with Eqs. (7), (18), and (19):

$$\eta_p^2=\frac{b}{A_p^{\mathrm{free}}}\approx\kappa . \tag{24}$$

With these notations, the full expression in Eq. (18) can be written as

$$\int d^3r\, \rho_{\mathrm{spin}}(\mathbf{r})\frac{Y_d(\mathbf{r})}{r^3}=\int d^3r\, \tilde{\rho}_{\mathrm{spin}}(\mathbf{r})\frac{Y_d(\mathbf{r})}{r^3} +\kappa\tfrac{2}{5}[\langle r^{-3}\rangle^{\mathrm{AE}}-\langle r^{-3}\rangle^{\mathrm{PS}}] . \tag{25}$$

We remind the reader that Y_d is defined as $Y_d=(3\cos^2\tau-1)/2$, i.e., Y_d is the spherical harmonic for $l=2$ (to within a constant factor $\sqrt{5/4\pi}$).

For practical purposes we once again choose a cutoff function defined by $f(r)=1$ for $r<r_c$ (where r_c is the core radius for the $l=1$ pseudopotential) and $f(r)=0$ for $r>r_c$. In order to test the sensitivity of the results to the choice of the cutoff function, we have investigated a different choice, namely, $f(r)=r^3$ for $r<r_c$, $f(r)=0$ for $r>r_c$. In this case the expectation value of the operator [the numerator of Eq. (23)] equals the contribution from the core region to the d component of the spin density, while the denominator represents the core charge associated with the atomic p wave function. In the test cases to be discussed in Sec. II, we have found that this alternative choice of the cutoff function yields values for κ which agree with the results using a step function to within 10%. The fact that the results are not sensitive to the particular choice of the cutoff function confirms the soundness of the approach.

3. Derivation of an expression for the isotropic hyperfine parameter

Now we apply the same formalism to the calculation of the isotropic hyperfine parameter, where the operator A in Eq. (14) is given by $\delta(\mathbf{r})$. This leads to

$$\begin{aligned}\langle\psi|\delta(\mathbf{r})|\psi\rangle&=\langle\tilde{\psi}|\delta(\mathbf{r})|\tilde{\psi}\rangle\\&\quad+\sum_{ij}\langle\tilde{\psi}|\tilde{\phi}_i\rangle(\langle\phi_i|\delta(\mathbf{r})|\phi_j\rangle\\&\qquad-\langle\tilde{\phi}_i|\delta(\mathbf{r})|\tilde{\phi}_j\rangle)\langle\tilde{\phi}_j|\tilde{\psi}\rangle .\end{aligned} \tag{26}$$

In the following we will make use of the fact that only s-like wave functions have nonzero amplitude at the nuclear site. Therefore, the sum over partial waves is once again, as in the case of the anisotropic hyperfine parameters, strongly restricted and only s-type partial waves contribute.

We form the equivalent of Eq. (17):

$$\langle\tilde{\psi}|\delta(\mathbf{r})|\tilde{\psi}\rangle=\langle\tilde{\psi}|\tilde{\phi}_s\rangle\langle\tilde{\phi}_s|\delta(\mathbf{r})|\tilde{\phi}_s\rangle\langle\tilde{\phi}_s|\tilde{\psi}\rangle , \tag{27}$$

from which we extract the expansion coefficients needed for the augmentation.

It is then a trivial exercise to verify that we obtain the following equation [analogous to Eq. (18)]:

$$\begin{aligned}\rho_{\mathrm{spin}}(0)&=\tilde{\rho}_{\mathrm{spin}}(0)+\frac{\tilde{\rho}_{\mathrm{spin}}(0)}{|\tilde{\phi}_s(0)|^2}[|\phi_s(0)|^2-|\tilde{\phi}_s(0)|^2]\\&=\tilde{\rho}_{\mathrm{spin}}(0)\frac{|\phi_s(0)|^2}{|\tilde{\phi}_s(0)|^2} .\end{aligned} \tag{28}$$

This corresponds exactly to our intuitive picture of "scaling up the spin density" by the ratio of AE to PS atomic values.

Once again, it is a common practice to express the measured value of the isotropic hyperfine parameter a with respect to an atomic reference.[17,29] We find, based upon Eqs. (6) and (28),

$$A_s^{\mathrm{free}}=\frac{2\mu_0}{3}g_e\mu^e g_I\mu^I|\phi_s(0)|^2 , \tag{29}$$

where $|\phi_s(0)|^2$ is the charge density at the nucleus obtained from an (AE) atomic calculation. The ratio of the hyperfine parameter a to A_s^{free} is denoted η_s^2.

4. Practical details

Here we give some details about the practical procedure for evaluating Eqs. (23), (25), and (28). For the defect in the solid (i.e., in the supercell calculations), the nu-

TABLE I. Theoretical values of A_s^{free} and A_p^{free}, in MHz, for various atoms. Apart from our own present spin-density-functional results, we also list values obtained from Ref. 17 [Morton and Preston (MP)] and from Ref. 29 [Koh and Miller (KM); the value for the neutral atom is given here]. For easy reference, we also list the value of the nuclear gyromagnetic ratio γ (expressed in MHz/T) (from Ref. 16).

		A_s^{free}			A_p^{free}		
Nucleus	γ (MHz/T)	Present	MP	KM	Present	MP	KM
Muonium	133.81	4246					
^{1}H	42.58	1351					
^{29}Si	-8.46	-4191	-4594	-3380	-106	-114	-86
^{67}Zn	2.66	1830	2087	1270			
^{69}Ga	10.22	9832	12 210	7430	195	204	148
^{75}As	7.29	11 787	14 660	9531	302	334	254
^{77}Se	8.12	16 225	20 120	13 420	444	492	378

merical integrations are performed on a grid in a spherical coordinate system. The only integrations which need to be performed over "all space" are those which contain a factor $1/r^3$; the integrand then falls off sufficiently fast to obtain converged values if we integrate out to a certain finite sphere radius R_{cut}. Tests have shown that convergence is reached for cutoff spheres which fit comfortably inside our 16- or 32-atom supercells; values for R_{cut} on the order of the interatomic distance (bond length) in the semiconductor suffice. Regarding grid spacings, we found that the following choices are sufficient to achieve an accuracy of better than 1%: 40 intervals for the azimuth ($\in[0,2\pi]$), 20 for the polar coordinate ($\in[0,\pi]$), and a grid spacing of 0.1 a.u. for the radial coordinate. Another possible route (not explored here) would be to transform the integration into a sum in Fourier space after calculating the Fourier components of the operator either analytically or on a radial grid.

Another practical issue has to do with basis-set convergence in the first-principles calculations. Ideally, one would like to work with a sufficiently large basis set so that all quantities are fully converged. In practice, this ideal cannot always be achieved, due to limitations in computing facilities. One therefore often tries to formulate problems in such a way that "absolute convergence" is not required in order to obtain reliable numbers. For example, in calculating structural energies as a function of atomic positions, one is really interested in energy *differences*, which usually converge much faster as a function of basis-set size than do absolute energies.[23] Inspection of Eqs. (23), (25), and (28) shows that the calculation of hyperfine parameters may offer a similar possibility to enhance accuracy without requiring absolute convergence. Suppose our spin densities in the defect supercell are calculated with a given basis set. We see that our formulas contain a quantity in the denominator which in principle would be obtained from an atomic calculation on the pseudoatom. Instead of performing the usual atomic calculation, we can alternatively perform a supercell calculation for a large vacuum supercell with one atom at the center, with exactly the same basis set as used for the defect calculation. One can then hope that any inaccuracies due to insufficient convergence will tend to cancel in the ratio. This procedure has proven to lead to dramatic improvement in convergence. For most of the examples discussed below, absolute convergence was within reach, except for the isotropic hyperfine parameters on hydrogen or Zn atoms, where we have taken explicit advantage of faster convergence in the ratio.

The results we will present below have been obtained by direct application of Eqs. (25) and (28), as outlined above. Equations (8) and (9) are then used to obtain the hyperfine parameters a and b. We also report the ratios η_s^2 and η_p^2. The required values of γ were taken from the CRC tables[16] and are given in Table I.

III. APPLICATIONS

A. Free-atom values

We start by giving some results for free atoms. Such an investigation is relevant, since in a sense the atomic values are used to "scale up" the pseudopotential results [see Eqs. (25) and (28)]. Table I contains results for all atoms that we will discuss in the examples below. These results were obtained from spin-polarized density-functional calculations on the free atom, using the Ceperley-Alder exchange and correlation potential.[18] For comparison, we also list theoretical values from two references. The results of Morton and Preston[17] were obtained based upon Hartree-Fock-Slater calculations by Herman and Skillman.[30] Morton and Preston also apply a relativistic correction factor. The values of Koh and Miller[29] are based upon self-consistent-field Hartree-Fock wave functions obtained by Clementi and Roetti.[31]

We note that, in the cases investigated here, A_s^{free} and A_p^{free} agree reasonably well with the values published in Ref. 17, with larger deviations for the heavier atoms. The values of Koh and Miller deviate significantly, both from the Morton and Preston results and from the present calculations. Even after applying a relativistic correction factor,[17] the Koh and Miller values for A_s^{free} are still much lower than those of Morton and Preston (MP). Koh and Miller give results as a function of the ionization state of the atom. We noticed that in many cases the result for the $+1$ ionized state was much closer to the MP result, and to our result, than that for the neutral atom. An investigation of the cause and nature of this behavior is outside the scope of this work. We only point out these features to indicate that caution should be exercised whenever experimental results are expressed as a ratio to theoretical atomic values, since such ratios could vary significantly depending on what reference is used. We stress that the values from Morton and Preston and Koh and Miller listed in Table I are only given for illustrative purposes, and are not used in our calculations in any way. Our approach here is to use consistently quantities obtained within the framework of pseudopotential-spin-density-functional theory.

The values for hydrogen and muonium can be obtained from an analytical expression for the spin density; they are 4463 MHz for muonium and 1420 MHz for hydrogen. We note that our density-functional value is slightly too small; a similar deviation was found from the comparison with the Morton and Preston values for other atoms. This might indicate a general tendency for the density-functional AE results to underestimate the values of the hyperfine parameters; indeed, we will see below that our calculated values for defects, although always close to experiment, tend to be on the low side. It is for this reason that we also report the results for the ratios η_s^2 and η_p^2, which could potentially be combined with more accurate AE atomic values to yield the values of a and b.

B. Hydrogen- or muonium-related defects

The behavior of hydrogen in semiconductors has been the focus of intense experimental and theoretical interest in recent years. The observation that hydrogen can passivate shallow impurities[7] highlighted the technological relevance of the subject; it also emphasized the need for a more profound understanding of hydrogen as an impurity in a semiconductor lattice. Theory was able to enhance significantly insight into the interactions between hydrogen (H) and the semiconductor host atoms, and with other impurities.[23] In the case of isolated interstitial hydrogen, an unambiguous identification of the proposed structures with the experimentally observed defects was lacking for a long time. Most of the experimental information about these defect configurations was obtained from muon spin rotation (μSR). Indeed, it has proven very difficult to obtain EPR results for an isolated hydrogen atom, and only one experimental group has reported positive results so far.[32] The most serious problem in this respect is the very high mobility of interstitial hydrogen, combined with its tendency to form complexes with other defects and impurities. This problem is much reduced for muonium, a pseudoisotope of hydrogen: the short lifetime of the muon (2.2 μs) ensures that μSR experiments observe single, isolated particles, because the particle decays before it is able to find suitable partners to form complexes. Muonium consists of an electron bound to a positive muon (μ^+). The mass of μ^+ is $\frac{1}{9}$ of that of the proton; therefore, the dynamical behavior of muonium may 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 Refs. 8 and 9. 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. 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 ⟨111⟩ symmetric hyperfine interaction (C_{3v} symmetry).[33,34]

1. Hydrogen or muonium in Si

Using pseudopotential-density-functional theory, we previously mapped out the complete total-energy surfaces for various charge states of hydrogen (or muonium) in Si.[23] Only the neutral charge state is relevant here, since we are looking for paramagnetic centers. Neutral H is most stable in the bond-center (BC) position. Large relaxations of the neighboring Si atoms (over 0.45 Å for the nearest neighbors) are required to accommodate the H atom. Neutral H may also occur at the tetrahedral interstitial (T_d) site, which is only slightly higher in energy than the BC site. A description of the atomic and electronic structure, as well as contour plots of the charge and spin densities, were given in Refs. 35 and 36.

Our calculated isotropic and anisotropic hyperfine parameters for muonium at the tetrahedral interstitial and at the bond-center site are reported in Tables II and III. They were obtained in a 32-atom supercell, at an energy cutoff of 12 Ry.[13,37] Convergence tests were reported in Ref. 10. We have carried out convergence tests as a function of supercell size by performing calculations in supercells containing 8, 16, and 32 Si atoms. Fast convergence as a function of supercell size may be expected for several reasons: (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 (note the r^{-3} dependence for the anisotropic parameter), and are therefore insensitive to the wave function far from the defect; and (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 (see, e.g., the plots in Ref. 23). In the present case, we found that the hyperfine parameters

TABLE II. Theoretical and experimental (Ref. 9) values of the isotropic hyperfine parameters for muonium at the tetrahedral interstitial site in Si. Values are given for the muon at the center of the defect, as well as for the first and second ^{29}Si neighbors. The experimental values for the Si neighbors have not been determined, but a value of −60 MHZ was estimated in Ref. 9.

	η_s^2	a (MHz)	
	Theoretical	Theoretical	Experimental
Muon	0.515	2187	2006
$\mathrm{Si}_{1\mathrm{NN}}$	0.012	−50	
$\mathrm{Si}_{2\mathrm{NN}}$	0.011	−46	

TABLE III. Theoretical and experimental (Ref. 33) values of the isotropic (a) and anisotropic (b) hyperfine parameters for muonium at the bond-center site in Si. Values are given for the muon at the center of the defect, as well as for the first and second ^{29}Si neighbors.

	η_s^2	a (MHz)		η_p^2	b (MHz)	
	Theoretical	Theoretical	Experimental	Theoretical	Theoretical	Experimental
Muon	-0.008	-35	-67.3		22.3	25.3
$\mathrm{Si}_{1\mathrm{NN}}$	0.020	-85	-95.1	0.202	-21.5	-21.2
$\mathrm{Si}_{2\mathrm{NN}}$	0.005	-23	-22.4	0.006	-0.6	-0.9

changed by less than 5% between the 16- and 32-atom calculations.

Our calculations indicate that contributions from spin polarization of valence states have significant effects, sometimes changing the hyperfine parameter by a factor of 2 compared to the contribution from the defect state alone.[10]

Because hydrogen and muonium are isoelectronic, the results obtained for muonium are, after appropriate scaling by the ratio of proton to muon magnetic moment, equally valid for hydrogen. A table comparing the experimental results for anomalous muonium and the so-called AA9 defect associated with hydrogen in Si can be found in Ref. 34. The EPR values for the AA9 center are very similar to the ones obtained for anomalous muonium, indicating the defects have the same structure. The experimental results from μSR are included for comparison in Tables II and III.

Hydrogen and muonium are very light, and can easily move around in the lattice. The measured hyperfine parameters will therefore correspond to some average over sites. We can determine which regions of space contribute by considering displacements in typical normal-mode vibrations. The magnitude of the effect can then be estimated by calculating the hyperfine parameters for a few relevant positions.[38] For the T_d configuration, we find that the maximum spin density (and isotropic hyperfine parameter) occurs when the muon is sitting at the T_d site itself. When the muon is moved by 0.27 Å in either the $\langle 111 \rangle$ or the $\langle 100 \rangle$ direction, the spin density is reduced by $\sim 12\%$. For a muon executing vibrational motions in the neighborhood of the T_d site, we therefore expect the observed hyperfine parameter to be just slightly lower than the value which we calculated at T_d itself. For the BC configuration, we found that when the muon is moved by 0.1 Å along the Si-Si bond direction (as in a stretching-mode displacement), with the (much heavier) Si atoms fixed, $|a|$ decreases by $\sim 11\%$ and b by only 2%. For displacements perpendicular to the Si-Si bond, $|a|$ decreases by 6% for a 0.33-Å displacement, if the Si atoms are kept fixed. If the Si atoms are allowed to relax, to keep the Si-muon distance constant, the same perpendicular displacement of the muon reduces $|a|$ by 12%. Once again, we see that motional averaging would have only a minor effect on the hyperfine parameters.

The results in Table II show that normal muonium can be identified with muonium at the tetrahedral interstitial site. Table III shows that anomalous muonium (as well as the AA9 center) can be identified with hydrogen (muonium) at the bond-center site.

The evidence in favor of identification of anomalous muonium with the bond-center position is therefore quite convincing. The so-called vacancy-associated model,[2] which had been proposed on the basis of hyperfine calculations for clusters, shows distinct disagreement with the experimental results,[33] which clearly establish that there are two equivalent Si neighbors along $\langle 111 \rangle$. The same cluster calculations[2] 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.

2. *Hydrogen or muonium in GaAs*

First-principles total-energy calculations within the pseudopotential-density-functional scheme for hydrogen in GaAs were carried out by Pavesi, Giannozzi, and Reinhart.[39] We have used their calculated atomic coordinates for the bond-center site and for the tetrahedral interstitial site, and performed spin-density-functional calculations of the hyperfine parameters on supercells containing 32 host atoms (i.e., 16 As and 16 Ga atoms) using a plane-wave basis set with an energy cutoff of 12 Ry.

The calculated hyperfine parameters are reported in

TABLE IV. 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. 40).

	η_s^2	a (MHz)
Muon	0.59	2497
$\mathrm{As}_{1\mathrm{NN}}$	0.009	106
$\mathrm{Ga}_{2\mathrm{NN}}$	0.005	46

TABLE V. 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. 40).

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

TABLE VI. Theoretical and experimental (Refs. 34 and 41) 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	Experimental	Theoretical	Theoretical	Experimental
Muon	0.025	106	131.4		33	43.6
$\mathrm{Ga}_{1\mathrm{NN}}$	0.103	1014	929.3	0.287	56	61.4
$\mathrm{As}_{1\mathrm{NN}}$	0.006	74	273.3	0.327	99	144.9

Tables IV, V, and VI. The experimental value measured for normal muonium in GaAs is $a = 2884$ MHZ (Ref. 40); it is close to the theoretical values both for the T_d^{As} and the T_d^{Ga} sites. For the bond center, the agreement with experiment[34,41] 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 the parameter becomes closer to experiment if the As atom is brought closer to the muon (i.e., the As atom 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;[42] the other was generated according to the Hamann-Schlüter-Chiang scheme,[19] but using somewhat larger core radii. The resulting hyperfine parameters agreed to better than 10%, confirming the general validity of the calculational approach.

3. Hydrogen or muonium in ZnSe

We have also investigated the behavior of hydrogen or muonium in the compound semiconductor ZnSe. The bond-center site is energetically unfavorable here; the tetrahedral interstitial sites are lower in energy, with the T_d^{Zn} site just slightly more stable than the T_d^{Se} site. Calculations were carried out in 16- and 32-atom supercells to check convergence. Details of the treatment of ZnSe are given in Sec. III C. The results for the 32-atom cells are listed in Table VII. μSR has produced a single value of $\eta_s^2 = 0.775$.[43] The difference between the calculated values for the T_d^{Se} and T_d^{Zn} sites is presumably small enough, and motion between the sites fast enough, for the two signals not to be resolved. The bond-center position is significantly higher in energy, in agreement with the absence of an anomalous muonium signal in ZnSe.

C. Defects in ZnSe

Native defects in II-VI materials have been studied in great detail using EPR and related techniques.[11] One reason for the continued interest in these defects is the widely held belief that they are responsible for self-compensation in wide band-gap materials. We have recently completed extensive first-principles calculations of native defects in ZnSe, showing that such defects are *not* responsible for the observed doping difficulties.[21]

To obtain accurate results for ZnSe, it is necessary to treat explicitly the Zn 3d electrons as valence electrons (rather than consider them part of the core, to be described with a pseudopotential).[22] Because of the localized nature of these d states, inordinately large numbers of plane waves would be required to obtain convergence with a plane-wave basis set; we therefore chose to use a mixed basis set, which contains localized basis functions in addition to the plane waves.[21,24] We have used a set of pseudoatomic basis functions to describe the Zn d states, along with plane waves with an energy cutoff of 9 Ry. Convergence of the hyperfine parameters was established by performing calculations on 16-atom and 32-atom supercells; the results changed by less than 5%. The results reported below are for 32-atom cells.

Here we concentrate on the properties of the Zn interstitial (Zn_i) in ZnSe. We have studied the Zn interstitial at two sites in the lattice: the tetrahedral interstitial (T_d) site surrounded by Se atoms (labeled T_d^{Se}) and the T_d site surrounded by Zn atoms (T_d^{Zn}). The calculated formation energy is very similar (within 0.1 eV) for these two sites. First-principles mixed basis calculations were carried out for the Zn_i in various charge states. The relevant paramagnetic center corresponds to the positive charge state. For Zn_i^+ at the tetrahedral interstitial site surrounded by Se atoms (T_d^{Se}), we find that the Se nearest neighbors (NN), along with the $\mathrm{Zn}_{4\mathrm{NN}}$ atoms to which they are bonded, move outward over 0.11 Å; the Zn second NN are relaxed outward (along ⟨100⟩ directions) by 0.05 Å.

We checked that our results for hyperfine parameters changed by less than 10% when the plane-wave cutoff was increased from 9 to 12 Ry. The calculated hyperfine

TABLE VII. Theoretical and experimental (Ref. 43) values of the isotropic hyperfine parameters for muonium at the T_d^{Se} and T_d^{Zn} sites in ZnSe.

	η_s^2	a (MHz)	
	Theoretical	Theoretical	Experimental
Muon at T_d^{Zn}	0.785	3333	3457
Muon at T_d^{Se}	0.765	3248	

TABLE VIII. Theoretical and experimental (Ref. 44) values of the isotropic (a) and anisotropic (b) hyperfine parameters for Zn_i^+ at the T_d^{Se} site in ZnSe. Values are given for the interstitial at the center of the defect, as well as for the first (^{77}Se), second (^{67}Zn), and third (^{77}Se) neighbors.

	η_s^2	a (MHz)		η_p^2	b (MHz)	
	Theoretical	Theoretical	Experimental	Theoretical	Theoretical	Experimental
$\mathrm{Zn}_{\mathrm{central}}$	0.588	1078	1089			
$\mathrm{Se}_{1\mathrm{NN}}$	0.045	736	481	0.024	11	16.8
$\mathrm{Zn}_{2\mathrm{NN}}$	0.005	10				
$\mathrm{Se}_{3\mathrm{NN}}$	0.003	55	37.5			

parameters for the Zn_i^+ are listed in Table VIII (Ref. 13), and compared with experimental values by Rong and Watkins.[44] We thus confirm the characterization of the observed defect as a Zn interstitial, and provide an accurate description of its structure. While the isotropic hyperfine parameters are not very sensitive to the details of the relaxation, the anisotropic parameter does vary significantly with atomic displacement. Indeed, the anisotropic parameter for the Se first nearest neighbors increases by almost a factor of 2 in going from the unrelaxed to the relaxed configuration.

We have also calculated the hyperfine parameters for the Zn_i^+ at the T_d^{Zn} site, where the relaxations are as follows: the Zn NN, along with the $\mathrm{Se}_{4\mathrm{NN}}$ atoms to which they are bonded, move outward over 0.09 Å; the Se second NN are relaxed outward (along $\langle 100 \rangle$ directions) by 0.03 Å. The results are listed in Table IX. Rong and Watkins[44] also observed a signal which they tentatively identified as a Zn interstitial at the T_d^{Zn} site, but the hyperfine parameters were not reported.

D. Isomer shifts

The hyperfine parameters are closely related to quantities which are of interest in the study of isomer shifts. For example, the resonant isomer-shift velocity, Δ_{IS} can be measured in a Mössbauer experiment:

$$\Delta_{\mathrm{IS}} = \alpha[\rho_a(0) - \rho_s(0)] \ , \tag{30}$$

where $\rho_a(0)$ and $\rho_s(0)$ are the electronic densities at the nuclear site (the contact density) in two different solid environments (the "absorber" and "source" materials) and α is the nuclear calibration constant. The latter is obtained by comparing experimental isomer shifts with calculated electron densities.[45]

Application of our approach to particular impurity problems is beyond the scope of the present study. It should be clear, however, that all the necessary ingredients to study the contact interaction are available, and could be used to great advantage for the analysis of Mössbauer experiments.

TABLE IX. Theoretical values of the isotropic hyperfine parameters for Zn_i^+ at the T_d^{Zn} site in ZnSe. Values are given for the interstitial at the center of the defect, as well as for the first (^{67}Zn), second (^{77}Se), and third (^{67}Zn) neighbors.

	η_s^2	a (MHz)
$\mathrm{Zn}_{\mathrm{central}}$	0.684	1252
$\mathrm{Zn}_{1\mathrm{NN}}$	≈ 0	≈ 0
$\mathrm{Se}_{2\mathrm{NN}}$	0.022	354
$\mathrm{Zn}_{3\mathrm{NN}}$	≈ 0	≈ 0

IV. CONCLUSIONS

We have presented a formalism to calculate hyperfine parameters for defects in semiconductors, within the pseudopotential-spin-density-functional method. This method has already proven its value for calculating structural properties of defects based on first-principles total-energy minimization. The present formalism renders the technique even more powerful, providing the ability to generate numbers which can be directly compared with experiment.

The complication which arises in the pseudopotential framework because of the difference between pseudo- and all-electron wave functions in the core region is addressed here by using an LAPW-inspired approach. This yields explicit formulas for the parameters, expressed in terms of pseudo spin densities and atomic quantities, all consistently calculated within the pseudopotential-spin-density-functional approach. We have applied the approach to a number of different test cases, consistently producing good agreement with experiment. While it is difficult to estimate a theoretical error bar, inspection of the test cases indicates that our results are nearly always within a factor of 2 of the experimental value, and more often deviate by less than 20%. In general, the theoretical values seem to be somewhat too small, which is probably related to the systematically too low values produced in the density-functional calculations for the all-electron atom. This may indicate that relative quantities such as η_s^2 and η_p^2, which are expressed with respect to the atomic values, may be more reliable. This leaves the problem of producing more accurate absolute values for the atomic quantities themselves, a topic which could benefit from further studies.

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