

Spin densities and related quantities in paramagnetic defects

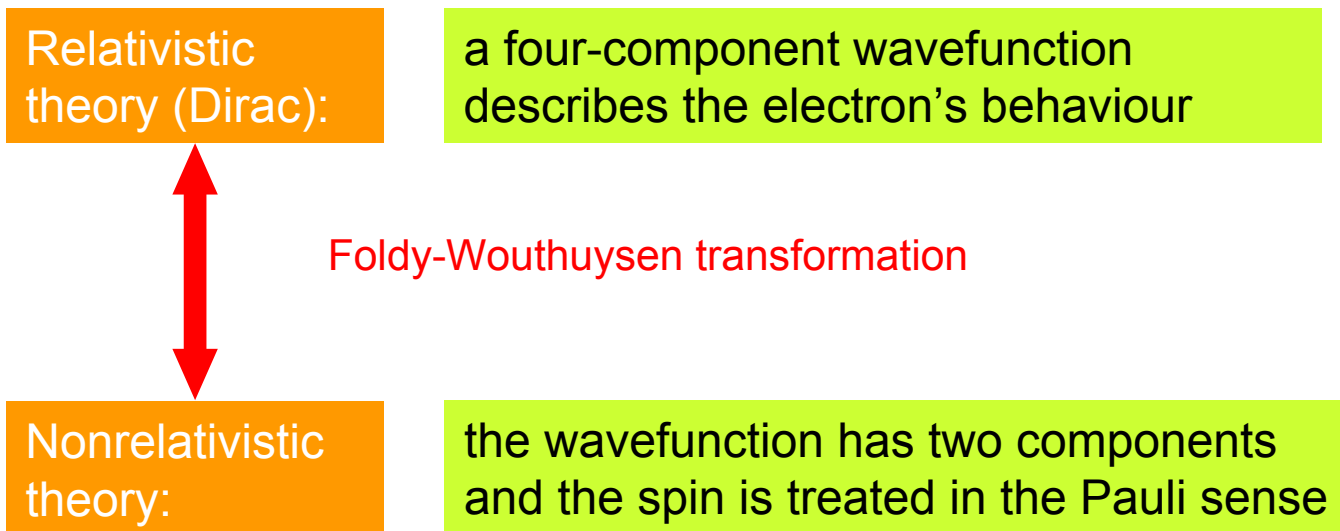
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Outline

- From the full Hamiltonian to a spin Hamiltonian
- The main terms in the EPR spin Hamiltonian
- Spin density, hyperfine structure and nuclear quadrupole interaction constants in paramagnetic defects: electron holes in alkaline earth oxides and alkali halides. Comparison with EPR and ENDOR experimental data.

Relativistic and nonrelativistic theories



The Foldy-Wouthuysen transformation converts the Dirac equation into a form that looks like a Schrödinger equation with perturbation corrections: the corresponding physical picture (model) allows easier interpretation.

The nonrelativistic Hamiltonian

A **full system** can be characterised by the following Hamiltonian:

$$\hat{H} = \hat{H}^0 + \hat{H}'$$

\hat{H}^0 **electrostatic Hamiltonian**

\hat{H}' the **small terms** obtained from a perturbation treatment of the relativistic Hamiltonian up to a given order

The eigenfunctions of \hat{H}^0 can be factorised in terms of the electronic and the nuclear wave functions (Born-Oppenheimer approximation):

$$\Phi_{kMK}^0 = \Psi_{kM}^0 \Theta_K$$

Ψ_{kM}^0 and Θ_K are chosen to be eigenfunctions of the electronic and nuclear spin operators.

Hamiltonian small terms

Term	Description	Operator	Coefficient	
			Atomic units	Gaussian units
Zero-order				
0.0	Nuclear–nuclear Coulomb interaction	$\sum_{v < v'} \left(\frac{Z_v Z_{v'}}{R_{vv'}} \right)$	$\mathcal{E}_0 a_0$	e^2
0.1	Kinetic energy	$\sum_j \left(-\frac{1}{2} \nabla_j^2 \right)$	$\mathcal{E}_0 a_0^2$	$\frac{\hbar^2}{m}$
0.2	Electron–nuclear Coulomb interaction (nuclear attraction)	$\sum_{j,v} \left(-\frac{Z_v}{r_{jv}} \right)$	$\mathcal{E}_0 a_0$	e^2
0.3	Electron–electron Coulomb interaction (electron repulsion)	$\sum_{j < k} \left(\frac{1}{r_{jk}} \right)$	$\mathcal{E}_0 a_0$	e^2
Relativistic corrections independent of spin and field				
1.1	Kinetic energy mass correction	$\sum_j \left(-\frac{1}{8} \nabla_j^4 \right)$	$\alpha^2 \mathcal{E}_0 a_0^4$	$\frac{\hbar^4}{m^3 c^2}$
1.2	(Electron–nuclear) Darwin term	$\sum_{j,v} Z_v \frac{\pi}{2} \delta(\mathbf{r}_{jv})$	$\alpha^2 \mathcal{E}_0 a_0^3$	$4\beta^2$
1.3	Electron–electron Darwin term	$\sum_{j < k} (-\pi \delta(\mathbf{r}_{jk}))$	$\alpha^2 \mathcal{E}_0 a_0^3$	$4\beta^2$
1.4	Electron–electron orbital interaction	$\sum_{j < k} \left[+\frac{1}{2} \left(\frac{\nabla_j \cdot \nabla_k}{r_{jk}} - \frac{(\mathbf{r}_{jk} \cdot \nabla_j)(\mathbf{r}_{jk} \cdot \nabla_k)}{r_{jk}^3} \right) \right]$	$\alpha^2 \mathcal{E}_0 a_0^3$	$4\beta^2$
1.5	Electron–electron orbital interaction	$\sum_{j < k} \left[+\frac{1}{4} \frac{1}{r_{jk}^3} (\mathbf{r}_{jk} \cdot \nabla_k - \mathbf{r}_{jk} \cdot \nabla_j) \right]$	$\alpha^2 \mathcal{E}_0 a_0^3$	$4\beta^2$
1.6	Electron–electron orbital interaction	$\sum_{j < k} [\pi \delta(\mathbf{r}_{jk})(\mathbf{r}_{jk} \cdot \nabla_j - \mathbf{r}_{jk} \cdot \nabla_k)]$	$\alpha^2 \mathcal{E}_0 a_0^3$	$4\beta^2$

Terms depending on spin but not field

(Electron spin)

2.1	Spin-orbit interaction	$\sum_{j,v} \left(-\frac{g'}{4} Z_{v,i} \frac{k_0^2(r_{jv})}{r_{jk}^3} \mathbf{S}_j \cdot (\mathbf{r}_{jv} \times \nabla_j) \right)$	$\alpha^2 \mathcal{E}_0 a_0^3$	$4\beta^2$
2.2	Spin-other-orbit interaction	$\sum_{j,k} \frac{i}{r_{jk}^3} \mathbf{S}_j \cdot [(\mathbf{r}_{kj}) \times \nabla_k]$	$\alpha^2 \mathcal{E}_0 a_0^3$	$4\beta^2$
2.3	Electron-electron spin-orbit interaction	$\sum_{j,k} \left(\frac{g' i}{4 r_{jk}^3} \mathbf{S}_j \cdot \mathbf{r}_{jk} \times \nabla_j \right)$	$\alpha^2 \mathcal{E}_0 a_0^3$	$4\beta^2$
2.4	Spin-spin dipolar interaction	$\sum_{j < k} \left(\frac{\mathbf{S}_j \cdot \mathbf{S}_k}{r_{jk}^3} - \frac{(\mathbf{S}_j \cdot \mathbf{r}_{jk})(\mathbf{S}_k \cdot \mathbf{r}_{jk})}{r_{jk}^5} \right)$	$\alpha^2 \mathcal{E}_0 a_0^3$	$4\beta^2$
2.5	Spin-spin contact interaction	$\sum_{j < k} \left(-\frac{8\pi}{3} \mathbf{S}_j \cdot \mathbf{S}_k \delta(\mathbf{r}_{jk}) \right)$	$\alpha^2 \mathcal{E}_0 a_0^3$	$4\beta^2$

(Nuclear spin)

2.6	Nuclear dipole-dipole interaction	$\sum_{v < v'} \frac{g_v g_{v'}}{4} \left[\frac{\mathbf{I}_v \cdot \mathbf{I}_{v'}}{R_{vv'}^3} - 3 \frac{(\mathbf{I}_v \cdot \mathbf{R}_{vv'})(\mathbf{I}_{v'} \cdot \mathbf{R}_{vv'})}{R_{vv'}^5} \right]$	$\left(\frac{m}{M_p} \right)^2 \alpha^2 \mathcal{E}_0 a_0^3$	$4\beta_N^2$
2.7	Nuclear quadrupole interaction	$\sum_{j,v} \left[\frac{Q_v}{2I_v(2I_v - 1)} \right] \left[\frac{I_v^2}{r_{jv}^3} - 3 \frac{(\mathbf{r}_{jv} \cdot \mathbf{I}_v)^2}{r_{jv}^5} \right]$	$\mathcal{E} a_0$	e^2
2.8	Orbital hyperfine interaction	$\sum_{j,v} \frac{-g_v}{2} k_0(r_{jv}) \frac{i}{r_{jv}^3} (\mathbf{r}_{jv} \times \nabla_j) \cdot \mathbf{I}_v$	$\left(\frac{m}{M_p} \right) \alpha^2 \mathcal{E}_0 a_0^3$	$4\beta\beta_N$
2.9	Orbital hyperfine correction	$\sum_{j,v} \frac{g_v}{4} k_0^3(r_{jv}) \nabla_j^2 \frac{i}{r_{jv}^3} (\mathbf{r}_{jv} \times \nabla_j) \cdot \mathbf{I}_v$	$\left(\frac{m}{M_p} \right) \alpha^2 \mathcal{E}_0 a_0^5$	$4 \left(\frac{\hbar}{mc} \right)^2 \beta\beta_N$
2.10	Electron coupled nuclear spin-spin interaction	$\sum_j \sum_{v,v'} \frac{g_v g_{v'}}{8} \frac{k_0(r_{jv})}{r_{jv}^3 r_{jv'}^3} \times [(\mathbf{I}_v \cdot \mathbf{I}_{v'}) (\mathbf{r}_{jv} \cdot \mathbf{r}_{jv'}) - (\mathbf{I}_v \cdot \mathbf{r}_{jv})(\mathbf{I}_{v'} \cdot \mathbf{r}_{jv'})]$	$\left(\frac{m}{M_p} \right)^2 \alpha^4 \mathcal{E}_0 a_0^4$	$\frac{4e^2}{mc^2} \beta_N^2$



(Electron and nuclear spins)

2.11	Dipolar hyperfine interaction	$\sum_{j,v} \left(-\frac{gg_v}{4} k_0(r_{jv}) \left[\frac{\mathbf{S}_{jv} \cdot \mathbf{I}_v}{r_{jv}^3} - 3 \frac{(\mathbf{S}_{jv} \cdot \mathbf{r}_{jv})(\mathbf{I}_v \cdot \mathbf{r}_{jv})}{r_{jv}^5} \right] \right)$	$\left(\frac{m}{M_p} \right) \alpha^2 \mathcal{E}_0 a_0^3$	$4\beta\beta_N$
2.12	(Fermi) contact hyperfine interaction	$\sum_{j,v} \frac{2\pi}{3} g' g_v \mathbf{S}_j \cdot \mathbf{I}_v \delta(\mathbf{r}_{jv})$	$\left(\frac{m}{M_p} \right) \alpha^2 \mathcal{E}_0 a_0^3$	$4\beta\beta_N$
2.13	Spin-orbit hyperfine correction	$\sum_j \sum_{v,v'} \frac{g_v g' Z_{v'} k_0^2(r_{jv'})}{8 r_{jv'}^3 r_{jv'}^3} \times [(\mathbf{r}_{jv'} \cdot \mathbf{r}_{jv})(\mathbf{S}_j \cdot \mathbf{I}_v) - (\mathbf{S}_j \cdot \mathbf{r}_{jv})(\mathbf{I}_v \cdot \mathbf{r}_{jv})]$	$\left(\frac{m}{M_p} \right) \alpha^4 \mathcal{E}_0 a_0^4$	$8 \frac{e}{\hbar c} \beta^2 \beta_N$
2.14	Spin-other-orbit hyperfine correction	$\sum_{j,k} \sum_v \frac{g_v}{4} \frac{1}{r_{jk}^3} \frac{1}{r_{jv}^3} \times [(\mathbf{r}_{kj} \cdot \mathbf{r}_{kv})(\mathbf{S}_j \cdot \mathbf{I}_v) - (\mathbf{r}_{kj} \cdot \mathbf{I}_v)(\mathbf{r}_{kv} \cdot \mathbf{S}_j)]$	$\left(\frac{m}{M_p} \right) \alpha^4 \mathcal{E}_0 a_0^4$	$8 \frac{e}{\hbar c} \beta^2 \beta_N$
2.15	Electron-electron spin-orbit hyperfine correction	$\sum_{j,k} \sum_v \frac{g' g_v}{8} \frac{1}{r_{jk}^3} \frac{1}{r_{jv}^3} \times [(\mathbf{r}_{kj} \cdot \mathbf{r}_{jv})(\mathbf{S}_j \cdot \mathbf{I}_v) - (\mathbf{S}_j \cdot \mathbf{r}_{jv})(\mathbf{I}_v \cdot \mathbf{r}_{kj})]$	$\left(\frac{m}{M_p} \right) \alpha^4 \mathcal{E}_0 a_0^4$	$8 \frac{e}{\hbar c} \beta^2 \beta_N$

Terms depending on field but not spin

3.1	Orbital Zeeman interaction	$\sum_j \left(-\frac{i}{2} (\mathbf{r}_j \times \nabla_j) \cdot \mathbf{B} \right)$	$\alpha a_0 e$	2β
3.2	Orbital Zeeman kinetic energy correction	$\sum_j \left(-\frac{i}{4} k_0^3(r_j) \nabla_j^2 (\mathbf{r}_j \times \nabla_j) \cdot \mathbf{B} \right)$	$\alpha^3 a_0^3 e$	$2\beta \left(\frac{\hbar}{mc} \right)^2$
3.3	Diamagnetic	$\sum_j \frac{1}{8} [B^2 r_j^2 - (\mathbf{B} \cdot \mathbf{r}_j)^2]$	$\alpha^2 v_0 / a_0$	$\frac{e^2}{mc^2}$

Terms depending on spins and field (electron spin)

4.1	(Electron spin) Zeeman	$\sum_j \frac{g}{2} \mathbf{S}_j \cdot \mathbf{B}$	$aa_0 e$	2β
4.2	(Electron spin) Zeeman kinetic energy correction	$\sum_j -\frac{g}{2} \nabla_j^2 \mathbf{S}_j \cdot \mathbf{B}$	$\alpha^3 a_0^3 e$	$2\beta \left(\frac{\hbar}{mc}\right)^2$
4.3	Spin-orbit Zeeman gauge correction	$\sum_{j,v} g' \frac{k_0^2}{8} \frac{Z_v}{r_{jv}^3} [(\mathbf{r}_{jv} \cdot \mathbf{r}_j)(\mathbf{S}_j \cdot \mathbf{B}) - (\mathbf{S}_j \cdot \mathbf{r}_j)(\mathbf{r}_j \cdot \mathbf{B})]$	$\alpha^3 a_0^2 e$	$2\beta \frac{e^2}{mc^2}$
4.4	Electron-electron spin-orbit Zeeman gauge correction	$\sum_{j,k} \frac{g'}{8} \frac{1}{r_{jk}^3} [(\mathbf{r}_{kj} \cdot \mathbf{r}_j)(\mathbf{S}_j \cdot \mathbf{B}) - (\mathbf{S}_j \cdot \mathbf{B})(\mathbf{r}_{kj} \cdot \mathbf{B}) - (\mathbf{S}_j \cdot \mathbf{r}_j)(\mathbf{r}_{kj} \cdot \mathbf{B})]$	$\alpha^3 a_0^2 e$	$2\beta \frac{e^2}{mc^2}$
4.5	Spin-other-orbit Zeeman gauge correction	$\sum_{j,k} \frac{1}{2} \frac{1}{r_{jk}^3} [(\mathbf{r}_{jk} \cdot \mathbf{r}_k)(\mathbf{S}_j \cdot \mathbf{B}) - (\mathbf{S}_j \cdot \mathbf{r}_k)(\mathbf{r}_{jk} \cdot \mathbf{B})]$	$\alpha^3 a_0^2 e$	$2\beta \frac{e^2}{mc^2}$

(Nuclear spin)

4.6	Nuclear Zeeman	$\sum_v \frac{g_v}{2} \mathbf{I}_v \cdot \mathbf{B}$	$\left(\frac{m}{M_P}\right) aa_0 e$	$2\beta_N$
4.7	Electronic nuclear Zeeman correction	$\sum_{j,v} \frac{g_v k_0}{4} \frac{1}{r_{jv}^3} [(\mathbf{r}_j \cdot \mathbf{r}_{jv})(\mathbf{I}_v \cdot \mathbf{B}) - (\mathbf{r}_j \cdot \mathbf{I}_v)(\mathbf{r}_{jv} \cdot \mathbf{B})]$	$\left(\frac{m}{M_P}\right) \alpha^3 a_0^2 e$	$2\beta_N \frac{e^2}{mc^2}$

J. H. Harriman – Theoretical Foundations of Electron Spin Resonance – Academic Press, 1978.

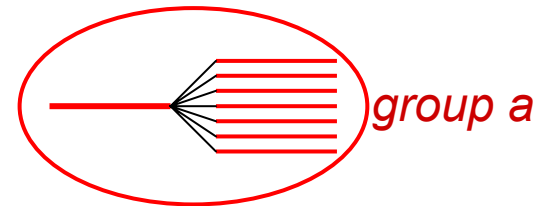
The partition method

The solutions of the time-independent Schrödinger equation

$$(\hat{H} - E) \Phi = 0$$

are sought as linear combinations of the set of the Φ_{kMK}^0 functions.

If we are interested only in the eigenfunctions of *group a* of nearly degenerate states, we can isolate these terms from all the others, which will belong to *group b*, and write Φ as:



$$\Phi = \sum_{k \in a} \sum_M \sum_K c_{kMK}^a \Psi_{kM}^0 \Theta_K + \sum_{\substack{\ell \in b \\ (b \neq a)}} \sum_M \sum_K c_{\ell MK}^b \Psi_{\ell M}^0 \Theta_K$$

The Schrödinger equation can be written in matrix form in such a way that the **a** and **b** blocks are clearly identified

$$\begin{pmatrix} (\mathbf{H}_{aa} - E\mathbf{1}_{aa}) & \mathbf{H}_{ab} \\ \mathbf{H}_{ba} & (\mathbf{H}_{bb} - E\mathbf{1}_{bb}) \end{pmatrix} \begin{pmatrix} \mathbf{c}_a \\ \mathbf{c}_b \end{pmatrix} = \mathbf{0}$$

and separate into the two following matrix equations:

$$\begin{cases} (\mathbf{H}_{aa} - E\mathbf{1}_{aa})\mathbf{c}_a + \mathbf{H}_{ab}\mathbf{c}_b = \mathbf{0} \\ \mathbf{H}_{ba}\mathbf{c}_a + (\mathbf{H}_{bb} - E\mathbf{1}_{bb})\mathbf{c}_b = \mathbf{0} \end{cases}$$

Since E refers to **group a**, the latter equation can formally be solved to give

$$\mathbf{c}_b = (E\mathbf{1}_{bb} - \mathbf{H}_{bb})^{-1} \mathbf{H}_{ba} \mathbf{c}_a$$

and substituting for \mathbf{c}_b in the first equation, this becomes

$$[\mathbf{H}_{aa} + \mathbf{H}_{ab}(E\mathbf{1}_{bb} - \mathbf{H}_{bb})^{-1} \mathbf{H}_{ba} - E\mathbf{1}_{aa}] \mathbf{c}_a = \mathbf{0}$$

or, equivalently,

$$[\mathbf{H}'_{aa} + (\mathbf{H}^0_{ab} + \mathbf{H}'_{ab})(E\mathbf{1}_{bb} - \mathbf{H}_{bb})^{-1}(\mathbf{H}^0_{ba} + \mathbf{H}'_{ba}) - (E - E_a^0)\mathbf{1}_{aa}] \mathbf{c}_a = \mathbf{0}$$

Since $\mathbf{H}^0_{ab} = \mathbf{H}^0_{ba} = \mathbf{0}$, $|E - E_a^0| \ll |E_a^0|$ and $\mathbf{H}'_{bb} \ll \mathbf{H}_{bb}$, the matrix equation relative to **a** is approximated as

$$[\mathbf{H}'_{aa} + \mathbf{H}'_{ab} (E_a^0 \mathbf{1}_{bb} - \mathbf{H}^0_{bb})^{-1} \mathbf{H}'_{ba} - (E - E_a^0)\mathbf{1}_{aa}] \mathbf{c}_a = \mathbf{0}$$

where we identify a **first** and a **second order** term

$$[\mathbf{H}^{(1)} + \mathbf{H}^{(2)} - E' \mathbf{1}_{aa}] \mathbf{c}_a = \mathbf{0}$$

$$\begin{cases} \mathbf{H}^{(1)} = \mathbf{H}'_{aa} \\ \mathbf{H}^{(2)} = \mathbf{H}'_{ab} (E_a^0 \mathbf{1}_{bb} - \mathbf{H}^0_{bb})^{-1} \mathbf{H}'_{ba} \\ E' = E - E_a^0 \end{cases}$$

$\mathbf{H}^{(1)}$ and $\mathbf{H}^{(2)}$ depend on space and spin operators that, however, after some manipulations can be replaced by **pure spin operators** and **parameters** to give a **spin hamiltonian**. Thus the behaviour of an actual system is simulated by means of a fictitious spin system, described by a phenomenological spin hamiltonian, that may be used conveniently in the interpretation of experimental results. Theory provides recipes for calculating the parameters.

The spin Hamiltonian

A spin hamiltonian that includes linear, quadratic and bilinear terms in magnetic field, electron spin and nuclear spin takes the form:

$$H^s = H^0 + H_B + H_S + H_I + H_{B^2} + H_{S^2} + H_{I^2} + H_{BS} + H_{BI} + H_{SI}$$

but for a state having its maximum degeneracy associated with M_S and M_I the linear terms do not contribute in first order, so that

$$H^s = H^0(B, S) + S \cdot \mathbf{D} \cdot S + S \cdot \mathbf{g} \cdot B + \sum_N I_N \cdot \mathbf{g}_n \cdot B + \sum_N S \cdot \mathbf{A} \cdot I_N + \sum_{M,N} I_M \cdot \mathbf{q}_{MN} \cdot I_N$$

$H^0(B, S)$ = diamagnetic term + Heisenberg term + ...

$S \cdot \mathbf{D} \cdot S$ = zero field splitting

$S \cdot \mathbf{g} \cdot B$ = electron Zeeman term

$I_N \cdot \mathbf{g}_n \cdot B$ = nuclear Zeeman terms

$S \cdot \mathbf{A} \cdot I_N$ = hyperfine interaction terms

$I_M \cdot \mathbf{q}_{MN} \cdot I_N$ = nuclear spin-nuclear spin coupling terms

$$H^0(B, S)$$

diamagnetic term: no splittings, not observable in EPR

Heisenberg term: effects of near degeneracies (rare, biradicals)

$$S \cdot D \cdot S$$

contributions independent of magnetic field strength

1st order: spin-spin contact term (independent of M_S , neglected)

spin-spin dipolar term (vanishes if $S < 1$)

2nd order: spin-orbit corrections (smaller than 1st order contributions)

$$S \cdot g \cdot B$$

interaction of electron magnetic moments with the external field.

The relevant parameter is tensor \mathbf{g} .

1st order: kinetic energy corrections

gauge corrections to the Zeeman interactions

2nd order: spin-orbit cross terms

orbital Zeeman cross terms

$$I_N \cdot g_n \cdot B$$

This includes a first-order nuclear Zeeman term independent of the electronic wave function and additional 1st and 2nd order terms leading to the shielding tensor and chemical shift effects (usually very small in EPR)

$$S \cdot A \cdot I_N$$

- 1st order: Fermi contact term (isotropic)
dipolar hyperfine interaction (anisotropic)
- 2nd order: orbital hyperfine and spin-orbit cross terms (negligible)

Considering terms up to 1st order for a one-unpaired-electron system, tensor **A** includes only the isotropic and anisotropic terms

$$\mathbf{A} = A_0 \mathbf{1}_3 + \mathbf{T}$$

The **isotropic term** depends on a scalar

$$A_0 = \frac{2\mu_0}{3} g \beta_e g_N \beta_n \rho^{spin}(\mathbf{r}_N)$$

The **anisotropic term** depends on \mathbf{T} , a **real traceless and symmetric tensor**, whose general element is expressed as

$$T_{ij}^N = -\frac{\mu_0}{4\pi} g \beta_e g_N \beta_n \int \rho^{spin}(\mathbf{r}) \left(\frac{r^2 \delta_{ij} - 3r_i r_j}{r^5} \right) d\mathbf{r}$$

\mathbf{T} , which depends on the mutual orientation of the field and the crystal, can be transformed into diagonal form

$$\mathbf{T} = b \begin{pmatrix} \eta - 1 & 0 & 0 \\ 0 & -\eta - 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

so that at this level of approximation the hyperfine interaction in spectra can be interpreted in terms of three scalars:

A_0	isotropic hyperfine constant
b	anisotropic hyperfine constant
η	deviation from uniaxial symmetry

$$I_M \cdot \mathbf{q}_{MN} \cdot I_N$$

Effects of nuclear structure and finite nuclear size

- 1st order: **nuclear quadrupole term**
 direct dipole-dipole interaction (negligible in EPR)
- 2nd order: **coupling of nuclear spins** (negligible in EPR)

The only really important contribution in EPR is that from the **nuclear quadrupole** term ($M = N$). \mathbf{q} is a **real traceless and symmetric tensor**, whose general element is expressed as

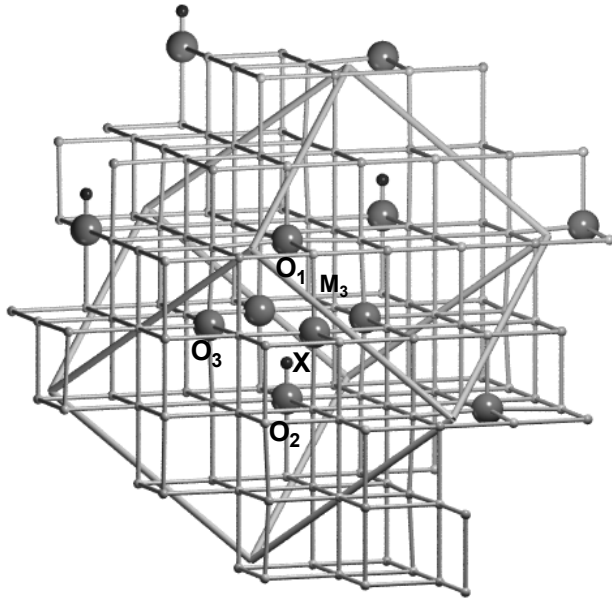
$$q_{ij}^N = \frac{e^2 Q_N}{4I(2I-1)h} \int \rho^{tot}(\mathbf{r}) \left(\frac{r^2 \delta_{ij} - 3r_i r_j}{r^5} \right) d\mathbf{r} = \frac{e Q_N}{4I(2I-1)h} e q_{ij}^{efg}$$

eQ_N and $e\mathbf{q}^{efg}$ denote the nuclear quadrupole moment and the **electric field gradient**, respectively. \mathbf{q} can be put in diagonal form

$$\mathbf{q} = P \begin{pmatrix} \eta - 1 & 0 & 0 \\ 0 & -\eta - 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

\mathbf{q} depends on two constants: P and η (deviation from uniaxial symmetry)

Electron holes in alkaline earth oxides



S_{16} supercell: 16 M^{2+} - O^{2-} ion pairs per cell

M = Mg, Ca, Sr

X = H, D, Li, Na

An electron hole is formed when a monovalent atom X is substituted for one divalent atom M in the oxide.

Formally:



The defective system is neutral and ionic, but one electron is lost after substitution has taken place:

the electron hole is localized at one O ion (O_1)

V_{OH} centres in alkaline earth oxides ($X = \text{H}$)

The substitution of H for M in alkaline earth oxides has been studied with the **Unrestricted Hartree-Fock (UHF)** approximation.

Relaxation (\AA) in $\text{MO}:[\text{H}]^0$ calculated with S_{16} .

System		Relaxed Atom			
		H	O ₁	O ₂	O ₃
MgO:[H] ⁰	Δz	-1.13	0.10	0.01	0.00
	Δr	—	—	—	0.11
CaO:[H] ⁰	Δz	-1.42	0.18	0.03	-0.01
	Δr	—	—	—	0.13
SrO:[H] ⁰	Δz	-1.62	0.24	0.03	0.00
	Δr	—	—	—	0.16

Displacements from the perfect lattice sites:

Δz along the O₁–H–O₂ axis
(positive sign: upward shift)

Δr radially and orthogonally
to the O₁–H–O₂ axis
(positive sign: outward shift)

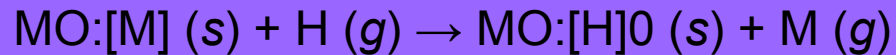
	Lattice parameter	O ₂ –H distance
MgO:[H] ⁰	4.21	0.969
CaO:[H] ⁰	4.83	0.965
SrO:[H] ⁰	5.19	0.947

Formation energy of V_{OH} centres

V_{OH} denotes a neutral cation vacancy, with formation of an hydroxyl group at O_2 and an electron hole at O_1

is formed upon irradiation

formation energy can be calculated for the following formal reaction:



Formation energy (hartree) of the $MO:[H]^0$ defect calculated with S_{16} .

System	ΔE	ΔE_H	$\Delta E_{H,O}$
MgO:[H] ⁰	0.429	0.297	0.279
CaO:[H] ⁰	0.427	0.242	0.217
SrO:[H] ⁰	0.443	0.233	0.204

ΔE : no relaxation, H at the perfect lattice site of M

ΔE_H : after relaxing H

$\Delta E_{H,O}$: after relaxing H and the six O nearest neighbours

Ionicity and spin distribution at V_{OH} centres

Net atomic charges (electrons) for the $MO:[H]^0$ defect calculated with S_{16} according to the Mulliken partition scheme of the electron charge density

System	H	O ₁	O ₂	O ₃	M ₃
MgO:[H] ⁰	0.545	-1.077	-1.592	-1.941	1.973
CaO:[H] ⁰	0.442	-1.054	-1.508	-1.907	1.941
SrO:[H] ⁰	0.383	-1.025	-1.416	-1.920	1.942

positive net charges correspond to an excess of nuclear charge

negative net charges correspond to an excess of electron charge

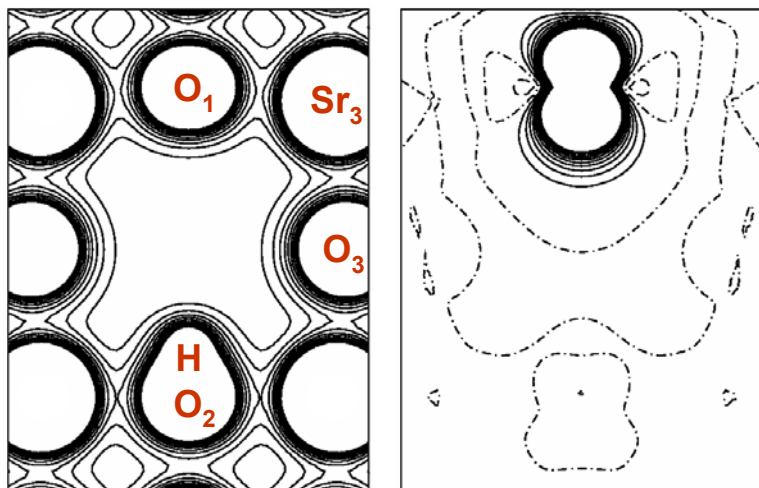
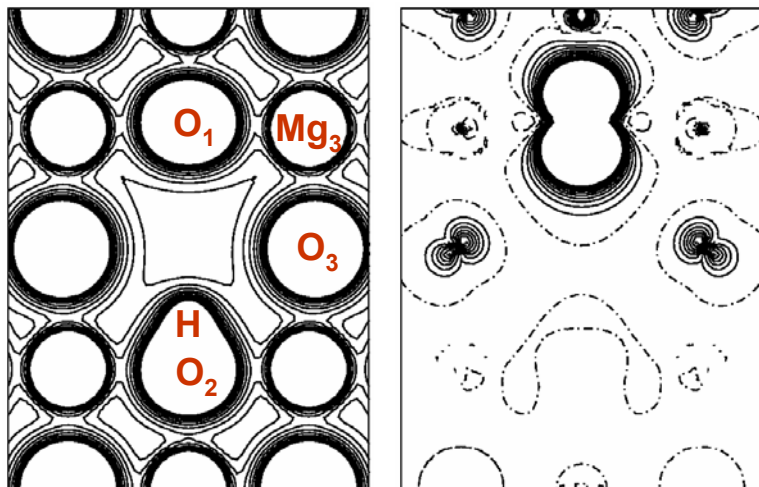
positive spin moments correspond to an excess of majority spin electrons (α)

negative spin moments correspond to an excess of minority spin electrons (β)

Spin moments (electrons) for the $MO:[H]^0$ defect calculated with S_{16} according to the Mulliken partition scheme of the electron spin density

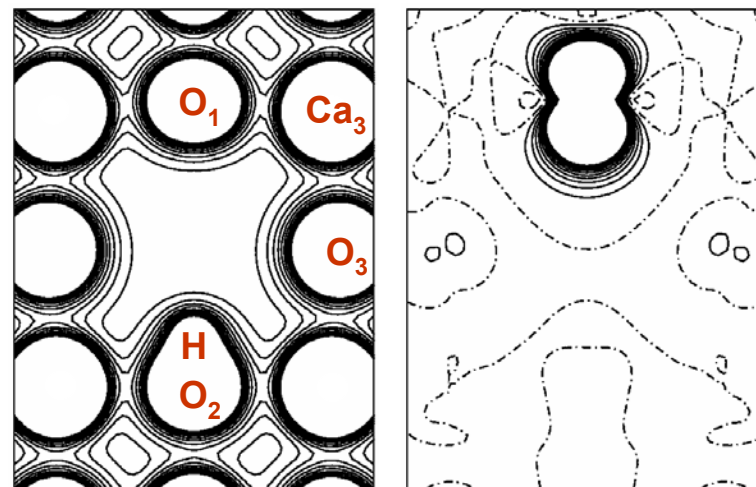
System	H	O ₁	O ₃
MgO:[H] ⁰	-0.001	0.974	0.004
CaO:[H] ⁰	0.000	0.986	0.001
SrO:[H] ⁰	0.000	0.991	0.001

Electron charge and spin densities at V_{OH}



Electron charge density maps:

$$\Delta\rho = 0.01 \text{ e/bohr}^3$$



Spin density maps:

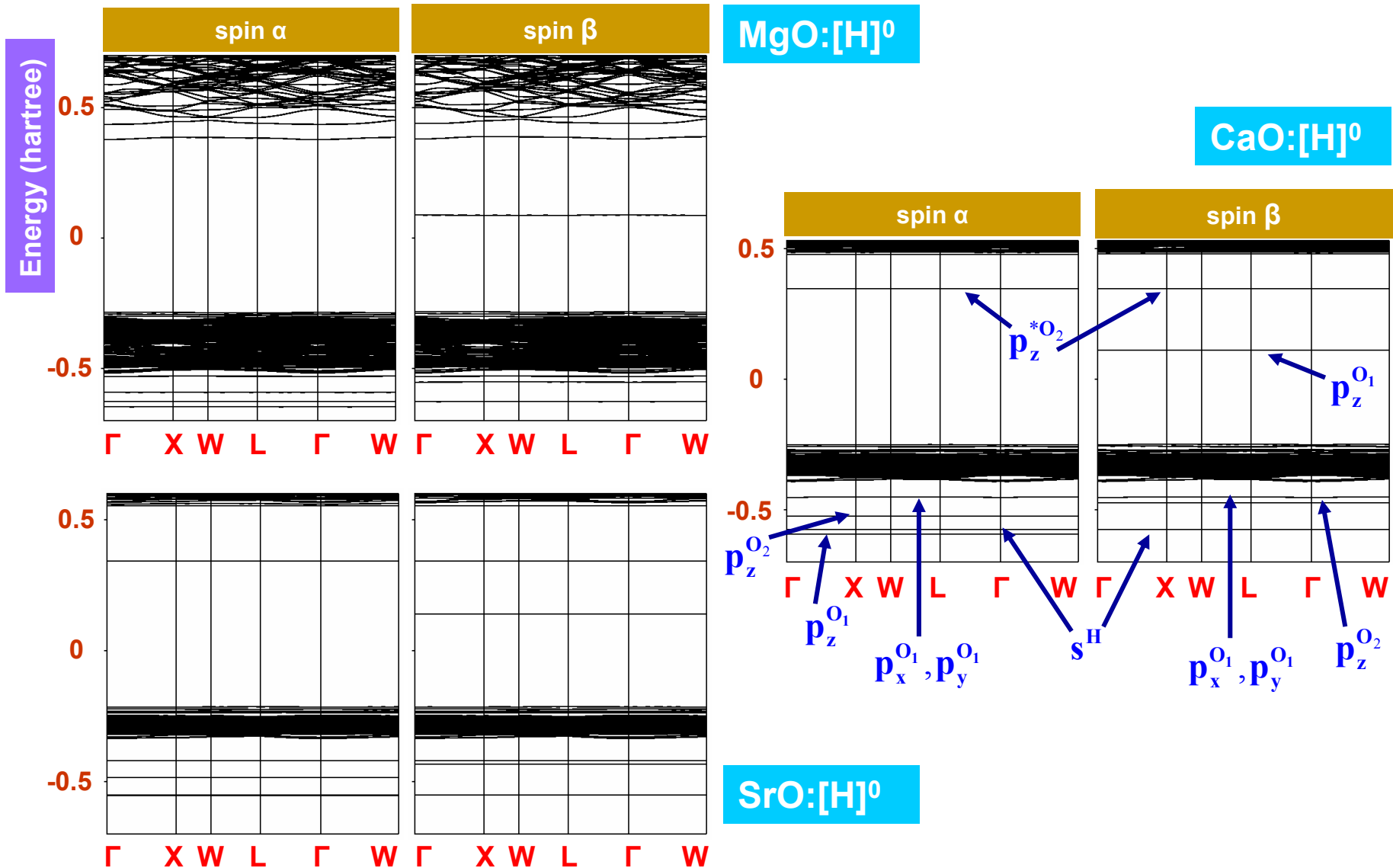
$$\Delta\rho = 0.001 \text{ e/bohr}^3$$

continuous lines: increase in α spin density

dashed lines: increase in β spin density

dot-dashed lines: zero spin density

Valence band structures of V_{OH} centres



EPR coupling constants for V_{OH} centres

Isotropic (a) and anisotropic (b) hyperfine coupling constants and nuclear quadrupole coupling constant (P) at H (D) for the MO:[H]⁰ (MO:[D]⁰) defect. The calculated values have been obtained with S_{48} .

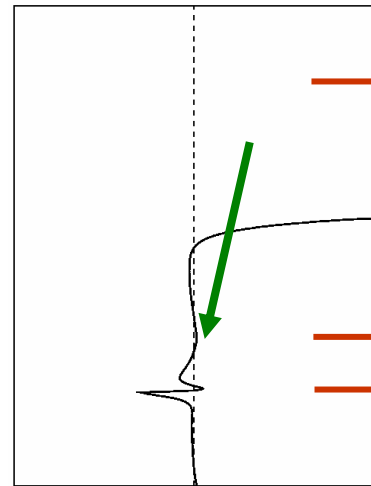
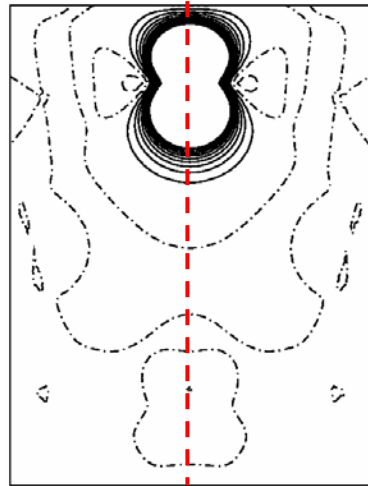
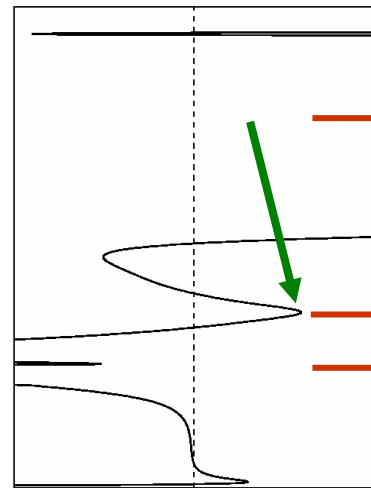
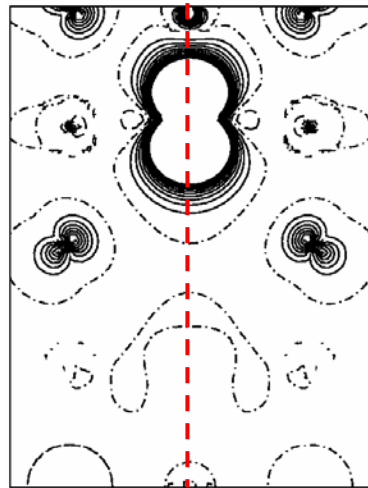
Units: MHz

$$a = A_0 \cdot 10^{-6} / h$$

The electron g factor has been approximated by the free electron g_e factor

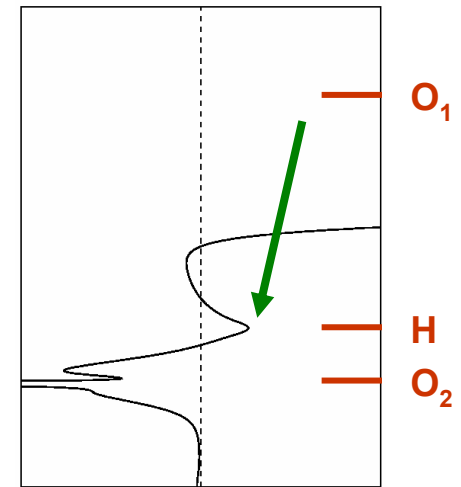
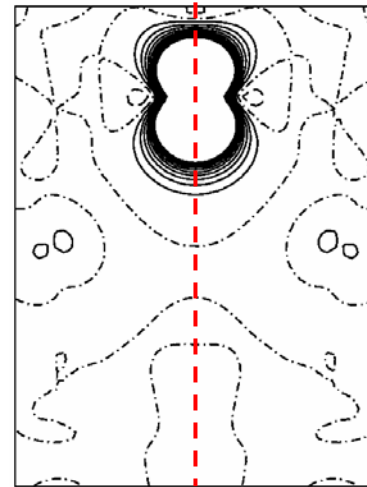
System	a		b		P	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
MgO:[H] ⁰	0.088	0.044	2.256	2.376		
		0.101		2.376		
		0.070		2.360		
MgO:[D] ⁰	0.014	0.007	0.346	0.363	0.160	0.173
CaO:[H] ⁰	0.030	0.028	1.323	±1.365		
		±0.011		1.365		
		0.026		1.356		
CaO:[D] ⁰	0.005	0.005	0.203	0.209	0.174	0.188
SrO:[H] ⁰	0.011	0.011	0.980	1.009		
		±0.010		±1.023		
SrO:[D] ⁰	0.002	0.007	0.150	0.195	0.202	0.158

Spin density along O_1-O_2 in V_{OH} centres



MgO:[H]⁰

Spin density profiles along the V_{OH} defect axis



CaO:[H]⁰

10^{-5} e/bohr^3

SrO:[H]⁰

10^{-5} e/bohr^3

Effect of the supercell size with V_{OH} centres

Importance of the supercell size in the determination of the defect formation energy $\Delta E_{H,O}$ (hartree), the isotropic (a) and anisotropic (b) hyperfine coupling constants and nuclear quadrupole coupling constant (P) at H for the $CaO:[H]^0$ defect.

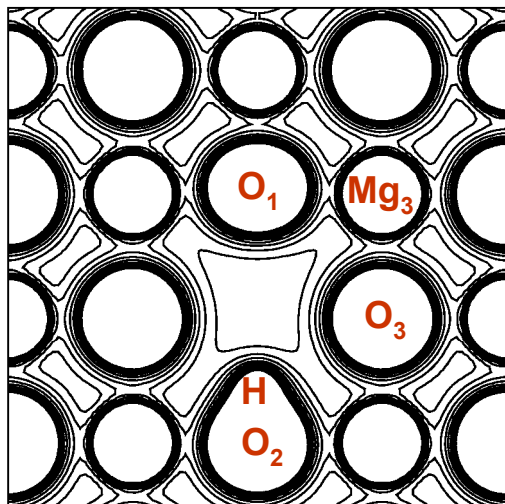
a and c cell parameters are given in units of the conventional CaO cell:

$$a_0 = 4.83 \text{ \AA}$$

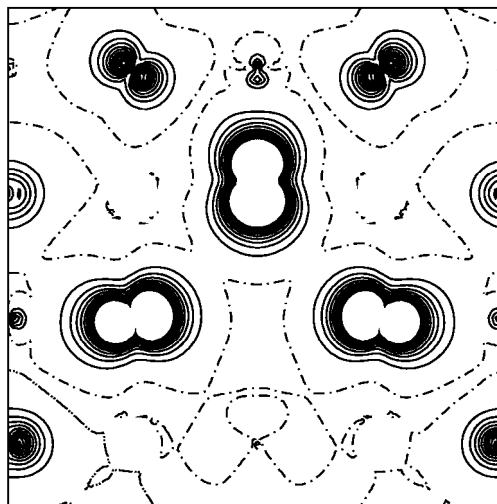
Cell	Lattice	a	c	α	$\Delta E_{H,O}$	a	b	P
S_{16}	I	$\sqrt{3} a_0$		109.5°	0.217	0.707	1.435	0.174
S_{32}	P	$2 a_0$		90°	0.225	0.731	1.771	0.174
S_{64}	F	$4 a_0$		60°	0.215	0.027	1.307	0.175
S_{24}	P	$\sqrt{2} a_0$	$3 a_0$		0.233	0.033	1.280	0.173
S_{32}	P	$\sqrt{2} a_0$	$4 a_0$		0.232	0.044	1.154	0.173
S_{48}	P	$2 a_0$	$3 a_0$		0.220	0.030	1.323	0.174
S_{64}	P	$2 a_0$	$4 a_0$		0.220	0.027	1.253	0.174
S_{80}	P	$2 a_0$	$5 a_0$		0.220	0.028	1.216	0.174
S_{96}	P	$2\sqrt{2} a_0$	$3 a_0$		0.216	0.028	1.371	0.174

V_{OH} centres with various Hamiltonians

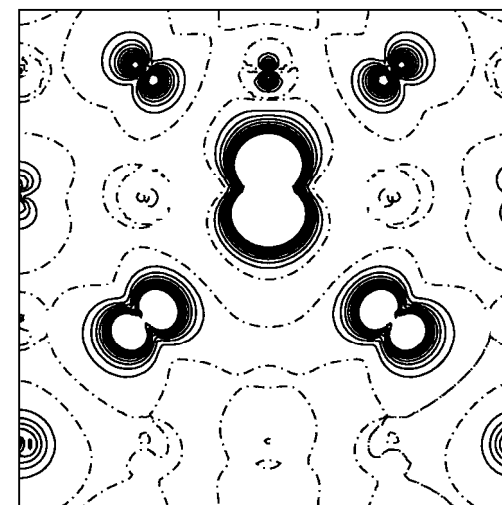
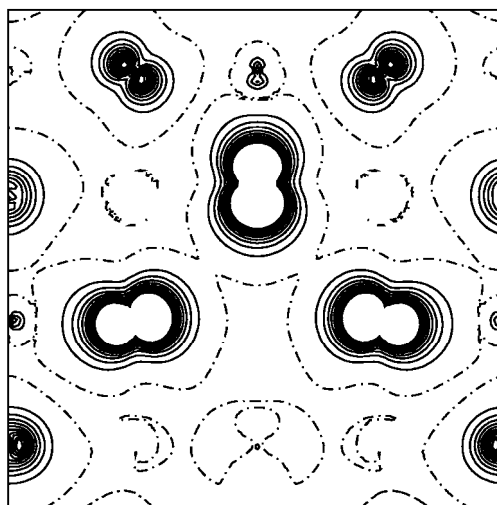
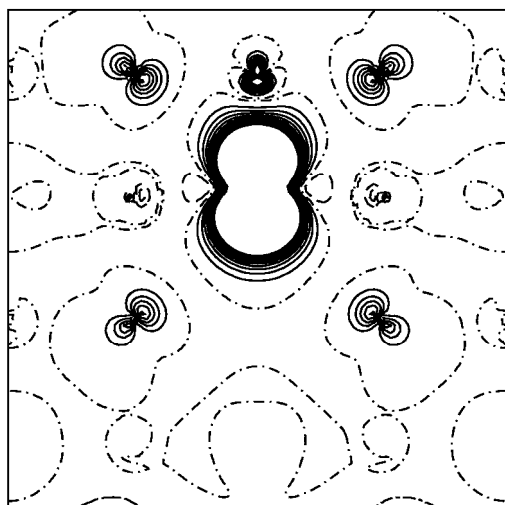
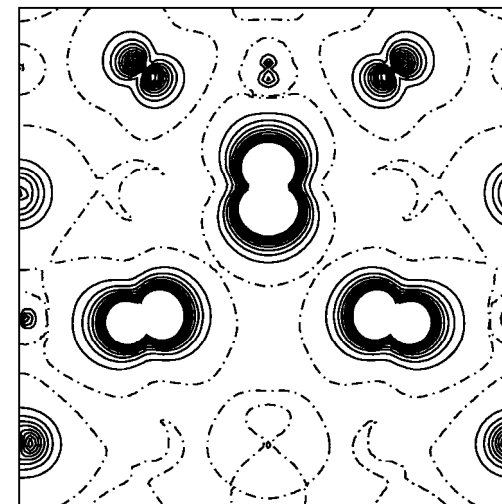
UHF



SPZ



PBE

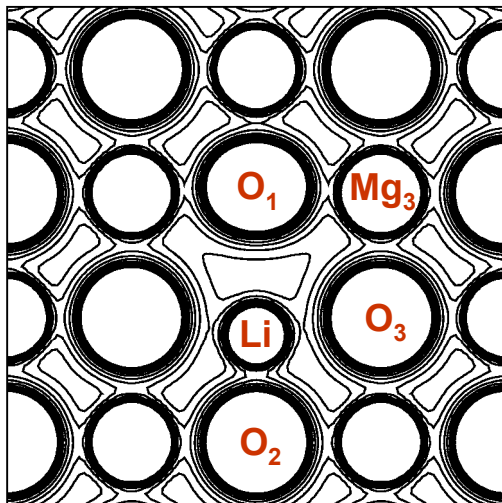


BLYP

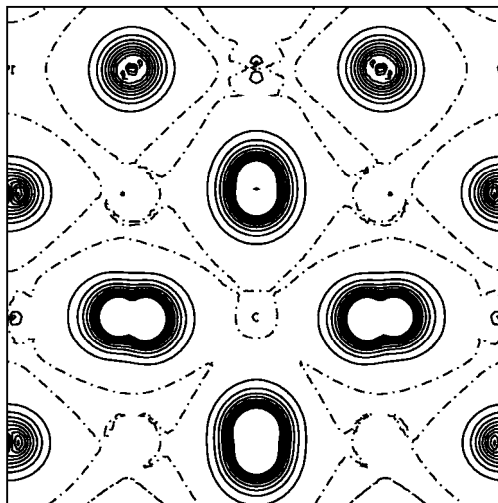
B3LYP

Li-doped MgO

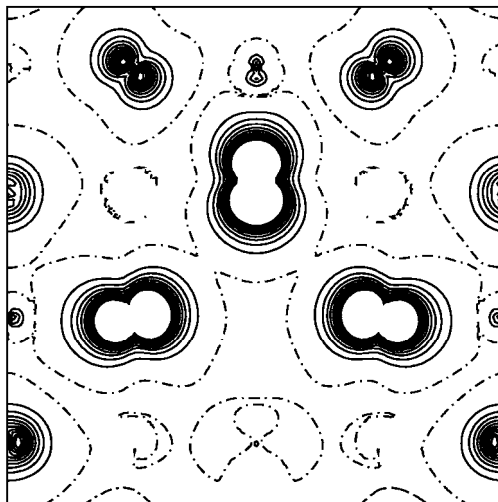
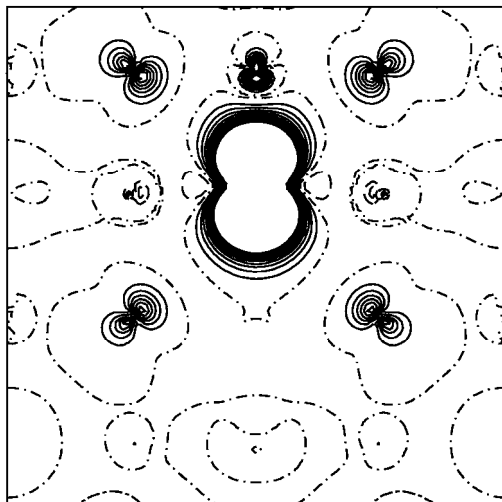
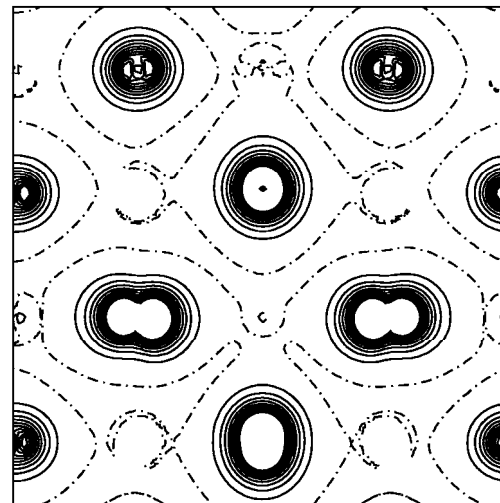
UHF



SPZ



PBE



BLYP

B3LYP

EPR constants for doped MgO

Isotropic (**a**) and anisotropic (**b**) hyperfine coupling constants and nuclear quadrupole coupling constant (**P**) at H for the MgO:[H]⁰ defect and at Li in MgO:[Li]⁰. The calculated values have been obtained with S₄₈.

Units: MHz

$$a = A_0 \cdot 10^{-6} / h$$

The electron *g* factor has been approximated by the free electron *g_e* factor

	MgO:[H] ⁰		MgO:[Li] ⁰		
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>P</i>
UHF	0.073	2.366	-2.393	2.258	-0.017
LDA	-0.256	-0.189	-3.691	-0.129	-0.003
BLYP	-0.694	-0.043	-3.078	0.092	-0.003
PBE	-0.379	0.115	-3.979	-0.202	-0.010
B3LYP	-0.074	1.142	-3.339	0.480	-0.004
Exp.	0.044	2.376	-4.539	2.313	-0.014
	0.101	2.371			
	0.070	2.360			

Exact exchange is crucial in the “correct” determination of spin density

Li/Na-doped alkaline earth oxides

System	M	O ₁	O ₂
MgO:[Li] ⁰	0.988	-1.084	-1.971
CaO:[Li] ⁰	0.980	-1.047	-1.932
SrO:[Li] ⁰	0.984	-1.025	-1.941
MgO:[Na] ⁰	1.114	-1.100	-1.998
CaO:[Na] ⁰	0.998	-1.053	-1.928
SrO:[Na] ⁰	0.986	-1.029	-1.937

Net atomic charges (electrons) for the MO:[Li]⁰ and MO:[Na]⁰ defects calculated with S₁₆ according to the Mulliken partition scheme of the **UHF** electron charge density.

System	M	O ₁	O ₂
MgO:[Li] ⁰	-0.001	0.964	0.000
CaO:[Li] ⁰	0.000	0.985	0.002
SrO:[Li] ⁰	0.000	0.990	0.003
MgO:[Na] ⁰	-0.004	0.970	0.000
CaO:[Na] ⁰	-0.002	0.986	0.003
SrO:[Na] ⁰	-0.001	0.990	0.004

Spin moments (electrons) for the MO:[Li]⁰ and MO:[Na]⁰ defects calculated with S₁₆ according to the Mulliken partition scheme of the **UHF** electron spin density

The unpaired electron is well localized at O₁, O₁ being essentially O⁻.

Li/Na-doped alkaline earth oxides

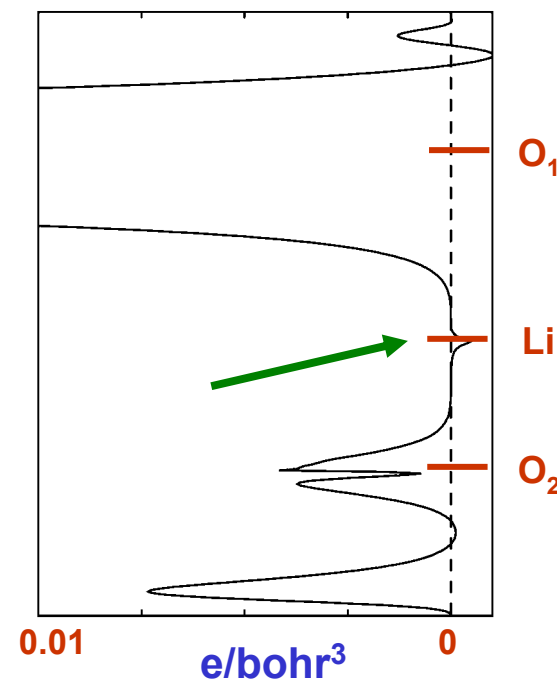
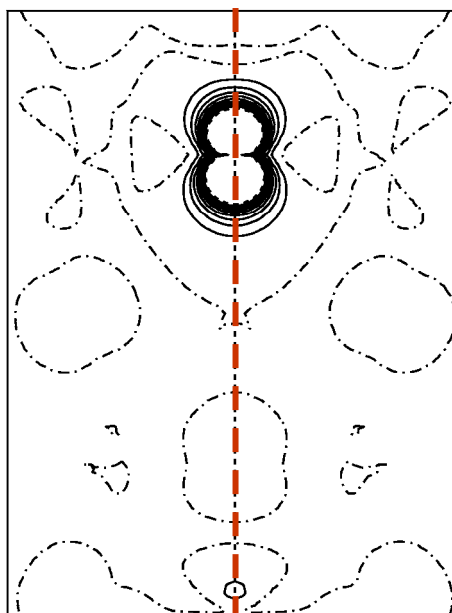
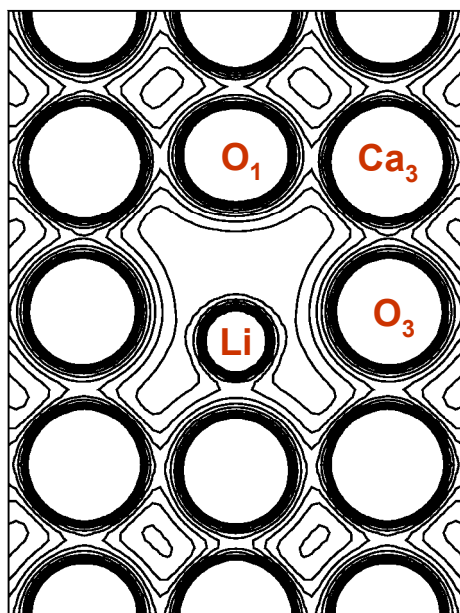
A. Lichanot, C. Larrieu, C. Zicovich-Wilson, C. Roetti, R. Orlando, R. Dovesi, *J. Phys. Chem. Solids* 59, 1119 (1998)

Isotropic (a) and anisotropic (b) hyperfine coupling constants and nuclear quadrupole coupling constant (P) at Li/Na for the $\text{MgO}:[\text{Li}/\text{Na}]^0$ defect. The calculated values have been obtained with S_{48} and the **UHF** approximation.

System	a		b		P	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
$\text{MgO}:[\text{Li}]^0$	-3.521	-4.539	2.580	2.313	-0.015	-0.014
$\text{CaO}:[\text{Li}]^0$	-0.819	-2.472	1.468	1.317	0.001	0.009
$\text{SrO}:[\text{Li}]^0$	-0.306	-1.198	1.060	0.866	0.012	0.013
$\text{MgO}:[\text{Na}]^0$	-1.715	-6.338	4.274	4.706	0.883	0.790
$\text{CaO}:[\text{Na}]^0$	-2.538	-9.145	1.558	1.877	0.449	0.446
$\text{SrO}:[\text{Na}]^0$	-1.620	-7.248	1.014	1.067	0.221	0.245

The accurate determination the isotropic hyperfine coupling constant a appears as critical: to what amount of spin density at the Li/Na nuclei do these values of a correspond?

Spin density in Li-doped CaO



The experimental technique is very sensitive to spin density: isotropic hyperfine coupling (constant a) at Li is determined by a very small amount of unbalanced spin density (β)

Sources of error in spin density calculations

- Lack of electron correlation: UHF does include part of the electron correlation as results from the exchange interaction, but disregards an important part of it; unfortunately, DFT cannot be used to estimate correlation in these cases, as no stable configuration with a localized unpaired electron is obtainable with DFT.
- UHF is a one-electron approximation for which eigenstates are not pure spin states; spin contamination is expected to affect spin density at the nuclei.
- Insufficient size of the supercell.
- Basis set inadequacies might be at the origin of a poor determination of spin density at nuclei.

EPR constants and basis set

Influence of the basis set in the UHF calculation of the isotropic (a) and anisotropic (b) hyperfine coupling constants and electric field gradient (P) at Li for the CaO:[Li]⁰ defect.

Basis set	a	b	P
A	-0.754	1.378	0.000
B	-0.626	1.379	0.001
C	-0.626	1.379	0.001
D	-0.774	1.363	0.002
E	-0.755	1.373	0.002

- A: 8-51G contraction for O
[Hay-Wadt] 31G(d) for Ca
6-11G contraction for Li
- B: same as A + decontraction of 1s shell of Li
- C: same as B + two p -type valence atomic orbitals for Li
- D: same as C, but 8-411G contraction for O
- E: same as D + one d polarization function for O

Improving the basis set does not correspond to real improvement in the hyperfine coupling constants.

Interionic distances in Li/Na-doped oxides

$M-O_1$ and O_1-O_2 distances (Å) in Li- and Na-doped alkaline earth oxides calculated with S_{48} and the UHF approximation.

Equilibrium geometry is one primary observable from *ab initio* calculations and is obtained by minimization of the total energy.

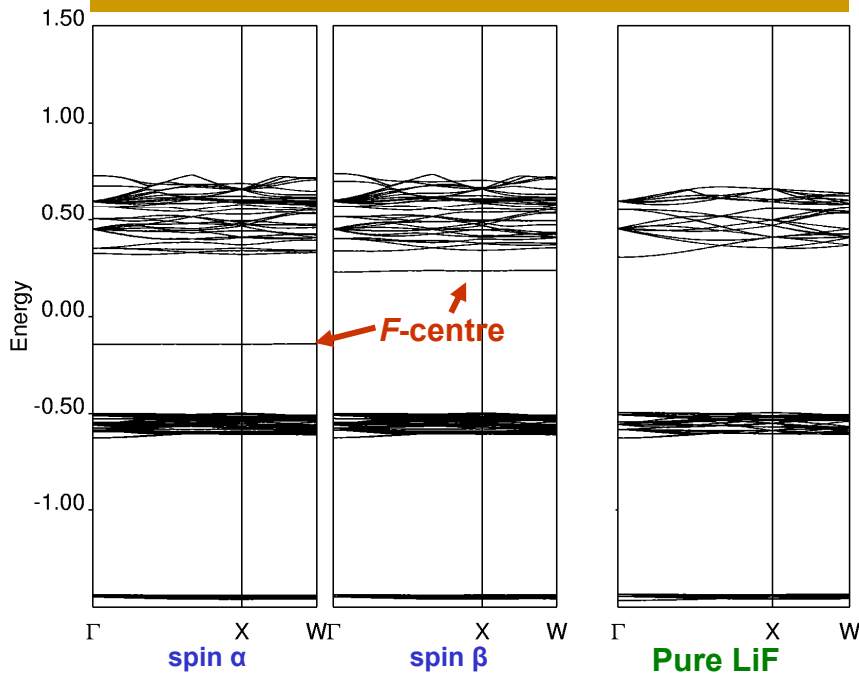
The spreading of the experimental values corresponds to the choice of various interpreting models used in their derivation from EPR data.

In parentheses: the lattice parameter of the conventional cubic cell.

System	$M-O_1$		O_1-O_2	
	Calc.	Exp.	Calc.	Exp.
MgO:[Li] ⁰	2.44	2.37–2.59	4.38	4.55
	(2.10)	2.56±0.17	(4.21)	
		2.55		
CaO:[Li] ⁰	2.91	2.86–3.05	5.04	5.02
	(2.52)	2.83±0.19	(4.83)	
SrO:[Li] ⁰	3.30	3.29–3.46	5.42	5.43
	(2.60)	3.56±0.51	(5.19)	
MgO:[Na] ⁰	2.30	1.64–1.91	4.39	4.21
	(2.10)		(4.21)	
CaO:[Na] ⁰	2.74	2.23–2.46	5.09	4.77
	(2.52)		(4.83)	
SrO:[Na] ⁰	3.02	2.70–2.90	5.47	5.21
	(2.60)		(5.19)	

F-centres in LiF

Valence and lower conduction band structure of an *F*-centre in LiF.



An *F*-centre is formed in LiF by abstraction of a Li atom: an unpaired electron localizes at the vacancy

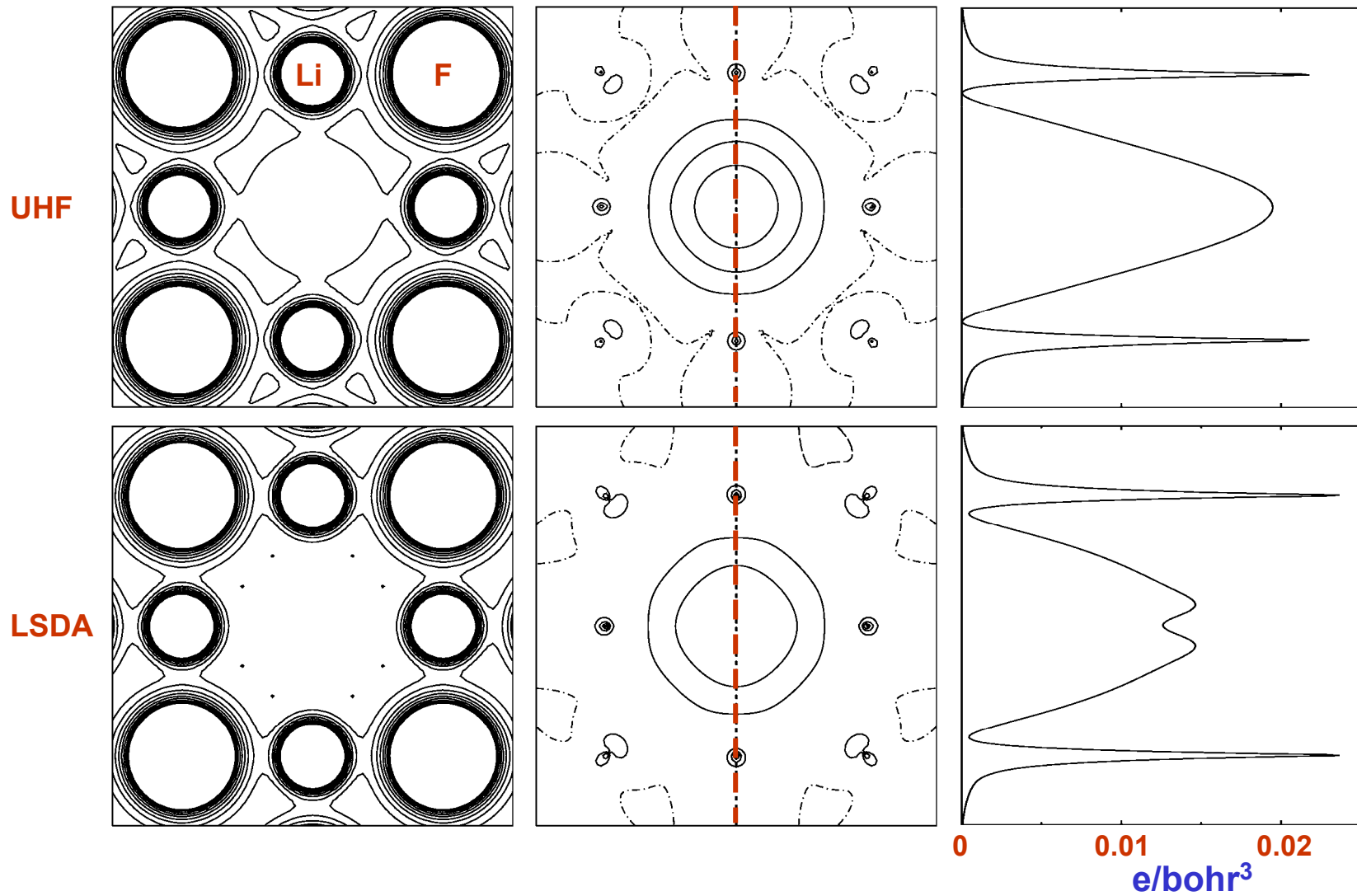
Net atomic charges (electrons) at an *F*-centre and its nearest neighbours in LiF calculated with S_{16} according to the Mulliken partition scheme of the electron charge density.

	<i>F</i> -centre	Li	F
UHF	-1.002	0.978	-0.975
LSDA	-0.887	0.986	-0.961

Mulliken spin moments (electrons) at an *F*-centre and its nearest neighbours in LiF.

	<i>F</i> -centre	Li	F
UHF	1.085	0.003	-0.009
LSDA	0.951	0.007	0.001

F-centres in LiF



EPR coupling constants for *F*-centres in LiF

Isotropic (*a*) hyperfine coupling constant at various neighbours of an *F*-centre in LiF. The calculated values have been obtained with S_{48} in the **UHF** and **LSDA** approximations.

	Li ₁₀₀	F ₁₁₀	Li ₁₁₁	F ₂₀₀	Li ₂₁₀	F ₂₁₁	F ₂₂₀
UHF	39.17	76.40	0.11	0.89	0.07	0.46	0.83
LSDA	47.20	145.20	1.49	-0.05	0.42	2.56	3.55
Exp.	39.06	105.94	0.50	0.48	0.27	0.88	1.34
δ_{UHF}	+0.3	-27.9	-78.4	+85.2	-73.3	-48.0	-38.4
δ_{LSDA}	+20.8	+37.1	+197.2	-110.4	+55.6	+191.1	+165.0

X_{hkl} denotes the X nucleus with cartesian coordinates (*h, k, l*) in units of Li⁺—F⁻ distance (1.995 Å)

δ percentage deviation from experiment

EPR coupling constants for *F*-centres in LiF

	Li ₁₀₀	F ₁₁₀	Li ₁₁₁	F ₂₀₀	Li ₂₁₀	F ₂₁₁	F ₂₂₀
UHF	3.25	11.47	0.72	1.17	0.34	0.66	0.43
LSDA	2.84	14.01	0.69	0.47	0.33	0.83	0.70
Exp.	3.20	14.96	0.68	1.12	0.28	0.69	0.56
δ_{HF}	+1.5	-23.3	+5.7	+4.2	+21.8	-3.9	-22.7
δ_{LDA}	-11.2	-6.4	+1.6	-57.7	+18.9	+19.9	+24.8

Anisotropic (*b*) hyperfine coupling constant at various neighbours of an *F*-centre in LiF. The calculated values have been obtained with S_{48} in the **UHF** and **LSDA** approximations.

Anisotropic ($c=b\eta$) hyperfine coupling constant at various neighbours of an *F*-centre in LiF. The calculated values have been obtained with S_{48} in the **UHF** and **LSDA** approximations.

	F ₁₁₀	Li ₂₁₀	F ₂₁₁	F ₂₂₀
UHF	0.38	0.00	0.03	0.07
LSDA	0.76	0.00	0.11	0.03

Conclusions

- The hyperfine structure of paramagnetic defects (electron holes) in alkaline earth oxides and alkali halides can be computed *ab initio* fairly accurately
- Despite of being a one-electron approximation (no correlation correction, no pure spin states), Unrestricted Hartree-Fock theory predicts most features of the hyperfine spectra correctly, mainly because of the presence of exact exchange
- The isotropic hyperfine coupling constant (Fermi contact) is the most delicate observable to calculate, because it depends on the very precise determination of an amount of spin density at a single point in space (a nucleus), where it can be extremely small.
- In some cases Density Functional Theory is unable to reproduced the localization of an unpaired electron in paramagnetic defects