J. Phys. Chem. A **2008,** *112,* 4521–4526

Implementation of a Density Functional Theory-Based Method for the Calculation of the Hyperfine *A*-tensor in Periodic Systems with the Use of Numerical and Slater Type Atomic Orbitals: Application to Paramagnetic Defects

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Received: January 17, 2008; Revised Manuscript Received: February 20, 2008

The *A*-tensor parameterizes the "hyperfine" interaction of an "effective" electronic spin with the magnetic field due to the nuclear spin as monitored in an electron paramagnetic resonance (EPR) experiment. In this account, we describe an implementation for the calculation of the *A*-tensor in systems with translational invariance based on the Kohn−Sham form of density functional theory (KS DFT). The method is implemented in the periodic program BAND, where the Bloch states are expanded in the basis of numerical and Slater-type atomic orbitals (NAOs/STOs). This basis is well-suited for the accurate representation of the electron density near the nuclei, a prerequisite for the calculation of highly accurate hyperfine parameters. Our implementation does not rely on the frozen core approximation tacitly assumed in the pseudopotential schemes. The implementation is validated by performing calculations on the *A*-tensor for small atoms and molecules within the supercell approach as well as for paramagnetic defects in solids. In particular, we consider the *A*-tensor of "normal" and "anomalous" muonium defects in diamond and of the hydrogen cyanide anion radical HCN^- in a KCl host crystal lattice.

I. Introduction

Since its discovery by Zavoisky in 1944,[6] electron paramagnetic resonance (EPR) spectroscopy (for a comprehensive review see, for example, ref 8) has become one of the most powerful experimental techniques that can provide a wealth of information about paramagnetic species. Due to the importance of the EPR spectroscopy, the first-principles calculation of EPR parameters is of great interest.

Paramagnetic interactions in EPR experiments are interpreted in terms of an "effective" EPR Hamiltonian (eq 1),

$$\widehat{H}_{\mathrm{EPR}} = \sum_C \mathbf{I}_C \cdot A_C \cdot \mathbf{S} + \mathbf{S} \cdot D \cdot \mathbf{S} + \frac{1}{2c} B \cdot g \cdot \mathbf{S} \qquad (1)$$

where the A_C-, D-, and g-tensors parametrize the hyperfine (for nucleus C), zero-field, and Zeeman splitting interactions, respectively. The first-principles calculation of some of these parameters (g-tensor) in molecules within the framework of Kohn−Sham DFT[1,2] (KS DFT) was developed by Ziegler and Schreckenbach in the mid-1990s.[9] Several other molecular DFT implementations and extensions for g-[4,10,11] and A-tensors[5,12] followed. A comprehensive review on the calculation of NMR and EPR parameters is available.[51] However, many of the EPR experiments are conducted in the crystalline environment and, therefore, can not be modelled with "molecular" codes. One of the early calculations of the hyperfine parameters in solids based on the periodic boundary conditions is described in a paper by Blügel et al.,[52] which also contains references to some previous work. The accurate first-principles calculation of the hyperfine *A*-tensor in solids using periodic boundary conditions is the main subject of the present account.

The effects of the crystal environment on the EPR spectra of paramagnetic species are known to be important. In a detailed study of muonium (a pseudoisotope of hydrogen) defects in a wide range of semiconductors, Cox and Johnson note[41] that the variation in the hyperfine parameters is huge, spanning almost 5 orders of magnitude. A standard way to model hyperfine interactions in solids is to perform calculations using periodic boundary conditions. For example, if we are dealing with a paramagnetic defect, the defect and its crystalline environment is periodically repeated using "supercells" that should be large enough to avoid interactions between the defects. The calculation of hypefine parameters within the pseudopotential approach has been pioneered by Van de Walle and Blöchl and applied to hydrogen and muonium defects in semiconductors.[13] Their computational approach is based on the all electron frozen core method, the PAW method.[14] The direct calculation of the magnetic hyperfine parameters using the PAW method followed later.[53] The PAW method assumes the frozen core approximation, which can significantly influence the isotropic component of the *A*-tensor.[54–56] Only recently, some hybrid schemes[22–24,47] have been proposed to overcome this difficulty. For example, Declerck el al.[22] use the "mixed" Gaussian augmented-plane-wave (APW) approach for the calculation of hyperfine parameters. The method of Declerck el al. employs plane-waves and all electron basis made up of Gaussian-type orbitals (GTOs) to describe the "host" system and paramagnetic defect, respectively. This method is implemented in the QUICKSTEP program.[20]

In this work, we develop a robust computational framework that allows one to predict EPR hyperfine parameters based on the KS DFT formalism with periodic boundary conditions using a Bloch basis set made up of numerical and Slater type atomic orbitals (AOs) (NAO/STO basis), a basis that is excellent for the accurate representation of the electron density near the nuclei. The advantages of the STOs used by us over GTOs for the calculation of hyperfine interactions are discussed, for example, in ref 42. The hyperfine parameters are implemented within the periodic BAND program[25–27] for the total energy calculations on systems with translational invariance. Because

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10.1021/jp800494m CCC: $40.75

"localizability" is the intrinsic property of the AOs that make up our Bloch basis, it can be computationally advantageous to use a high quality basis set to describe the paramagnetic defect and to treat the rest of the system with a basis of lower quality. Our implementation does not hinge upon the frozen core approximation; however, the frozen core approximation can be used, in principle, to describe the "host" core states without compromising the accuracy of the hyperfine calculation on the "guest". Our implementation includes scalar relativistic effects using the zeroth order regular approximation (ZORA) formalism.[3] The inclusion of spin−orbital coupling is straightforward within our approach and will be addressed in the future.

The paper is organized as follows. The next section summarizes the derivation of the A-tensor within the ZORA formalism. Our BAND implementation is described, including the use of symmetry. The next section presents results from numerical calculations of hyperfine parameters for localized systems, namely, atoms of group IB and the TiF_3 molecule. This is followed by calculations of EPR parameters of paramagnetic defects in solids and the concluding summary. Atomic units are used throughout unless otherwise specified.

II. ZORA and Hyperfine Hamiltonian

To derive the expression for the A-tensor, one needs to establish a one-to-one correspondence between a "microscopic" Hamiltonian (for example, the KS Hamiltonian) and the "effective" hyperfine Hamiltonian;

$$\hat{H}^{\mathrm{hyp}} = \sum_C \mathbf{I}_C \cdot A_C \cdot \mathbf{S} \tag{2}$$

where $\mathbf{S}$ is the "effective" spin of the paramagnetic substance and $\mathbf{I}_C$ is the nuclear spin of the Cth atom. Van Lenthe and coworkers derived such a correspondence[4,5] using a "microscopic" relativistic ZORA KS DFT Hamiltonian.[3] The nonrelativistic case can be obtained from the ZORA derivation by taking the appropriate limit. This section briefly summarizes the theory behind the ZORA approximation and the treatment of magnetic hyperfine interactions within the ZORA approach.

In the ZORA approach to relativistic effects,[3] the expansion in $E/(2c^2 - V)$ is used instead of the Pauli expansion in $(E - V)/2c^2$. As a result, the ZORA Hamiltonian, in contrast[49] to the Pauli Hamiltonian, is regular at the origin even for a Coulombic potential. In the ZORA approach, the kinetic energy operator $-1/2\mathbf{p}^2$ is replaced by the ZORA expression $\hat{T}^{\mathrm{ZORA}}$

$$-\frac{1}{2}\mathbf{p}^2 \Rightarrow \hat{T}^{\mathrm{ZORA}} = \vec{\sigma}\cdot\mathbf{p}\frac{K}{2}\vec{\sigma}\cdot\mathbf{p},\ K = \frac{1}{1 - V_s(\mathbf{r})/2c^2} \tag{3}$$

where $\mathbf{p}$ is the "momentum operator" ($\mathbf{p} = -i\nabla$) in the absence of a magnetic field), c is the speed of light (137.03921) in a.u.), $\vec{\sigma} = \{\sigma_x, \sigma_y, \sigma_z\}$ is a vector made up of the Pauli matrices, and $V_s(\mathbf{r})$ is the self-consistent KS potential. In practice, the requirement of self-consistency for the kinetic energy operator can be dropped, and the potential in the denominator of $\hat{T}^{\mathrm{ZORA}}$ is taken as a sum of atomic potentials which we denote by V. The nonrelativistic limit can be obtained by setting $K \to 1$.

Using a well known identity for Pauli matrices (eq 4),

$$(\vec{\sigma}\cdot\vec{a})(\vec{\sigma}\cdot\vec{b}) = \vec{a}\cdot\vec{b} + i\vec{\sigma}\cdot(\vec{a}\times\vec{b}) \tag{4}$$

$\hat{T}^{\mathrm{ZORA}}$ can be split into the so-called scalar relativistic and spin-orbital terms (eq 5).

$$\hat{T}^{\mathrm{ZORA}} = \hat{T}^{\mathrm{ZORA}}_{\mathrm{SR}} + \hat{T}^{\mathrm{ZORA}}_{\mathrm{SO}} = \mathbf{p}\frac{K}{2}\mathbf{p} + \frac{1}{2}\vec{\sigma}\times(\nabla K\times p) \tag{5}$$

Equation 5 constitutes the ZORA kinetic energy expression in the absence of a magnetic field. The ZORA formalism including the effects of spin-orbital coupling was implemented in BAND as described in ref 43.

The magnetic field is introduced into the Hamiltonian employing the so-called "minimum coupling" ansantz in which the momentum operator is modified as $\mathbf{p} \to \Pi = \mathbf{p} + \vec{A}/c$ (the sign of $\vec{A}/c$ is reversed for positively charged particles), where $\vec{A}$ is a vector potential corresponding to some current density. Then, again, use of eq 4 yields eq 6,

$$\begin{aligned}\hat{T}^{\mathrm{ZORA}} &= \vec{\sigma}\cdot\Pi\frac{K}{2}\vec{\sigma}\cdot\Pi \\ &= \Pi\frac{K}{2}\Pi + \frac{i\vec{\sigma}}{2}\cdot\left(\left(\mathbf{p}+\frac{\vec{A}}{c}\right)K\times\left(\mathbf{p}+\frac{\vec{A}}{c}\right)\right)\end{aligned} \tag{6}$$

After some vector algebra, the total expression for the ZORA kinetic energy operator in the presence of the magnetic field is obtained (eq 7).

$$\begin{aligned}\hat{T}^{\mathrm{ZORA}} = \mathbf{p}\frac{K}{2}\mathbf{p} + \frac{1}{2}\vec{\sigma}\cdot(\nabla K\times\mathbf{p}) + \frac{K}{2c}\vec{A}\mathbf{p} + \mathbf{p}\vec{A}\frac{K}{2c} + \frac{K}{2c^2}\vec{A}^2 + \\ \frac{K}{2c}\vec{\sigma}\cdot\vec{B} + \frac{1}{2c}\vec{\sigma}\cdot(\nabla K\times\vec{A}),\quad \vec{B} = \nabla\times\vec{A}\end{aligned} \tag{7}$$

The first and the second terms in eq 7 are readily identified as the scalar relativistic and spin-orbital ZORA terms in the absence of the magnetic field (eq 5). The third term in eq 7 couples the momentum operator $\mathbf{p} = -i\nabla$ and vector potential $\vec{A}$. We will omit this term from consideration because the electronic angular momentum of the unpaired electron is often quenched. The fourth term is quadratic in the magnetic vector potential and is also omitted from consideration because the hyperfine interaction is linear in the magnetic field. Finally, the last two terms couple electron spin operators with the magnetic field and, therefore, form the microscopic hyperfine Hamiltonian (eq 8).

$$\hat{H}^{\mathrm{hyp}}_{\mathrm{micr}} = \frac{g_e}{2}\frac{1}{2c}(K\vec{\sigma}\cdot\vec{B} + \vec{\sigma}\cdot(\nabla K\times\vec{A})) \tag{8}$$

Note that due to the quantum electrodynamic effects, the $\vec{\sigma}\cdot\vec{B}$ term acquires a factor $g_e/2$, which is close to unity. Following ref 5, this factor is included in the other terms in eq 8 as well. The "microscopic" hyperfine Hamiltonian (eq 8) acts on both the spatial and the spin part of the multiplet wavefunctions and was derived in ref 5. Integrating over the spatial coordinates followed by a comparison of the remainder to the effective hyperfine Hamiltonian (eq 2) allows us to determine the A-tensor.

The magnetic field in eq 8 is due to the magnetic dipole moment of the nuclear spin $\mathbf{I}_C$. The nucleus is modelled by a point dipole with magnetic moment (eq 9),

$$\mu_C = \frac{g_C}{2Mc}\mathbf{I}_C \tag{9}$$

where g_C is the nuclear g-value, and M is the proton mass in units of the electron mass. A more realistic model should take into account the finite size of the nucleus, and some steps in this direction were taken in ref 44. The vector potential corresponding to the magnetic dipole μ_C is

$$\vec{A} = \mu_C \times \frac{\Delta \mathbf{r}_C}{\Delta r_C^3} = -\mu_C \times \nabla \left(\frac{1}{\Delta r_C} \right) \tag{10}$$

where $\Delta\mathbf{r}_c = \mathbf{r} - \mathbf{R}_C$ is a displacement vector from C and $\Delta r_C = |\Delta\mathbf{r}_C|$ is a distance to the Cth nuclei. The magnetic field is given by eq 11.

$$\vec{B} = \nabla \times \vec{A} = -\nabla \times \left[\mu_C \times \nabla \left(\frac{1}{\Delta r_c} \right) \right] \tag{11}$$

Substituting eq 10 and 11 in eq 8, we obtain the microscopic hyperfine Hamiltonian (eq 12).

$$\widehat{H}_{\mathrm{micr}}^{\mathrm{hyp}} = \sum_C \frac{g_e g_C}{8Mc^2} \vec{\sigma} \cdot \left\{ -\mathbf{I}_C \left(\nabla \cdot K \nabla \left(\frac{1}{\Delta r_C} \right) \right) + (\mathbf{I}_C \cdot \nabla) K \nabla \left(\frac{1}{\Delta r_C} \right) \right\} \tag{12}$$

Suppose now that $|\psi_1\rangle$ and $|\psi_2\rangle$ are two degenerate states (Kramer's doublet). Note that in the crystalline environment, the degeneracies of paramagnetic defects are often lifted. The energy splitting can be determined from the degenerate first-order perturbation theory. The A-tensor elements can be obtained using eq 13

$$\begin{pmatrix} \langle \Psi_1 | \widehat{H}_{\mathrm{micr}}^{\mathrm{hyp}} | \Psi_1 \rangle & \langle \Psi_1 | \widehat{H}_{\mathrm{micr}}^{\mathrm{hyp}} | \Psi_2 \rangle \\ \langle \Psi_2 | \widehat{H}_{\mathrm{micr}}^{\mathrm{hyp}} | \Psi_1 \rangle & \langle \Psi_2 | \widehat{H}_{\mathrm{micr}}^{\mathrm{hyp}} | \Psi_2 \rangle \end{pmatrix} = \sum_C \sum_{ij} (\mathbf{I}_C)_i (A_C)_{ij} \begin{pmatrix} \langle \alpha | \sigma_j | \alpha \rangle & \langle \alpha | \sigma_j | \beta \rangle \\ \langle \beta | \sigma_j | \alpha \rangle & \langle \beta | \sigma_j | \beta \rangle \end{pmatrix} \tag{13}$$

by comparing the right hand side of eq 13, which involves the microscopic Hamiltonian (eq 12) acting on spatially- and spin-dependent degenerate states with the left hand side that involves the effective hyperfine Hamiltonian acting on the spin states.

In the case of spin-polarized scalar-relativistic calculations, the A-tensor for nucleus C is[5] given by eq 14,

$$\begin{aligned} (A_C)_{kl} &= \frac{g_e g_C}{4Mc^2} \int m(\mathbf{r}) \left(\delta_{kl} \nabla \cdot \left(K \frac{\Delta \mathbf{r}_C}{\Delta r_C^3} \right) - \nabla_k \left(K \frac{(\Delta \mathbf{r}_C)_l}{\Delta r_C^3} \right) \right) \mathrm{d}\mathbf{r} \\ &= \frac{g_e g_C}{4Mc^2} \int \frac{K}{\Delta r_C^3} ((\Delta \mathbf{r}_C)_l \nabla_k m(\mathbf{r}) - \delta_{kl} \Delta \mathbf{r}_C \cdot \nabla m(\mathbf{r})) \, \mathrm{d}\mathbf{r} \end{aligned} \tag{14}$$

where $m(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$ is the spin density. To obtain the second equation in eq 14, use was made of partial integration in order to avoid differentiation of quantities of the type $K\Delta r_l/(\Delta r)^3$. In using partial integration, it was assumed that spin density vanishes at the surface which encloses the integration region. The latter is the case for the paramagnetic defects embedded in the host and modelled within the supercell approach. The Wigner−Seitz (WS) cell should be "sufficiently large" to avoid cell-to-cell interaction, and the spin density $m(\mathbf{r})$ should vanish on the WS surface. In the nonrelativistic case, $K = 1$ and the A-tensor can also be obtained by eq 15.

$$(A_C)_{kl} = \frac{g_e g_C}{4Mc^2} \int m(\mathbf{r}) \left(\frac{8\pi}{3} \delta(\Delta \mathbf{r}_C) \delta_{kl} + 3 \frac{(\Delta \mathbf{r}_C)_k (\Delta \mathbf{r}_C)_l}{\Delta r_C^5} - \frac{\delta_{kl}}{\Delta r_C^3} \right) \mathrm{d}\mathbf{r} \tag{15}$$

We have implemeted both formulas for the calculation of the hyperfine tensor in BAND:[27] the second equation in eq 14 as well as in eq15. The first term in eq 15 (the "Fermi" contact term or isotropic term) is deduced from the value of spin density at the grid points of the Boerrigter−te Velde−Baerends grid[33] near the nucleus (eq 16).

$$(A_C)_{\mathrm{iso}} = \frac{2\pi g_e g_C}{3Mc^2} m(\mathbf{R}_C), \quad m(\mathbf{R}_C) = \rho_\alpha(\mathbf{R}_C) - \rho_\beta(\mathbf{R}_C) \tag{16}$$

The rest of the terms in eqs 14 and 15 are obtained using numerical integration. It is expected that the results obtained using eq 14 are more accurate as we integrate over the smoother functions of the type $\Delta r_l/\Delta r^3$ as opposed to terms of the type $\Delta r_l \Delta r_k/\Delta r^5$ (eq 15). In eq 14, A_{iso} is determined as an integral quantity that should be more accurate than the "local" expression (eq 16). The disadvantage of eq 14 is that one has to construct (and, in BAND, store) gradients of Bloch basis set functions. The construction of the density gradient from Bloch functions in BAND is described in ref 34.

In practice, the A-tensor for atom C is computed using equation 17,

$$A_{\hat{o}C} = \frac{g_e g_{\hat{o}C}}{4Mc^2} \sum_{\hat{o}} o \tilde{A}_C o^\dagger \tag{17}$$

where the sum is over symmetry operations $\hat{o}\,\mathbf{r} = \{\mathbf{o}; \mathbf{t}_o\}\mathbf{r} = \mathbf{or} + \mathbf{t}_o$, and ôC denotes an atom which is symmetry related to atom C. The symmetry operations always map one sublattice of atoms into another apart from, perhaps, a primitive lattice vector.[40] $\tilde{A}_C$ is evaluated from the symmetry unique wedge of the WS cell – irreducible Wigner-Seitz (IWS) cell using either eq 18 or 19.

$$\tilde{A}_C = \int_{\mathrm{IWS}} \frac{K}{\Delta r_C^3} (\Delta \mathbf{r}_C (\nabla m(\mathbf{r}))^\dagger - \hat{1} (\Delta \mathbf{r}_C)^\dagger \cdot \nabla m(\mathbf{r})) \, \mathrm{d}\mathbf{r} \tag{18}$$

$$\tilde{A}_C = \int_{\mathrm{IWS}} \frac{m(\mathbf{r})}{\Delta r_C^3} \left(3 \frac{(\Delta \mathbf{r}_C)(\Delta \mathbf{r}_C)^\dagger}{\Delta r_C^2} - \hat{1} \right) \mathrm{d}\mathbf{r} \tag{19}$$

In eqs 18 and 19 we used the "matrix" notation, for example, $\mathbf{r}_C$ is a three-component column vector (a displacement from atom C) and $(\nabla m)^\dagger$ is a three-component row vector; $\hat{1}$ is a 3×3 unity matrix. We use eq 18 or 19 to evaluate $\tilde{A}$ for all the atoms and, then, perform symmetization (eq 17).

III. Results

We verified our BAND implementation of EPR hyperfine parameters by comparing our results with experiment, with calculations reported in the literature, and, for "localized systems", with calculations using the "molecular" ADF code.[28–30] Unless otherwise stated, we perform spin unrestricted SCF calculations using the local spin density approximation (LSDA)[35] for the exchange−correlation (xc) energy. The parametrization of the correlation energy follows that of Vosko, Wilk, and Nusair (formula V).[36] We employ mixed NAO/STO basis sets of triple-ζ quality with two sets of polarization functions (TZ2P in BAND's notation) from BAND's database. These basis sets are often modified in the actual calculations to avoid basis set dependence problems and to strike a balance between accuracy and computational effort. The numerical accuracy parameter in BAND's calculations is set to five for atoms and molecules and to four for the calculation on solids. The reciprocal space is sampled using the Γ-point only, for the periodic systems under consideration this sampling is deemed sufficient.

TABLE 1: Absolute Isotropic Values of A-tensor A_{iso} in MHz for IB Group of (Coinage) Metals[a]

	NR		SR		
atom	BAND	ADF	BAND	ADF	EXP
^{63}Cu ($I = 3/2$)	5978	5971	6746	6750	5867
^{107}Ag ($I = 1/2$)	1359	1360	1925	1909	1713
^{197}Au ($I = 3/2$)	1016	1018	3149	3134	3053

[a] BAND: results of BAND, all electron LSDA calculations with triple-zeta basis (LSDA/TZ2P); ADF: LSDA calculations of van Lenthe et al.;[5] NR: nonrelativistic calculations; SR: scalar relativistic ZORA calculations; EXP: experiment (gas phase).[31,32]

TABLE 2: A-tensor (MHz) for ^{47}Ti and ^{19}F in a TiF$_3$ Molecule[a]

		A-tensor ^{47}Ti ($I = 5/2$)				A-tensor ^{19}F ($I = 1/2$)			
		ΔA_{xx}	ΔA_{yy}	ΔA_{zz}	A_{iso}	ΔA_{xx}	ΔA_{yy}	ΔA_{zz}	A_{iso}
BAND	LDA	9.7	9.7	−19.3	−237.4	33.8	6.0	−39.9	10.6
ADF	LDA	9.2	9.2	−18.4	−234.2	33.5	5.6	−39.2	10.5
BAND	GGA	8.4	8.4	−16.8	−223.0	29.0	7.2	−36.1	14.4
ADF	GGA	7.9	7.9	−15.9	−220.5	28.6	6.2	−34.7	12.9
EXP		8.1	8.1	−16.2	−185				

[a] BAND: results of all electron nonrelativistic calculations with BAND using TZ2P NAO/STO basis; ADF: results of all-electron nonrelativistic calculations with molecular ADF code using TZ2P STO basis. LSDA: results of spin unrestricted LSDA calculations using parameterization of correlation energy due to Vosko et al.;[36] GGA: results of spin unrestricted calculations using Becke's GGA correction for exchange[38] and Perdew's GGA correction for correlation;[39] EXP: experiment;[37] $A_{\mathrm{iso}} = 1/3$ Tr A; $\Delta A_{xx} = A_{xx} - A_{\mathrm{iso}}$; $\Delta A_{yy} = A_{yy} - A_{\mathrm{iso}}$; $\Delta A_{zz} = A_{zz} - A_{\mathrm{iso}}$.

Table 1 shows results from our BAND calculation of the isotropic hyperfine parameters of a single Cu, Ag, and Au atom. In our calculations, the atom is placed in a cubic supercell with $a = 20$ Å. Our results are compared to the LSDA calculations of van Lenthe et al.[5] carried out using the molecular ADF program for a single atom[28–30] and gas phase experiments.[31,32]

The agreement between our results and that of van Lenthe et al. is excellent; the largest discrepancy is 15 MHz, and very often the discrepancy is just several MHz. We attribute the small differences between our BAND calculations and that of van Lenthe et al. to a number of small technical differences between the BAND and ADF programs, most notably BAND's usage of NAOs. Examining Table 1, one also notices that the inclusion of scalar relativistic effects in calculation of hyperfine parameters is already important for Ag atom and is absolutely necessary for Au.

The procedure for the calculation of hyperfine parameters was further tested on small molecules, in particular, on TiF$_3$. We used a ZORA GGA optimized geometry from ref 4, a D_{3h} structure with Ti−F bond length of 1.78 Å. Results of our calculations and experimental data[37] are summarized in Table 2. In the case of TiF$_3$, the agreement between BAND calculations, molecular ADF calculations, and the experiment[37] is also good.

Calculations reported in Tables 1 and 2 can be reproduced using any molecular quantum chemistry program that contains capabilities for calculation of EPR parameters. The real applications of our approach is the calculation of hyperfine parameters in solids. We explore two applications of our method: calculation of hyperfine parameters of muonium defects in diamond and calculation of hyperfine parameters of anion radicals in halide crystal lattices.

Hyperfine Parameters of Muonium in Diamond. The properties of hydrogen as a semiconductor impurity is of great importance to the industry producing electrical semiconductor devices. Recently, a growing interest has emerged in hydrogen defects in diamond due to the development of novel materials using improved plasma-assisted chemical vapour deposition techniques.[48] An extensive review on the theory of hydrogen in diamond is available.[46]

Because of the very high mobility and reactivity of hydrogen, it turned out to be difficult to obtain EPR parameters for an isolated hydrogen in semiconductors. However, unambiguous information about the structure of a hydrogen impurity can be obtained from muon spin rotation (μ SR) experiments. Muonium consists of an electron bound to a positive muon, which is lighter than a proton by a factor of nine. For the static calculations in the Born−Oppenheimer approximation, the treatment of hydrogen and muonium is identical as both particles have the same charge. In this work, we calculate hyperfine parameters of hydrogen and, then, scale our results to compare to μ SR experiments. The values of the isotropic hyperfine paramaters in vacuum are 4463 MHz and 1420 MHz for muonium and hydrogen atoms, respectively, corresponding to the spin density of $1/\pi$ at the nucleus.

As in the case of Si,[13] muonium in diamond is observed in, at least, two sites: the tetrahedral interstitial site (TD site, "normal" Mu) and bond centered site (BC site, "anomalous" Mu). These sites are shown on Figure 1of ref 46.

The hyperfine spectra of muonium is isotropic (the A-tensor is proportional to the unit matrix) and "axially" symmetric (the A-tensor is diagonal with two distinct elements, A_+ and $A_\|$, the third element is equal to A_+) at the TD and BC sites, respectively. The BC site is known to be more energetically favorable with energies in the range of 1–2 eV (23–46 kcal/mol) according to ab initio calculations (ref 46, p R561). LDA DFT caculation using a 64 atom supecell[50] puts the BC site 0.95 eV more energetically favorable than the TD site. It was also found that stabilization of the BC site is accompanied by substantial streching of the the C−C bond, with values ranging from 39 to 52% (ref 46, p R562).

With the objective of determining hypefine parameters of a muonium defect in diamond, we first performed constrained LSDA geometry optimizations of hydrogen in TD and BC sites using a 65 atom cubic supercell containing 64 C atoms and one hydrogen atom using the VASP code.[16–19,57] The PAW formalism[14] was employed in these calculations as implemented in VASP.[15] The LDA lattice constant for diamond is $a = 3.54$ Å and agrees well with experimental lattice constant $a = 3.57$ Å. In the case of the TD site, a hydrogen atom and its six nearest carbon atom neighbors were allowed to relax. All other C atoms were kept fixed according to their equilibrium positions. The relaxation of neighboring carbon atoms was found to be negligible in the TD site, giving an early indication that the "atomic" character of muonium (hydrogen) might be well preserved at this site. In the case of the BC site, hydrogen as well as two bonded C atoms and their three nearest C neighbors were allowed to relax. The rest of the C atoms were fixed according to their equilibrium position. In agreement with earlier calculations (ref 46, p R562 and the references therein), our LSDA relaxiation resulted in a streching of the C−C bond by 45% (1.53 Å → 2.22 Å). The BC site was found to be more energetically favourable by 0.89 − 0.79 eVs, for the calculation with dispersion and the Γ-point calculation, respectively.

The optimized geometries were used in the BAND LSDA Γ-point calculations of hyperfine parameters. The TZ2P all electron basis set for the C was modified by excluding the 4F STO polarization function in order to speed up the calculations,

TABLE 3: Hyperfine Constants for Normal (Mu) and Anomalous Muonium (Mu*) in Diamond Computed with BAND[a]

	Mu		Mu*	
	A_{iso}	f	A_{iso}	A_{p}
BAND	3345	0.77	−117.7	217.9
EXP	3711	0.83	−205.7	186.6
LDA-GF			−137.0	200.0

[a] $f = A_{\mathrm{iso}}/A_{\mathrm{vac}}$ ($A_{\mathrm{vac}} = 1389$ MHz is the LSDA isotropic hyperfine parameter of hydrogen in vacuum); $A_{\mathrm{iso}} = {}^1/_3\mathrm{Tr}\ A$; In Mu*, the tensor is axially symmetric: $A_{xx} = A_{yy} = A_{+}$ and $A_{zz} = A_{\|}$. $A_{\mathrm{iso}} = {}^1/_3\mathrm{Tr}\ A$. In this case, anisitropy is defined as $A_{\mathrm{p}} = (A_{\|} - A_{+})/3$. BAND: results of all electron LSDA BAND calculations; LDA-GF: results of self-consistent Green's function−LSDA method;[45] EXP: experiment (from ref 46, Table 3).

TABLE 4: *A*-tensor (MHz) of HCN^- Anion Radical in KCl Crystal Lattice[a]

	ΔA_{xx}	ΔA_{yy}	ΔA_{zz}	A_{iso}
		Carbon		
BAND	45.1	−23.5	−21.6	213.7
ADF	42.4	−21.6	−20.7	301.7
EXP	42.8	−25.6	−17.2	209.4
		Nitrogen		
BAND	82.1	−41.5	−40.6	16.2
ADF	42.3	−21.1	−21.1	5.5
EXP	39.1	−19.5	−19.5	19.5
		Hydrogen		
BAND	−4.7	−8.3	13.1	316.9
ADF	−5.7	−8.3	13.9	332.7
EXP	0.3	−14.2	13.8	382.2

[a] $A_{\mathrm{iso}} = {}^1/_3\mathrm{Tr}\ A$, $\Delta A_{xx} = A_{xx} - A_{\mathrm{iso}}$, $\Delta A_{yy} = A_{yy} - A_{\mathrm{iso}}$, and $\Delta A_{zz} = A_{zz} - A_{\mathrm{iso}}$ are anisotropies; BAND: results of Γ-point LSDA calculation in 66 atom supercell; K and Cl 1s, 2s, and 2p core states are frozen; HCN^- anion radical is described with all-electron basis; ADF: results of LSDA calculation on HCN^- using "molecular" ADF program; EXP: experimental results of Adrian et al.[7]

and the H basis set was modified to exclude one of the 1S STOs to avoid basis set dependency problems. The modified TZ2P basis set was used in the calculation of the hyperfine parameters for the TD and BC sites. Note that the "modified" TZ2P basis reproduces structural and electronic parameters of diamond quite well, with a 3.54 Å equilibrium lattice constant and a band gap of 4.65 eV in good agreement with other LDA calculations.[21] The hyperfine parameters of the muonium defect in TD and BC sites of diamond are summarized in Table 3.

We find a good agreement between our calculation and experimental hyperfine parameters for normal muonium as well as for the anisotropic hyperfine parameter in anomalous Mu. The results for the isotropic hyperfine parameter are worse but agree well with the previously reported LDA−Green's function calculations.[45] The discrepancy between theory and experiment is explained by a higher sensitivity of the isotropic hyperfine parameter to the computational details. The extent to which the isotropic hyperfine parameter varies in different calculations can be fully appreciated from Table 3 of ref 46, some of the isotropic hyperfine parameters reported there are in the −700 to −1000 MHz range. The other sources of discrepancy between theory and experiment is the zero-point motion of the muon itself and the LSDA approximation for the xc energy. Overall, we consider our calculation of hyperfine parameters of muonium defect in diamond to be quite successful.

B. Hyperfine Parameters of HCN^- Anion Radical in a KCl Lattice. We have used a similar procedure to determine, for the first time to our knowledge, the hyperfine parameters of the hydrogen cyanide anion radical HCN^- in a KCl crystal host lattice.

We followed a procedure similar to the one used in for the calculation of the hyperfine parameters of muonium defects in diamond. First, the structure of a HCN^- defect in a KCl crystal lattice was optimized using PAW LSDA calculations with the VASP code. The calculations were performed on a 66 atom cubic supercell in which one of the halogen atoms was replaced by HCN, which results in the formation of a HCN^- anion radical. The LSDA-optimized lattice constant for KCl is 6.09 Å. It was found that the anion radical lies in the crystal's $\{1\bar{1}0\}$ plane, with the C−N bond almost parallel to the (110) crystal axis.

The optimized geometry was used in the BAND LSDA Γ-point calculation of hyperfine parameters of HCN^- in KCl. K and Cl atoms were described with a TZ2P frozen core basis set in which the 1s, 2s, and 2p core states are frozen and represented by NAOs. C, N, and H atoms are described with an all electron TZ2P basis sets in which the 4F polarization functions have been removed. We also remove one of the 1S and 4S STOs from the H and K basis sets, respectively, to avoid linear dependence problems.

Our results for the carbon and hydrogen atoms compare well with the experimental data. In particular, for the C atom, the presence of the crystalline environment decreases the isotropic hyperfine constant, which leads to an excellent agreement with experiment. For the hydrogen atom, the presence of the environment does not seem to influence the hyperfine parameters by much, the isotropic hyperfine parameter is underestimated, but that also seems to be the case in the vacuum. For the N atom, we find that the presence of the environment leads to an increase in the isotropic hyperfine parameter; however, this increase is rather small. We find, within our LSDA calculation, that the inclusion of the environment effects makes the agreement between theory and the experiment slightly worse for the anisotropic components of the hyperfine tensor. The small discrepancy between theory and experiment in the case of N is probably due to the well-known shortcomings of the LDA: underestimation of lattice constant and of the band gap, which might cause a "spurious" interaction between N and neighboring K atoms of the host crystal lattice. Therefore, to better the agreement between experimental and calculated hyperfine parameters, futher improvements in the approximate xc energy functionals are deemed important.

IV. Concluding Remarks. We described the theory and implementation of the hyperfine *A*-tensor in the BAND program for the calculation of systems with translational invariance based on the KS DFT. In BAND, the Bloch states are expanded in the basis of numerical and Slater-type atomic orbitals (NAOs/STOs) which are excellent for the accurate representation of (spin) electron density near the nuclei. It is expected that the present approach minimizes errors due to the choice of basis set functions. Our implementation does not rely on the frozen core approximation tacitly assumed in the pseudopotential schemes.

The implementation is validated by performing calculations of the *A*-tensor for small atoms and molecules within the supercell approach. We find a good agreement between the results of our calculations, experiment, and other calculations.

The real application of our method lies in the computation of the EPR hypefine parameters in solids, especially for paramagnetic defects in "host" crystal lattices.

Within the present approach, we have calculated the *A*-tensor of normal and anomalous muonium defects in diamond. We find a good agreement between our calculations and experimental hyperfine parameters for normal muonium as well as for the anisotropic hyperfine parameter in anomalous muonium. The results for the isotropic hyperfine parameter of the anomalous Mu are worse but agree with some of the previously reported calculations. The discrepancy between theory and experiment is explained by a higher sensitivity of the isotropic hyperfine parameter to the computational details and by the effects of the zero-point motion of the muon.

Calculations of the hyperfine parameters are also presented on the cyanide anion radical HCN^- in the KCl crystal host lattice. Our results for the carbon and hydrogen atoms compare well with the experimental data. We find, within our LDA calculation, that the results for the nitrogen atom are slightly worse. We speculate that the small discrepancies between the theory and experiment in the case of N are due to the well known shortcomings of LDA: underestimation of the lattice constant and the band gap that, in turn, causes a "spurious" interaction between the nitrogen atom and the neighboring atoms of the host crystal lattice.

Acknowledgment. E. K. acknowledges financial support from the Alberta Ingenuity Fund and stimulating discussions with Dr. P. H. T. Philipsen and Dr. E. van Lenthe.

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JP800494M