First-Principles Theory of the EPR g Tensor in Solids: Defects in Quartz

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A theory for the reliable prediction of the EPR g tensor for paramagnetic defects in solids is presented. It is based on density functional theory and on the gauge including projector augmented wave approach to the calculation of all-electron magnetic response. The method is validated by comparison with existing quantum chemical and experimental data for a selection of diatomic radicals. We then perform the first prediction of EPR g tensors in the solid state and find the results to be in excellent agreement with experiment for the E_1' and substitutional phosphorus defect centers in quartz.

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Electron paramagnetic resonance (EPR), also known as electron spin resonance, is the most powerful spectroscopic technique for the study of paramagnetic defects in solids. Indeed, defect centers are often named directly after their EPR spectra. Applications of EPR extend to any situation where there are unpaired electrons, including the understanding of reactions involving free radicals in both biological and chemical contexts or the study of the structure and spin state of transition metal complexes.

EPR spectra of spin $1/2$ centers are made up of two contributions: (i) the hyperfine parameters, which can be computed from the ground state spin density, and have been used to connect theoretical studies of defects to available experimental data [1–6], and (ii) the g tensor. Only recently have there been attempts to calculate the g tensor in molecules from first principles using density functional theory (DFT) [7,8]. However, these approaches are valid only for finite systems and, thus, are not useful for the calculation of the g tensor for paramagnetic defects in solids, except possibly within a cluster approximation. In the absence of a predictive scheme, experimentally determined g tensors are, of necessity, interpreted in terms of their symmetry alone, leaving any remaining information unexploited. A reliable, first-principles approach to the prediction of g tensors in solids, in combination with structural and energetic calculations, would access this information, and could be used for an unequivocal discrimination between competing microscopic models proposed for defect centers. In this Letter we describe an approach for the calculation of the g tensor in extended systems, using periodic boundary conditions and supercells.

In a previous paper [9] we have shown how to compute the all-electron magnetic linear response, in finite and extended systems, using DFT and pseudopotentials. To achieve this we introduced the gauge including projector augmented wave (GIPAW) method, which is an extension of Blöchl's projector augmented wave (PAW) method [10]. In Ref. [9], we used GIPAW to compute the NMR chemical shifts in molecules and solids. Here we apply the GIPAW approach to the first-principles prediction of EPR g tensors for paramagnetic defects in solids. We validate our theory and implementation for diatomic radicals, for which both all-electron quantum chemical calculations and experimental data exist. As, until now, there have been no first-principles calculations of g tensors in solids, we validate our method in the solid state by a direct comparison with experiment. In particular, we interpret, from first principles, the EPR spectrum of the well characterized and technologically important defects in quartz, the E_1' and phosphorus substitutional centers.

The g tensor is an experimentally defined quantity, arising from the recognition that the EPR spectrum can be modeled using the following effective Hamiltonian, bilinear in the total electron spin $\mathbf{S}$, and the applied uniform magnetic field or nuclear spins, $\mathbf{B}$ and $\mathbf{I}_I$, respectively:

$$H_{\text{eff}} = \frac{\alpha}{2}\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B} + \sum_I \mathbf{S}\cdot\mathbf{A}_I\cdot\mathbf{I}_I\,. \tag{1}$$

Here, and in the following, atomic units are used, α is the fine structure constant, and the summation I runs over the nuclei. The tensors $\mathbf{A}_I$ are the hyperfine parameters (a PAW based theory for its calculation has been described elsewhere by Van de Walle and Blöchl [1,3]), and the tensor $\mathbf{g}$ is the EPR g tensor.

In order to calculate the g tensor we start from the electronic Hamiltonian which includes terms up to order α^3, in the presence of a constant external magnetic field $\mathbf{B}$ [7,11]:

$$H = \sum_i \left\{ \frac{[\mathbf{p}_i + \alpha\mathbf{A}(\mathbf{r}_i)]^2}{2} - \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{j\neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right\} + H_{\text{Z}} + H_{\text{Z-KE}} + H_{\text{SO}} + H_{\text{SOO}}\,. \tag{2}$$

The summations over i and j run over the electrons and H_{Z}, $H_{\mathrm{Z\text{-}KE}}$, H_{SO}, and H_{SOO} are the electron Zeeman, the electron Zeeman kinetic energy correction, the spin-orbit, and the spin-other-orbit terms, respectively:

$$H_{\mathrm{Z}} = \frac{\alpha g_e}{2} \sum_i \mathbf{S}_i \cdot \mathbf{B}, \qquad H_{\mathrm{Z\text{-}KE}} = -\frac{\alpha^3 g_e}{2} \sum_i \frac{p_i^2}{2} \mathbf{S}_i \cdot \mathbf{B},$$

$$H_{\mathrm{SO}} = \frac{\alpha^2 g'}{4} \sum_i \mathbf{S}_i \cdot \left(\sum_I Z_I \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} - \sum_{j \neq i} \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|^3} \right) \times [\mathbf{p}_i + \alpha \mathbf{A}(\mathbf{r}_i)], \tag{3}$$

$$H_{\mathrm{SOO}} = \alpha^2 \sum_{i, j \neq i} \mathbf{S}_i \cdot \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|^3} \times [\mathbf{p}_j + \alpha \mathbf{A}(\mathbf{r}_j)].$$

The constant g' is related to g_e, the electronic Zeeman g factor in vacuum, by $g' = 2(g_e - 1)$, and $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}$ is the vector potential.

Starting from the Hamiltonian of Eq. (2), we can expand the total energy in powers of α, up to $O(\alpha^3)$, using perturbation theory. In the resulting expansion, the term bilinear in $\mathbf{S}_i$ and $\mathbf{B}$ is identified as the first term of Eq. (1). This term can be rewritten within the formalism of spin polarized DFT to obtain an explicit expression for the g tensor:

$$\mathbf{g} = \mathbf{g}_e + \Delta\mathbf{g}_{\mathrm{Z\text{-}KE}} + \Delta\mathbf{g}_{\mathrm{SO}} + \Delta\mathbf{g}_{\mathrm{SOO}} = \mathbf{g}_e + \Delta\mathbf{g}, \tag{4}$$

where $\mathbf{g}_e = g_e \mathbf{I}$, $\mathbf{I}$ being the identity matrix, and

$$\Delta\mathbf{g}_{\mathrm{Z\text{-}KE}} = -\alpha^2 g_e (T_\uparrow^{(0)} - T_\downarrow^{(0)}) \mathbf{I}, \tag{5}$$

$$\Delta\mathbf{g}_{\mathrm{SO}} \cdot \mathbf{B} = \frac{\alpha}{2} g' \int d^3r \, [\mathbf{j}_\uparrow^{(1)}(\mathbf{r}) \times \nabla V_{\mathrm{ks},\uparrow}^{(0)}(\mathbf{r}) - \mathbf{j}_\downarrow^{(1)}(\mathbf{r}) \times \nabla V_{\mathrm{ks},\downarrow}^{(0)}(\mathbf{r})], \tag{6}$$

$$\Delta\mathbf{g}_{\mathrm{SOO}} \cdot \mathbf{B} = 2 \int d^3r \, \mathbf{B}^{(1)}(\mathbf{r}) [\rho_\uparrow^{(0)}(\mathbf{r}) - \rho_\downarrow^{(0)}(\mathbf{r})]. \tag{7}$$

Here $\uparrow$ denotes the majority spin channel and $\rho_\uparrow^{(0)}(\mathbf{r})$, $T_\uparrow^{(0)}$, and $V_{\mathrm{ks},\uparrow}^{(0)}(\mathbf{r})$ are the unperturbed electron probability density, kinetic energy, and Kohn-Sham potential of the $\uparrow$-spin channel, respectively. $\mathbf{j}_\uparrow^{(1)}(\mathbf{r})$ is the electronic charge current linearly induced by the constant magnetic field $\mathbf{B}$ in the $\uparrow$-spin channel. Finally, $\mathbf{B}^{(1)}(\mathbf{r})$ is the magnetic field produced by the total induced current, $[\mathbf{j}_\uparrow^{(1)}(\mathbf{r}) + \mathbf{j}_\downarrow^{(1)}(\mathbf{r})]$, which we correct for self-interaction by removing the contribution from the current of the unpaired electron, $[\mathbf{j}_\uparrow^{(1)}(\mathbf{r}) - \mathbf{j}_\downarrow^{(1)}(\mathbf{r})]$.

We can interpret the physical origin of deviation of the g tensor from its value in vacuum. The spin-other-orbit correction, $\Delta\mathbf{g}_{\mathrm{SOO}}$, describes the screening of the external field $\mathbf{B}$ by the induced electronic currents, as experienced by the unpaired electron. The unpaired electron itself is not at rest and in the reference frame of the unpaired electron the electric field due to the ions and to the other electrons is Lorentz transformed so as to appear as a magnetic field. The interaction between the spin of the unpaired electron and this magnetic field results in the spin-orbit correction, $\Delta\mathbf{g}_{\mathrm{SO}}$ [12]. Finally, the electron Zeeman kinetic energy correction, $\Delta\mathbf{g}_{\mathrm{Z\text{-}KE}}$, is a purely kinematic relativistic correction.

Equations (5)–(7) show that the evaluation of the g tensor requires, besides ground state quantities, the linear magnetic response currents $\mathbf{j}^{(1)}(\mathbf{r})$. Mauri, Pfrommer, and Louie [13] showed how to calculate the magnetic response of a system of electrons in an infinite insulating crystal, and our recent paper [9] reformulated this so as to be strictly valid for nonlocal pseudopotentials, and to reproduce the valence all-electron currents even within the pseudization core region. An accurate description of the all-electron currents in the core regions is essential for the evaluation of the SO term, Eq. (6). Indeed, the dominant contribution to the integral in Eq. (6) comes from the core region as a result of the divergence of $V_{\mathrm{ks}}^{(0)}(\mathbf{r})$ at the nuclei.

Using our GIPAW approach to the calculation of the all-electron magnetic response using pseudopotentials, described in detail in Ref. [9], we break the SO term into three parts which derive from the three GIPAW contributions to the induced current, Eq. (34) of Ref. [9]:

$$\Delta\mathbf{g}_{\mathrm{SO}} = \Delta\mathbf{g}_{\mathrm{SO}}^{\mathrm{bare}} + \Delta\mathbf{g}_{\mathrm{SO}}^{\Delta d} + \Delta\mathbf{g}_{\mathrm{SO}}^{\Delta p}. \tag{8}$$

The $\Delta\mathbf{g}_{\mathrm{SO}}^{\mathrm{bare}}$ term is evaluated from Eq. (6) using a spin dependent version of the $\mathbf{j}_{\mathrm{bare}}^{(1)}(\mathbf{r})$ of Ref. [9] and a local Kohn-Sham potential consisting of a sum of the self-consistent contribution to the local potential and the local parts of the pseudopotentials.

The diamagnetic correction term $\Delta\mathbf{g}_{\mathrm{SO}}^{\Delta d}$ can be evaluated from the ground state valence pseudo wave functions $|\bar{\Psi}_{o,\uparrow}^{(0)}\rangle$ using the following expression:

$$\Delta\mathbf{g}_{\mathrm{SO}}^{\Delta d} \cdot \mathbf{B} = \sum_{I,o,n,m} \langle \bar{\Psi}_{o,\uparrow}^{(0)} | \tilde{p}_{I,n} \rangle \mathbf{e}_{n,m}^{I} \langle \tilde{p}_{I,m} | \bar{\Psi}_{o,\uparrow}^{(0)} \rangle - \sum_{I,o,n,m} \langle \bar{\Psi}_{o,\downarrow}^{(0)} | \tilde{p}_{I,n} \rangle \mathbf{e}_{n,m}^{I} \langle \tilde{p}_{I,m} | \bar{\Psi}_{o,\downarrow}^{(0)} \rangle. \tag{9}$$

The summation o is over occupied states. The projector functions $|\tilde{p}_{I,n}\rangle$ are defined in Ref. [9] and satisfy $\langle \tilde{p}_{I,n} | \tilde{\phi}_{I',m} \rangle = \delta_{I,I'} \delta_{n,m}$, where $|\tilde{\phi}_{I,n}\rangle$ are a set of pseudo partial waves corresponding to the all-electron partial waves $|\phi_{I,n}\rangle$. The projector weights $\mathbf{e}_{n,m}^{I}$ are given by the following atom centered integrals:

$$\mathbf{e}^{I}_{n,m} = -\frac{\alpha^2 g'}{4} [\langle \phi_{I,n} | (\mathbf{B} \times \mathbf{r}) \times \nabla V(r) | \phi_{I,m} \rangle - \langle \tilde{\phi}_{I,n} | (\mathbf{B} \times \mathbf{r}) \times \nabla \tilde{V}(r) | \tilde{\phi}_{I,m} \rangle] . \tag{10}$$

The potentials $V(r)$ and $\tilde{V}(r)$ in Eqs. (10) and (11) are the screened atomic all-electron and local channel pseudopotentials, respectively.

The evaluation of the paramagnetic correction term $\Delta \mathbf{g}^{\Delta p}_{\mathrm{SO}}$ is more involved as it requires the first order linear response wave functions. However, the required evaluation can be described by analogy with the calculation of paramagnetic correction to the NMR chemical shifts, $\sigma^{\Delta p}_{\mathrm{GIPAW}}$, replacing the weights $\mathbf{f}^{I}_{n,m}$ in Eq. (60) of Ref. [9] by

$$\mathbf{f}^{I}_{n,m} = \langle \phi_{I,n} | \frac{g'}{2} \frac{\mathbf{L}}{r} \frac{\partial V(r)}{\partial r} | \phi_{I,m} \rangle - \langle \tilde{\phi}_{I,n} | \frac{g'}{2} \frac{\mathbf{L}}{r} \frac{\partial \tilde{V}(r)}{\partial r} | \tilde{\phi}_{I,m} \rangle , \tag{11}$$

where $\mathbf{L}$ is the angular momentum operator.

The electron Zeeman kinetic energy correction term $\Delta \mathbf{g}_{\text{Z-KE}}$ is evaluated by combining a straightforward PAW correction with the quantity evaluated from the ground state pseudo valence wave functions using Eq. (5). In this work the SOO term is evaluated from the induced field $\mathbf{B}^{(1)}(\mathbf{r})$ derived from the bare induced current, and the spin density due to the pseudo wave functions. It is expected that a full GIPAW treatment would result in only minor corrections since (i) the SOO term is small in comparison to the SO term, and (ii) both the induced field and the spin density do not diverge at the nuclei.

To validate our new expressions for the evaluation of the g tensor, and our implementation of them into a parallelized plane-wave pseudopotential code, we compare with the all-electron gauge including atomic orbital (GIAO) DFT results obtained by Schreckenbach and Ziegler [7] for a series of diatomic radicals. We use their calculated bond lengths for the dimers, but approximate the isolated dimers by using large supercells. Troullier-Martins pseudopotentials [14] and the (spin polarized) generalized gradient approximation due to Perdew *et al.* [15] (GGA-PBE) are used throughout our calculations. Table I shows the excellent agreement between our two approaches. The exception is the AlO radical, for which we obtain much closer agreement with experiment. The otherwise close agreement between these two very different approaches suggests a technical rather than fundamental problem in the GIAO calculation for AlO. Comparison with experiment is made through Table 2 of Ref. [7], while acknowledging that most measurements are performed in solid matrices, which strongly influence the g tensor (most notably the $\Delta g_{\parallel}$ components), and that the experimental errors are of the order of several hundred parts per million (ppm).

TABLE I. Calculated Δg tensors, in parts per million (ppm), for diatomic molecules. For comparison with Ref. [7] we omit (in this table only) the SOO contribution to our calculations. A 100 Ry plane-wave cutoff is used.

	$\Delta g_{\parallel}$		$\Delta g_{\perp}$	
Molecule	GIPAW	SZ [7]	GIPAW	SZ [7]
H_2^+	−39	−39	−41	−42
CO^+	−134	−138	−3223	−3129
CN	−138	−137	−2577	−2514
AlO	−141	−142	−2310	−222
BO	−69	−72	−2363	−2298
BS	−80	−83	−9901	−9974
MgF	−49	−60	−2093	−2178
KrF	−340	−335	61 676	60 578
XeF	−333	−340	157 128	151 518

Finally, by analyzing the different contributions, including the SOO term, we found that in all dimers apart from H_2^+, the SO term accounts for more than 90% of $\mathrm{Tr}\Delta g/3$, and that the paramagnetic correction term $\Delta \mathbf{g}^{\Delta p}_{\mathrm{SO}}$ accounts for the overwhelming majority of the SO term.

To further validate our approach to the calculation of the g tensor and to apply it for the first time in the solid state, we study two defects of α quartz.

The E'_1 center is associated with a positively charged oxygen vacancy, with the unpaired electron on a Si dangling bond. As in previous calculations [2,3,17], we model the defect with a 71 atom (24 Si and 47 O), positively charged (+1) hexagonal supercell. We use the theoretical GGA-PBE lattice parameters (which are 1% larger than in experiment) and relax the atoms. For the structural optimization we use a Γ only k-point sampling and a plane-wave cutoff of 50 Ry. The resulting relaxed structure is very close to that of Ref. [3]. The EPR g tensor is calculated using our relaxed structure, a plane-wave cutoff of 70 Ry and 4 inequivalent k points. In Table II we compare our theoretical g tensor with the experimental results [16], finding excellent agreement.

The $P2$ defect center is neutral and associated with a fourfold coordinated P atom, substituting for a Si atom. The center exists as two variants at low temperature (<140 K) in quartz, labeled $P2$(I) in the ground state and $P2$(II) in the excited state [18]. Only recently have these P defect centers been examined using DFT based total energy approaches [4,6]. However, up until now, the connection with experiment has been made using the

TABLE II. Calculated $\Delta \mathbf{g}$ tensors for our model E'_1 defect, and corresponding experimental data [16].

Principal values		Principal directions			
GIPAW (ppm)	Expt. (ppm)	GIPAW		Expt.	
		θ	ϕ	θ	ϕ
−651	−530	110.0°	223.5°	114.5°	227.7°
−2255	−1790	142.3°	341.6°	134.5°	344.4°
−2481	−2020	120.4°	121.1°	125.4°	118.7°

TABLE III. Calculated total energies, with respect to our lowest energy configuration. For nontetrahedral configurations, OPO indicates the largest O-P-O angle after the relaxation, and OSiO the corresponding angle in the unrelaxed α-quartz structure. With l and s we specify whether the two SiO bonds forming in the OSiO angle are short or long in the unrelaxed structure. The number of symmetry equivalent structures is N_c. We report our assignment of the experimental centers based on the comparison of Table IV.

SiO	OSiO	OPO	N_c	Energy (meV)	Species
Tetrahedral configuration			1	730	
ls	108.8°	147.4°	2	243	
ss	108.9°	155.4°	1	178	
ll	109.5°	157.6°	1	79	$P2$(I)
ls	110.4°	155.1°	2	0	$P2$(II)

TABLE IV. Calculated $\Delta \mathbf{g}$ tensors for our model $P2$ defect centers, and corresponding experimental data [18].

Principal values		Principal directions			
GIPAW (ppm)	Expt. (ppm)	GIPAW		Expt.	
		θ	ϕ	θ	ϕ
Configuration $P2$(I)					
1249	900	65.0°	90.0°	64.8°	90.0°
−980	−1100	90.0°	0.0°	90.0°	0.0°
−3414	−3200	25.0°	270.0°	25.2°	270.0°
Configuration $P2$(II)					
1146	1100	47.1°	13.1°	46.5°	11.8°
−824	−1000	99.0°	94.7°	101.1°	91.1°
−3454	−3200	135.7°	355.4°	134.4°	350.1°

hyperfine parameters alone, and the two variants of the defects, $P2$(I) and $P2$(II), have not been distinguished theoretically.

Using the method described above, and a supercell of 72 atoms, 5 distinct total energy local minima are found as a function of the initial configuration, Table III. The configuration with the highest energy corresponds to a symmetric relaxation with the P remaining tetrahedrally coordinated, and O-P-O angles of about 109°. In the 4 other configurations the P atom moves off-center, opening up one of the 6 O-P-O angles, which reaches a value of about 150°. We computed the EPR g tensors for our two lowest energy structures and compare them with the experimental results [18] in Table IV. Again, we obtain an excellent agreement between theory and experiment, which confirms that the two lowest energy theoretical structures correspond to the two lowest energy experimental structures. However, the comparison between g tensors shows that the energy ordering between the $P2$(I) and $P2$(II) species is not correctly described by theory. This is not surprising given the small energy separation between the two configurations. This is expected to be sensitive to both the size of the supercell and the use of approximated DFT functionals.

To summarize, we have calculated the EPR g tensor for a paramagnetic defect in an extended solid for the first time and find our results to be in excellent agreement with experimental results for the E_1' defect. On applying the method to the $P2$ defect, we show that comparison with experimental g tensors can provide structural information where the accuracy of DFT for energetics is insufficient. Combined with the calculation of hyperfine parameters [1–6], we expect that our GIPAW based first-principles approach to the prediction of EPR g tensors will be of great use in the assessment of models proposed for less well characterized paramagnetic defects, and add significantly to the tools available to the electronic structure community.

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