First principles theory of the EPR g-tensor in solids

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Introduction

- Electron Paramagnetic Resonance (EPR) is the most powerful spectroscopic technique for the study of paramagnetic defects in solids

- Defect centers are often named directly after their EPR spectra

- Applications extend to any situation with unpaired electrons
  - reactions involving free radicals in both chemical and biological contexts
  - study of structure and spin state of transition metal complexes

- Sometimes also known as Electron Spin Resonance (ESR)

- Complements NMR spectroscopy

Anatomy of EPR spectra

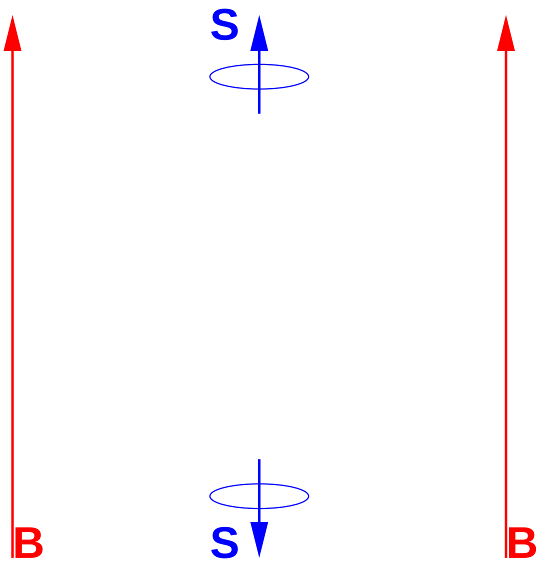
- EPR spectra of spin 1/2 centers are made up of two contributions

- Hyperfine parameters
  - can be computed from the ground state spin density at sites neighbouring the defect
  - widely used to connect theoretical models of defects with available experimental data

- The g-tensor
  - often easier to measure than hyperfine parameters, and available first
  - often available to higher accuracy

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

Electron Paramagnetic resonance



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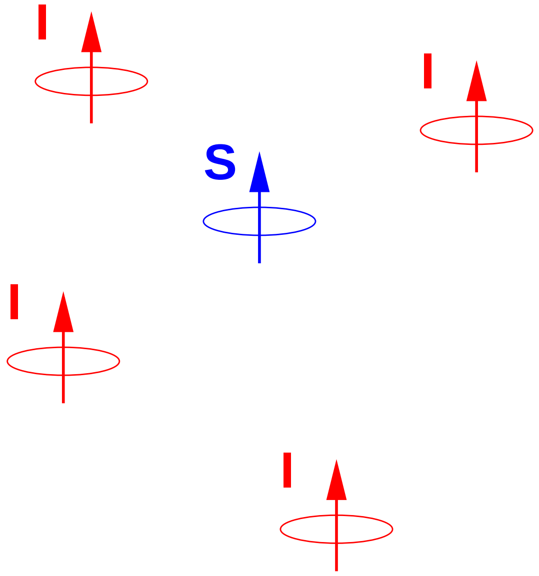

g-tensors: The state of the art

- Some old HF and MRCI (accurate) calculations exist for small radicals
- DFT used for the first time by Ziegler (1997) and Malkina (2000)
- Theory only strictly valid for finite systems
- Only small systems presented
- No defects in solids attempted at all (even in the cluster approx.)

Motivation

- 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.

The EPR Hamitonian

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

$$H_{\mathrm{Z}} = \frac{\alpha \mathrm{g_e}}{2} \sum_i \mathbf{S}_i \cdot \mathbf{B}$$

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

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

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

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}$$

The derivation

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

- Aim to write the full Hamiltonian in the form of the model hamiltonian
- Expand total energy in powers of α to to O(α^3), using perturbation theory
- Identify the terms bilinear in $\mathbf{S}$ and $\mathbf{B}$ as the first term in the effective hamiltonian
- Rewrite in the formalism of spin-polarised DFT

Expressions for the g-tensor

$$\mathbf{g} = \mathbf{g}_{\mathrm{e}} + \Delta\mathbf{g}_{\mathrm{Z-KE}} + \Delta\mathbf{g}_{\mathrm{SO}} + \Delta\mathbf{g}_{\mathrm{SOO}} = \mathbf{g}_{\mathrm{e}} + \Delta\mathbf{g}$$

$$\Delta\mathbf{g}_{\mathrm{Z-KE}} = -\alpha^2 \mathrm{g}_{\mathrm{e}} (T_{\uparrow}^{(0)} - T_{\downarrow}^{(0)})\mathbf{I}$$

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

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

Physical interpretation of the expressions

The spin-other-orbit correction The screening of the external $\mathbf{B}$ field by induced electronic currents, as experienced by the unpaired electron.

The spin-orbit correction The unpaired electron is not at rest. In the frame of the unpaired electron the electric field due to the ions and the other electrons is Lorentz transformed to appear as a magnetic field. The interaction of the spin of the unpaired electron and this magnetic field is the spin-orbit correction.

Zeeman kinetic energy correction This is a purely kinematic relativistic correction.

The tools of the trade

- Mauri, Pfrommer and Louie showed how to calculate the magnetic response of electrons in an infinite insulating crystal

- We showed how to generalise this so as to be valid for non-local pseudopotentials

- Gauge Including Projector Augmented Wave (GIPAW) approach
  - corrects for deviation of pseudo from all-electron wavefunctions in the core (important for the SO term as $V_{\mathrm{ks}}^{(0)}(\mathbf{r})$ diverges at the nucleus)
  - is gauge invariant

- Our NMR code (PARATEC) calculates $\mathbf{j}^{(1)}_{\uparrow/\downarrow}(\mathbf{r})$

- Minor changes needed to the GIPAW operators $(\mathbf{r}/r^3 \rightarrow \nabla V(\mathbf{r}))$

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A first test: diatomic radicals

- Validate against existing high quality AE diatomic calculations of Ziegler (no SOO term)
- Excellent agreement apart from AlO (we are much closer to experiment for this one)

Molecule	$\Delta g_{\parallel}$		$\Delta g_{\perp}$	
	GIPAW	SZ	GIPAW	SZ
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	61676	60578
XeF	-333	-340	157128	151518

Diatomic radicals: breakdown of contributions

Mol	Z-KE	SO_{bare}	$SO_{\Delta d}$	$SO_{\Delta p}$	SOO_{bare}
H_2^+	-64	22	1	0	0
CO^+	-179	-419	9	-1604	-5
CN	-179	-354	7	-1237	29
AlO	-186	376	15	-1792	2
BO	-92	-332	5	-1180	-5
BS	-105	-197	5	-6330	1
MgF	-76	-217	4	-1122	11
KrF	-444	4427	50	36972	-412
XeF	-441	2326	63	102694	-134

- The SO term dominates
- The GIPAW corrections are essential

Diatomic Radicals: experiment vs. theory

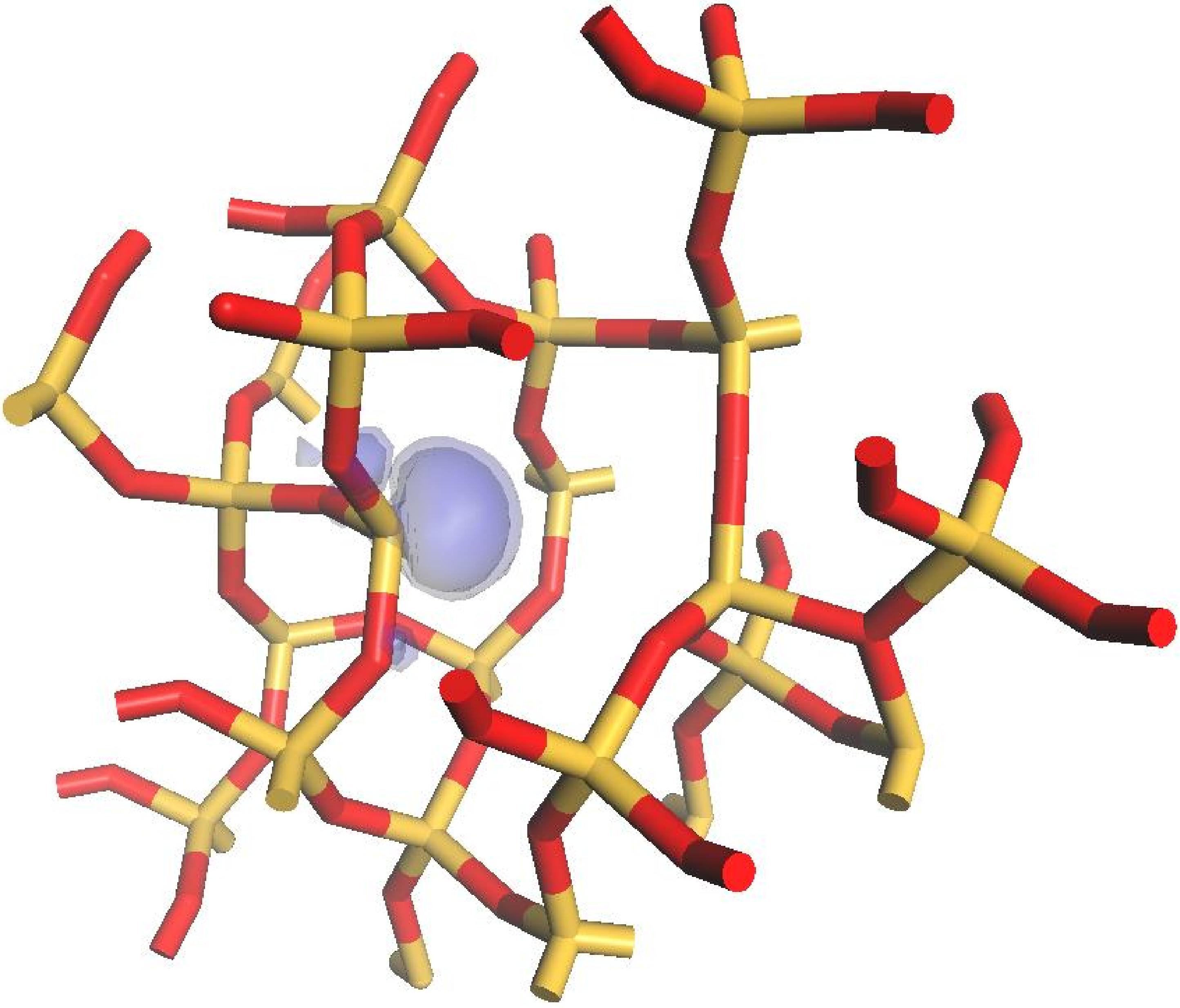
Molecule	$\Delta g_{\parallel}$		$\Delta g_{\perp}$	
	GIPAW	Expt.	GIPAW	Expt.
CO^+	-100	-1200	-3247	-2800
		-1800		-2600
		-1400		-3200
				*-2400
CN	-78	-800	-2564	-2000
AlO	-88	-800	-2334	-1900
		-900		-2600
		-3000		-8600
BO	-52	-1100	-2379	-800
BS	-51	-700	-9913	-8100
		-800		-7900
MgF	-34	-300	-2084	-1300
KrF	-208	-2000	60992	66000
XeF	-212	-28000	156867	124000

- Matrix effects

The E'$_1$ defect in quartz

- Positively charged oxygen vacancy
- Unpaired electron on Si dangling bond
- Low symmetry
  - all six components independent (orientation and eigenvalues)
- Well characterised
  - many good experiments and first principles calculations of the structures and hyperfine parameters
- Technologically important
  - silicon devices and optical fibres
- Model using 71 atom cell (+1 charge), spin polarized GGA-PBE

The E'$_1$ defect state in quartz



The EPR g-tensor of E'$_1$ in quartz

Principle values		Principle directions			
GIPAW	Expt.	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°

- Agreement impressive
- Angles of error 4.5°, 8.1°, and 5.4°
- Relative magnitude of principle values perfect
- Absolute magnitude overestimated by 20%
- Can relate tensor to geometry

Conclusions

- A reliable theory for the calculation of the EPR g-tensor for paramagnetic defects in solids has been presented

- It has allowed the first ever first principles calculation of the EPR g-tensor in the solid state

- With the calculation of hyperfine parameters, the method will be of great use in investigating less well characterised paramagnetic defects

- It adds significantly to the tools available to the electronic structure community