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Hands-on Tutorial on Electronic Structure Computations

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NMR and EPR Spectroscopy (Part II)

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NMR and EPR spectroscopy (part II)

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based on material by

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Outline

- **PART I:**
  - Basic principles of magnetic resonance spectroscopy
  - Introduction to experimental NMR
  - Interpretation of NMR spectra
  - Solid state NMR
- **PART II:**
  - Effective NMR spin hamiltonian
  - The GIPAW method
  - Examples
  - Brief introduction to EPR spectroscopy and EPR parameters
- **PART III: (Emine Kuçukbenli)**
  - GIPAW pseudopotentials
  - The gipaw.x code: input file and description of the output

Effective NMR Hamiltonian

$$\mathcal{H}_S(\mathrm{NMR}) = -\hbar \sum_I \gamma_I \mathbf{B}_{\mathrm{ext}} \left(\bar{\bar{1}} - \bar{\bar{\sigma}}\right) \mathbf{I}_I$$

chemical shift

$$+ \frac{1}{2}\hbar^2 \sum_I \sum_{J \neq I} \gamma_I \gamma_J \mathbf{I}_I \left(\bar{\bar{\mathrm{D}}}_{IJ} + \bar{\bar{\mathrm{J}}}_{IJ}\right) \mathbf{I}_J$$

J coupling

$$+ \sum_{I, |\mathbf{I}_I| \geq 1} \mathbf{I}_I \bar{\bar{\mathrm{Q}}}_I \mathbf{I}_I$$

nuclear quadrupole (I>1/2)

$\mathbf{I}_I = \mathrm{Nuclear\ spin};\ \mu_I = \gamma_I \hbar \mathbf{I}_I\ ;\ \sigma = \mathrm{Nuclear\ chemical\ shielding\ tensor}$

$\bar{\bar{\mathrm{D}}}_{IJ} = \mathrm{Nuclear\ magnetic\ dipolar\ coupling\ tensor}$

$\bar{\bar{\mathrm{J}}}_{IJ} = \mathrm{Indirect\ nuclear\ spin} - \mathrm{spin\ coupling\ tensor}$

$\bar{\bar{\mathrm{Q}}}_{II} = \mathrm{Nuclear\ quarupolar\ coupling\ tensor}$

The chemical shift

From the NMR Hamiltonian the shielding tensor is defined as:

$$\mathbf{B}_{\mathrm{ind}} = -\bar{\bar{\sigma}}\mathbf{B}_{\mathrm{ext}}$$

It is the second derivative of energy w.r.t. field and nuclear moment:

$$\overleftrightarrow{\sigma}_I = \frac{\partial^2 E}{\partial \boldsymbol{\mu}_I \partial \mathbf{B}}$$

The chemical shift is then defined by:

$$\delta = -\left(\sigma - \sigma_{\mathrm{ref}}\right)$$

σ_{ref} is a reference value in a well-characterized material.

“Direct” and “converse” methods

Direct approach (traditional):

- linear response to external magnetic field
- calculate the induced current, then the induced field
- Mauri, Louie (1996); GIPAW: Pickard, Mauri (2001)

$$\overleftrightarrow{\sigma}_I = - \left. \frac{\partial \mathbf{B}_{\mathrm{ind}}}{\partial \mathbf{B}_{\mathrm{ext}}} \right|_{r=r_I}$$

$$\mathbf{B}_{\mathrm{ind}}(\mathbf{r}) = \frac{1}{c} \int d^3\mathbf{r}' \, \frac{\mathbf{j}_{\mathrm{ind}}(\mathbf{r}') \times (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}$$

Converse approach:

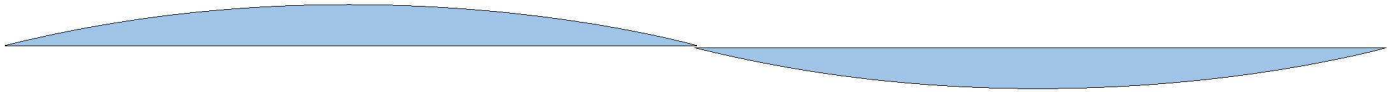
- no linear response, no magnetic field, no gauge-origin problem
- calculate the change of orbital magnetization due to nuclear magnetic moment
- based on the “Modern Theory of the Orbital Magnetization”

$$\overleftrightarrow{\sigma}_I = -\Omega \frac{\partial \mathbf{M}_{\mathrm{orb}}}{\partial \boldsymbol{\mu}_I}$$

$$\mathbf{M}_{\mathrm{orb}} = \frac{\alpha}{2} \mathrm{Im} \sum_{n\mathbf{k}} f_{n\mathbf{k}} \left\langle \partial_{\mathbf{k}} u_{n\mathbf{k}} \right| \times \left(H_{\mathbf{k}} + E_{n\mathbf{k}} - 2\mu \right) \left| \partial_{\mathbf{k}} u_{n\mathbf{k}} \right\rangle$$

Outline of linear response

Vector potential **A**(**r**)=(1/2)**B** x **r** is incompatible with crystal periodicity
Solution: apply a long-wavelength magnetic field (q << 1)



$$B(r) \propto \frac{\cos(q\,r)}{q}\hat{z} \qquad A(r) \propto \frac{\sin(q\,r)}{q}\hat{z}\times\hat{q}$$

The response to an incommensurate perturbation is obtained by Density Functional Perturbation Theory (DFPT):

DFPT to magn. field

Biot-Savart

$$|\phi^{(0)}_{n\sigma}\rangle \longrightarrow |\phi^{(1)}_{n\sigma}\rangle \longrightarrow \mathbf{j}^{(1)}_{\sigma}(\mathbf{r}') \longrightarrow \mathbf{B}^{(1)}_{\sigma}(\mathbf{r}')$$

GS wfcs — perturbed wfcs — induced current — induced field

EFG: electric field gradient tensor

Quadrupolar nuclei (I>1/2); non-zero only when no cubic symmetry:

$$\bar{\bar{\mathbf{Q}}}^{I}_{\alpha\beta} = \frac{eQ}{h} \langle \psi_0 | \frac{\delta \mathbf{E}_\alpha}{\delta \mathbf{r}_\beta} | \psi_0 \rangle = \frac{eQ}{h} \bar{\bar{\mathbf{V}}}_{\alpha\beta}$$

$$\mathbf{E} = \text{electric field} \; ; \; eQ = \text{electric quadrupole moment}$$

Principal axis system: Eigenvectors and -values of $\bar{\bar{\mathbf{V}}}_{\alpha\beta}$

Convention: $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$

Observables:

- Quadrupolar coupling constant $Cq = \frac{eQ\,V_{zz}}{h}$
- Asymmetry parameter $\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$

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GIPAW

PHYSICAL REVIEW B, VOLUME 63, 245101

All-electron magnetic response with pseudopotentials: NMR chemical shifts

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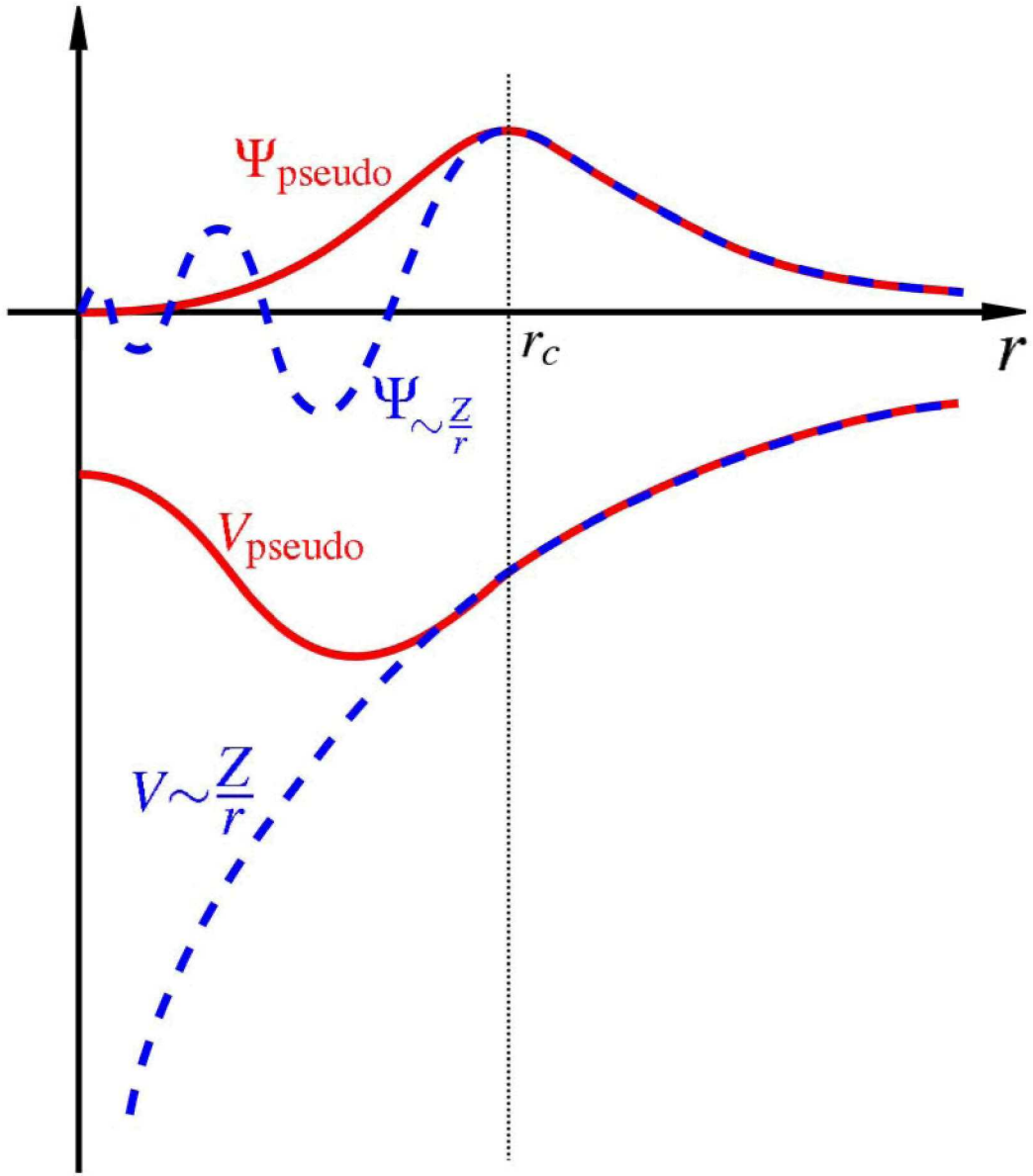
A theory for the *ab initio* calculation of all-electron NMR chemical shifts in insulators using pseudopotentials is presented. It is formulated for both finite and infinitely periodic systems and is based on an extension to the projector augmented-wave approach of Blöchl [P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994)] and the method of Mauri *et al.* [F. Mauri, B. G. Pfrommer, and S. G. Louie, Phys. Rev. Lett. **77**, 5300 (1996)]. The theory is successfully validated for molecules by comparison with a selection of quantum chemical results, and in periodic systems by comparison with plane-wave all-electron results for diamond.

DOI: 10.1103/PhysRevB.63.245101 PACS number(s): 71.45.Gm, 76.60.Cq, 71.15.−m

Need to reconstruct the wavefunction near the nuclei!

Pseudopotential / all-electron



AE wfc (blue) oscillates rapidly near the nucleus

PS wfc (red) smooth, no nodes in the core region

PAW idea

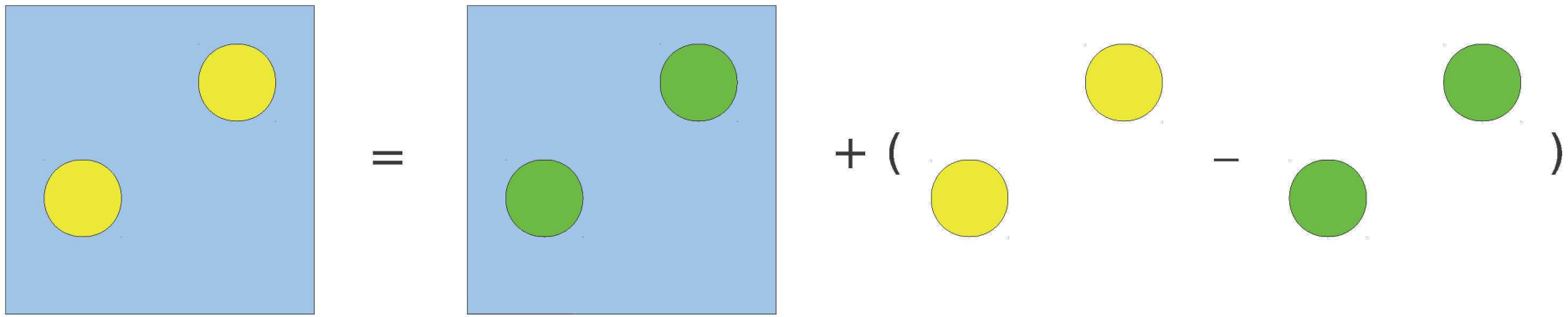
PAW (Blöchl, 1994) = projector augmented wave
Idea: “reconstruct” the AE wfc from the PS wfc

valence wfcs

$$|\psi^{\mathrm{AE}}\rangle = |\psi^{\mathrm{PS}}\rangle + \sum_{R,n} \left(|\phi^{\mathrm{AE}}_{r,n}\rangle - |\phi^{\mathrm{PS}}_{R,n}\rangle\right) \langle p_{R,n}|\psi^{\mathrm{PS}}\rangle$$

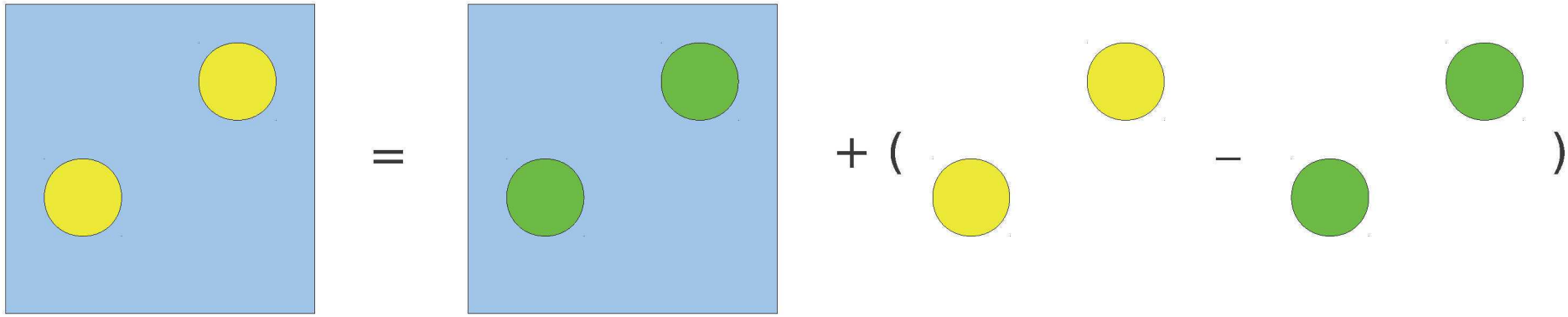
atomic partial waves

atomic projectors



PAW idea

$$|\psi^{\mathrm{AE}}\rangle = |\psi^{\mathrm{PS}}\rangle + \sum_{R,n} \left(|\phi^{\mathrm{AE}}_{r,n}\rangle - |\phi^{\mathrm{PS}}_{R,n}\rangle\right) \langle p_{R,n}|\psi^{\mathrm{PS}}\rangle$$



$$\mathcal{T} = 1 + \sum_{\mathbf{R},n} \left(|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle\right)\langle \tilde{p}_n|$$

$$|\Psi\rangle = \mathcal{T}|\tilde{\Psi}\rangle \qquad \langle\Psi|O|\Psi\rangle = \langle\tilde{\Psi}|\mathcal{T}^{\dagger}O\mathcal{T}|\tilde{\Psi}\rangle \qquad \tilde{O} = \mathcal{T}^{\dagger}O\mathcal{T}$$

$$\tilde{O} = O + \sum_{ij} |\tilde{p}_i\rangle[\langle\phi_i|O|\phi_j\rangle - \langle\tilde{\phi}_i|O|\tilde{\phi}_j\rangle]\langle\tilde{p}_j|$$

Gauge Including PAW

Hamiltonian in uniform magnetic field

$$H=\frac{1}{2}\left(\mathbf{p}+\frac{1}{c}\mathbf{A}(\mathbf{r})\right)^2+V(\mathbf{r}) \qquad \mathbf{A}(\mathbf{r})=\frac{1}{2}\mathbf{B}\times(\mathbf{r}-\mathbf{d})$$

$$H=\frac{1}{2}\mathbf{p}^2+V(\mathbf{r})+\frac{1}{2c}\mathbf{L}\cdot\mathbf{B}+\frac{1}{8c^2}(\mathbf{B}\times\mathbf{r})^2$$

Translation in magnetic field yields a gauge phase factor:

$$H'=\frac{1}{2}\left(\mathbf{p}+\frac{1}{c}\mathbf{A}(\mathbf{r})\right)^2+V(\mathbf{r}-\mathbf{t}) \qquad \Psi'(\mathbf{r})=e^{(i/2c)\mathbf{r}\cdot\mathbf{t}\times\mathbf{B}}\Psi(\mathbf{r})$$

from PAW $$\mathcal{T}=1+\sum_{\mathbf{R},n}(|\phi_{\mathbf{R},n}\rangle-|\tilde{\phi}_{\mathbf{R},n}\rangle)\langle\tilde{p}_n|$$

to GIPAW = PAW + magnetic field

$$\mathcal{T}_{\mathbf{B}}=\mathbf{1}+\sum_{\mathbf{R},n}e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}[|\phi_{\mathbf{R},n}\rangle-|\tilde{\phi}_{\mathbf{R},n}\rangle]\langle\tilde{p}_{\mathbf{R},n}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}$$

(1) wfc reconstruction (2) gauge-invariance

The GIPAW Hamiltonian

Hamiltonian in uniform magnetic field

$$H = \frac{1}{2}\left(\mathbf{p} + \frac{1}{c}\mathbf{A}(\mathbf{r})\right)^2 + V(\mathbf{r})$$

GIPAW transformation

$$\mathcal{T}_{\mathbf{B}} = \mathbf{1} + \sum_{\mathbf{R},n} e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}\left[|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle\right]\langle\tilde{p}_{\mathbf{R},n}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}$$

$$\bar{O} = T_{\mathbf{B}}^{+} O T_{\mathbf{B}}$$

$$\bar{O} = O + \sum_{\mathbf{R},n,m} e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\tilde{p}_{\mathbf{R},n}\rangle \times \left[\langle\phi_{\mathbf{R},n}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}} O e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\phi_{\mathbf{R},m}\rangle - \langle\tilde{\phi}_{\mathbf{R},n}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}} O e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\tilde{\phi}_{\mathbf{R},m}\rangle\right] \times \langle\tilde{p}_{\mathbf{R},m}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}$$

After some algebra...

$$\bar{H}^{(1)} = \frac{1}{2c}\left(\mathbf{L} + \sum_{\mathbf{R}} \mathbf{R}\times\frac{1}{i}[\mathbf{r}, V_{\mathbf{R}}^{\mathrm{nl}}] + \sum_{\mathbf{R}} \mathbf{L}_{\mathbf{R}} Q_{\mathbf{R}}\right)\cdot\mathbf{B}$$

$$Q_{\mathbf{R}} = \sum_{n,m} |\tilde{p}_{\mathbf{R},n}\rangle q_{\mathbf{R},nm}\langle\tilde{p}_{\mathbf{R},m}| \qquad q_{\mathbf{R},nm} = \langle\phi_{\mathbf{R},n}|\phi_{\mathbf{R},m}\rangle - \langle\tilde{\phi}_{\mathbf{R},n}|\tilde{\phi}_{\mathbf{R},m}\rangle$$

Calculating Shielding tensor

$$\mathbf{B}_{\text{in}}^{(1)}(\mathbf{r}) = -\vec{\sigma}(\mathbf{r})\mathbf{B}_{\text{ext}} = \frac{1}{c}\int d^3r'\,\mathbf{j}^{(1)}(\mathbf{r}') \times \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}$$

Current operator

$$\mathbf{J}(\mathbf{r}') = \mathbf{J}^d(\mathbf{r}') + \mathbf{J}^p(\mathbf{r}')$$

$$\mathbf{J}^d(\mathbf{r}') = \frac{1}{c}\mathbf{A}(\mathbf{r}')|\mathbf{r}'\rangle\langle\mathbf{r}'| \qquad \mathbf{J}^p(\mathbf{r}') = -\frac{\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p}}{2}$$

$$\Delta\mathbf{J}_{\mathbf{R}}^d(\mathbf{r}') = -\frac{\mathbf{B}\times(\mathbf{r}'-\mathbf{R})}{2c}\sum_{n,m}|\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|\mathbf{r}'\rangle\langle\mathbf{r}'|\phi_{\mathbf{R},m}\rangle - \langle\tilde{\phi}_{\mathbf{R},n}|\mathbf{r}'\rangle\langle\mathbf{r}'|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle\tilde{p}_{\mathbf{R},m}|$$

$$\Delta\mathbf{J}_{\mathbf{R}}^p(\mathbf{r}') = \sum_{n,m}|\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|\mathbf{J}^p(\mathbf{r}')|\phi_{\mathbf{R},m}\rangle - \langle\tilde{\phi}_{\mathbf{R},n}|\mathbf{J}^p(\mathbf{r}')|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle\tilde{p}_{\mathbf{R},m}|$$

Expanding in powers of B:

$$\bar{\mathbf{J}}^{(0)}(\mathbf{r}') = \mathbf{J}^p(\mathbf{r}') + \sum_{\mathbf{R}}\Delta\mathbf{J}_{\mathbf{R}}^p(\mathbf{r}')$$

$$\bar{\mathbf{J}}^{(1)}(\mathbf{r}') = -\frac{\mathbf{B}\times\mathbf{r}'}{2c}|\mathbf{r}'\rangle\langle\mathbf{r}'| + \sum_{\mathbf{R}}\left\{\Delta\mathbf{J}_{\mathbf{R}}^d(\mathbf{r}') + \frac{1}{2ci}[\mathbf{B}\times\mathbf{R}\cdot\mathbf{r}, \Delta\mathbf{J}_{\mathbf{R}}^p(\mathbf{r}')]\right\}$$

Calculating Shielding tensor

$$\bar{\mathbf{J}}^{(0)}(\mathbf{r}') = \mathbf{J}^{p}(\mathbf{r}') + \sum_{\mathbf{R}} \Delta\mathbf{J}^{p}_{\mathbf{R}}(\mathbf{r}')$$

induced current

$$\bar{\mathbf{J}}^{(1)}(\mathbf{r}') = -\frac{\mathbf{B}\times\mathbf{r}'}{2c}|\mathbf{r}'\rangle\langle\mathbf{r}'| + \sum_{\mathbf{R}}\left\{\Delta\mathbf{J}^{d}_{\mathbf{R}}(\mathbf{r}') + \frac{1}{2ci}[\mathbf{B}\times\mathbf{R}\cdot\mathbf{r}, \Delta\mathbf{J}^{p}_{\mathbf{R}}(\mathbf{r}')]\right\}$$

$$\mathbf{j}^{(1)}(\mathbf{r}') = 2\sum_{o}\left[\langle\bar{\Psi}^{(1)}_{o}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}^{(0)}_{o}\rangle + \langle\bar{\Psi}^{(0)}_{o}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}^{(1)}_{o}\rangle + \langle\bar{\Psi}^{(0)}_{o}|\bar{\mathbf{J}}^{(1)}(\mathbf{r}')|\bar{\Psi}^{(0)}_{o}\rangle\right]$$

$$\bar{H}^{(1)} = \frac{1}{2c}\left(\mathbf{L} + \sum_{\mathbf{R}}\mathbf{R}\times\frac{1}{i}[\mathbf{r}, V^{nl}_{\mathbf{R}}] + \sum_{\mathbf{R}}\mathbf{L}_{\mathbf{R}}Q_{\mathbf{R}}\right)\cdot\mathbf{B}$$

$$\mathbf{B}^{(1)}_{in}(\mathbf{r}) = -\vec{\sigma}(\mathbf{r})\mathbf{B}_{ext} = \frac{1}{c}\int d^{3}r'\,\mathbf{j}^{(1)}(\mathbf{r}')\times\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^{3}}$$

All needed first order wfc variations can be calculated b
DFPT

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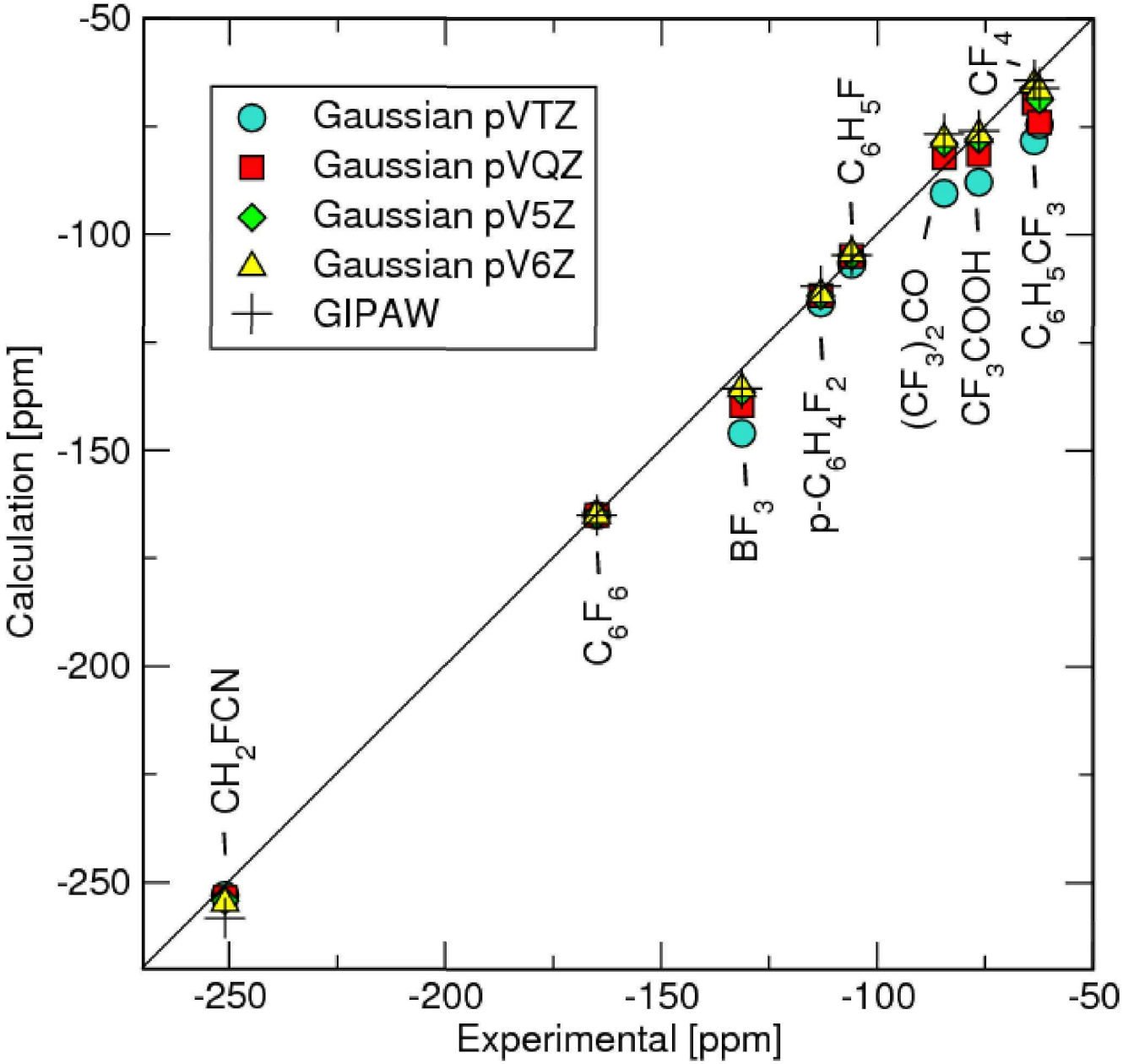
Example: molecules

Molecule	Core	σ_{GIPAW} bare	Δd	Δp	Total	σ_{IGAIM} Total
H atom						
CH_4	0.00	30.47	0.40	0.00	30.87	30.99
CH_3F	0.00	25.71	0.41	0.00	26.13	26.50
C_6H_6	0.00	22.33	0.41	0.00	22.74	23.25
TMS	0.00	30.41	0.40	0.00	30.80	31.02
SiH_3F	0.00	24.92	0.38	0.00	25.30	25.13
Si_2H_4	0.00	24.53	0.36	0.00	24.90	24.78
SiH_4	0.00	26.96	0.37	0.00	27.33	27.28
C atom	1*s*					
CO	198.88	−126.25	4.59	−100.15	−22.93	−21.16
CH_4	198.88	16.86	3.97	−28.76	190.96	191.22
CH_3F	198.88	−49.64	3.93	−54.70	98.47	99.66
CH_3NH_2	198.88	−13.98	3.91	−39.05	149.77	150.44
C_6H_6	198.88	−89.51	4.07	−77.32	36.12	39.52
CF_4	198.88	−92.12	3.51	−76.05	34.22	35.29
TMS	198.88	9.12	3.97	−32.65	179.33	182.08
Si atom	1*s*2*s*2*p*					
SiF_4	832.39	−19.43	5.28	−408.26	409.97	409.69
SiH_3F	832.39	−19.50	5.70	−510.30	308.29	305.45
Si_2H_4	832.39	−9.04	5.80	−622.45	206.70	202.99
SiH_4	832.39	−0.21	5.98	−410.20	427.97	424.37
TMS	832.39	−17.39	5.70	−518.00	302.70	304.39
P atom	1*s*2*s*2*p*					
PF_3	902.47	−32.94	6.08	−697.61	178.00	172.52
P_2	902.47	−33.84	7.58	−1236.95	−360.75	−375.45
P_4	902.47	49.84	7.42	−126.79	832.94	826.62

red = GIPAW
Blue=Gaussian™

Pickard, Mauri
PRB **63**, 245101 (2001)

Example: ^{19}F



GIPAW ~ Gaussian 6Z
(140 basis/atom)

Ceresoli, Marzari, Lopez, Thonhauser
PRB **81**, 184424 (2010)

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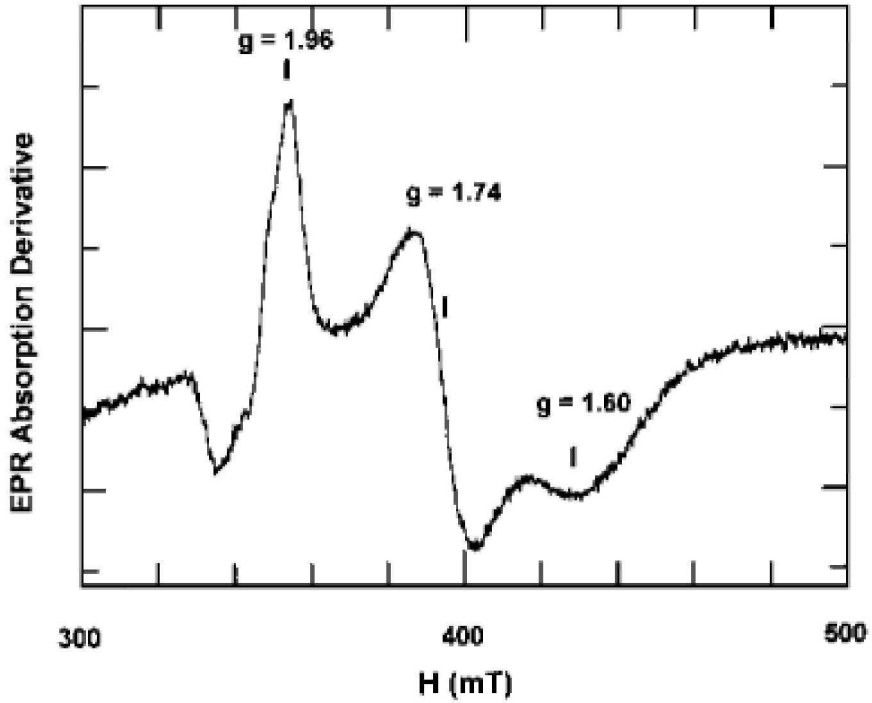
EPR/ESR spectroscopy

Electron Paramagnetic Resonance / Electron Spin Resonance

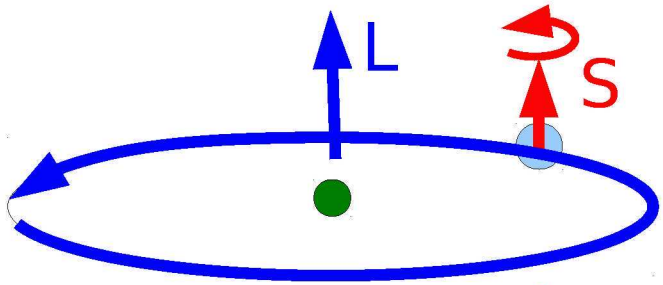


Tipical fields ~0.5 T
Resonance ~14 GHz

- Paramagnetic defects in solids, radicals in proteins
- Sensitive to local geometry and electronic structure (charge, hybridization)
- Non destructive, small samples, dilute spins

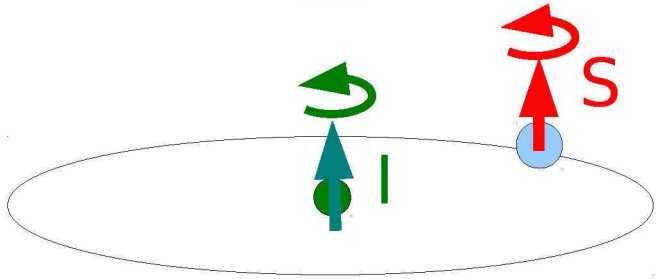
Interpretation of EPR spectra

$$B_{tot} = B_{ext} + B_{ind}$$



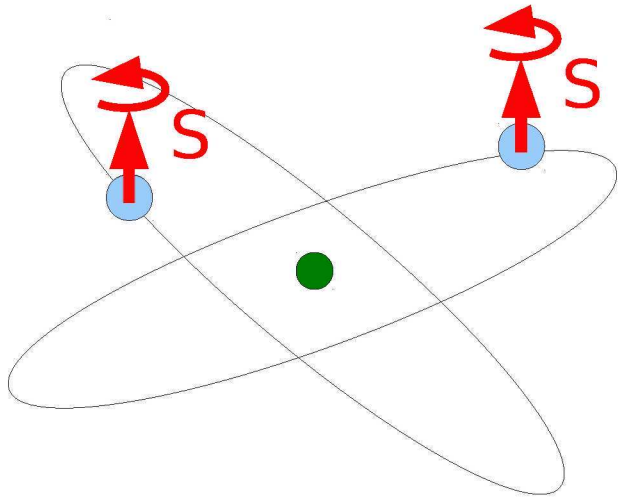
Spin-Orbit, SOO

$$+ B_{nucl}$$



Hyperfine

$$+ B_{other\text{-}spin}$$



Zero Field Splitting

Effective Spin Hamiltonian

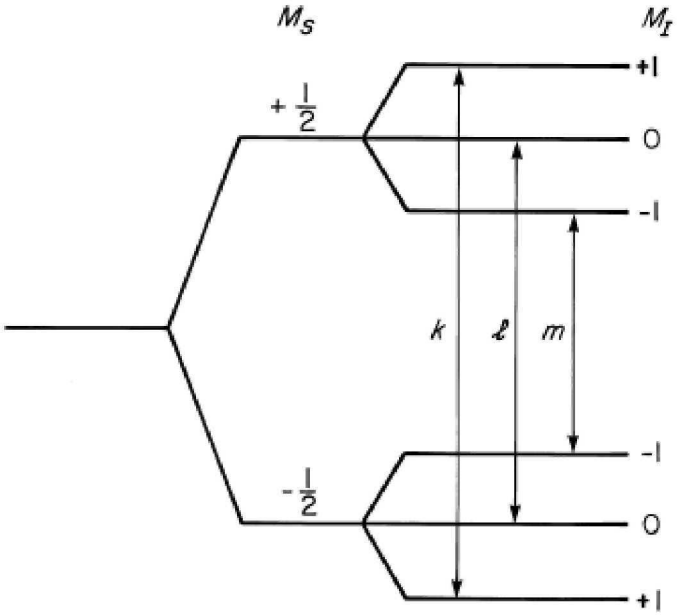
$$\mathcal{H}_{\text{eff}} = \frac{\alpha}{2}\mathbf{S}\cdot\overleftrightarrow{g}\cdot\mathbf{B} + \sum_R \mathbf{S}\cdot\overleftrightarrow{A}_R\cdot\mathbf{I}_R + \mathbf{S}\cdot\overleftrightarrow{D}\cdot\mathbf{S}$$

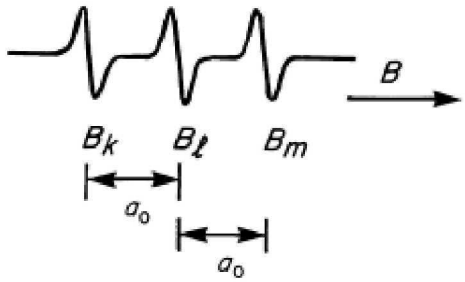
$\alpha = 1/c$

g-tensor

hyperfine

ZFS





Selection rules:

$|\Delta M_S| = 1$

$|\Delta M_I| = 0$

Zero Field Splitting

In case: S > 1/2

$$\mathcal{H}_{\mathrm{ZFS}} = \frac{g_e\,\mu_B}{r^5}\left[(\mathbf{s}_1\cdot\mathbf{s}_2)\,r^2 - 3\,(\mathbf{s}_1\cdot\mathbf{r})\,(\mathbf{s}_2\cdot\mathbf{r})\right]$$

- Two electron integrals
- Usually small (?)
- Not implemented in Espresso

$$\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$$

Theory of EPR parameters

The effective spin Hamiltonian allows to extract EPR parameters from the experiments, but in order to calculate EPR parameters, we need a “physical” Hamiltonian. The simplest non-relativistic Hamiltonian that accounts for spin is the Pauli Hamiltonian:

Mass velocity and Darwin

$$\mathcal{H}_{\text{Pauli}} = \frac{p^2}{2m} + V(\mathbf{r}) - \frac{1}{8c^2}(p^4 - \nabla^2 V) +$$

$$+ \frac{g_e}{2c}\mathbf{S}\cdot\mathbf{B} - \frac{g_e}{2c^3}\frac{p^2}{2}\mathbf{S}\cdot\mathbf{B} +$$

Zeeman and Zeeman-KE

$$+ \frac{g'}{4c^2}\mathbf{S}\cdot(\nabla V \times \mathbf{p}) + \mathcal{H}_{\text{SOO}} + \cdots$$

Spin orbit

Spin other-orbit

$g_e = 2.0023192778$ $g' = 2(g_e - 1)$ $c = 1/\alpha = 137.03599$

$\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}$ ($\boldsymbol{\sigma}$ = Pauli matrixes)

… plus other terms

Table 2.2. Partial listing of $\mathcal{O}(\alpha^2)$ terms of the approximate Hamiltonian.

Label	Description	Operator
	Scalar relativistic corrections	
h^{mv}	Mass-velocity term	$-\frac{1}{8}\alpha^2 \sum_i \nabla_i^4$
$h^{\mathrm{Dar}(1)}$	Electron-nuclear Darwin term	$\frac{\pi}{2}\alpha^2 \sum_{i,K} Z_K \delta(\mathbf{r}_{iK})$
$h^{\mathrm{Dar}(2)}$	Electron-electron Darwin term	$-\frac{\pi}{2}\alpha^2 \sum'_{i,j} \delta(\mathbf{r}_{ij})$
h^{OO}	Electron-electron orbital interaction	$\frac{1}{4}\alpha^2 \sum'_{i,j} \frac{\nabla_i \cdot \nabla_j}{r_{ij}} - \frac{(\nabla_i \cdot \mathbf{r}_{ij})(\mathbf{r}_{ij} \cdot \nabla_j)}{r_{ij}^3}$
	Spin-dependence, no field-dependence	
	Electron spin	
$h^{\mathrm{SO}(1)}$	Spin-orbit interaction	$\frac{1}{4}\alpha^2 g_e \sum_{i,K} \frac{Z_K}{r_{iK}^3} \mathbf{s}_i \cdot \mathbf{l}_{iK}$
$h^{\mathrm{SSO}(2)}$	Electron-electron spin-orbit interaction	$-\frac{1}{4}\alpha^2 g_e \sum_{i,j}{}' \mathbf{s}_i \cdot \frac{\mathbf{l}_{ij}}{r_{ij}^3}$
$h^{\mathrm{SOO}(2)}$	Electron-electron spin-other-orbit interaction	$-\frac{1}{2}\alpha^2 g_e \sum'_{i,j} \mathbf{s}_j \cdot \frac{\mathbf{l}_{ij}}{r_{ij}^3}$
$h^{\mathrm{SSD}(2)}$	Spin-spin dipolar interaction	$\frac{1}{4}\alpha^2 g_e^2 \sum'_{i,j} \frac{r_{ij}^2 (\mathbf{s}_i \cdot \mathbf{s}_j) - (\mathbf{s}_i \cdot \mathbf{r}_{ij})(\mathbf{r}_{ij} \cdot \mathbf{s}_j)}{r_{ij}^5}$
$h^{\mathrm{SSC}(2)}$	Spin-spin contact interaction	$-\frac{\pi g_e^2}{3}\alpha^2 \sum'_{i,j} \mathbf{s}_i \cdot \mathbf{s}_j \delta(\mathbf{r}_{ij})$
	Nuclear spin	
h_K^{PSO}	Orbital hyperfine interaction	$\alpha^2 \gamma_K \sum_i \mathbf{l}_K \cdot \frac{\mathbf{l}_{iK}}{r_{iK}^3}$
	Electron and nuclear spins	
h_K^{SD}	Dipolar hyperfine interaction	$\frac{1}{2}\alpha^2 g_e \gamma_K \sum_i \mathbf{s}_i \cdot \frac{3\mathbf{r}_{iK}\mathbf{r}_{iK} - 1 r_{iK}^2}{r_{iK}^5} \cdot \mathbf{I}_K$
h_K^{FC}	Fermi contact hyperfine interaction	$\frac{4\pi}{3}\alpha^2 g_e \gamma_K \sum_i \delta(\mathbf{r}_{iK}) \mathbf{s}_i \cdot \mathbf{I}_K$

From: Pekka Manninen PhD thesis, University of Oulo, Finland (2004).
http://herkules.oulu.fi/isbn9514274318/

g-tensor: the easy part

From the effective spin Hamiltonian, the g-tensor is defined as:

$$\overleftrightarrow{g} = \frac{2}{\alpha}\frac{\partial^2 \mathcal{H}}{\partial \mathbf{S} \partial \mathbf{B}}$$

The Zeeman and Zeeman-Kinetic Energy term yield:

$$\overleftrightarrow{g}_{\mathrm{Z}} = g_e \overleftrightarrow{1}$$

$$\Delta\overleftrightarrow{g}_{\mathrm{Z-KE}} = -\frac{g_e \alpha^2}{2}\left(\sum_{S=\pm 1/2} S\, T_S\right)\overleftrightarrow{1}$$

Kinetic energy of occupied orbitals

g-tensor: SO and SOO

The SO and SOO don't depend explicitly on the magnetic field, but implicitly through the wavefunctions. Their contribution can be calculated in perturbation theory:

DFPT to magn. field

Biot-Savart

$$|\phi_{n\sigma}^{(0)}\rangle \longrightarrow |\phi_{n\sigma}^{(1)}\rangle \longrightarrow \mathbf{j}_{\sigma}^{(1)}(\mathbf{r}') \longrightarrow \mathbf{B}_{\sigma}^{(1)}(\mathbf{r}')$$

GS wfcs — perturbed wfcs — induced current — induced field

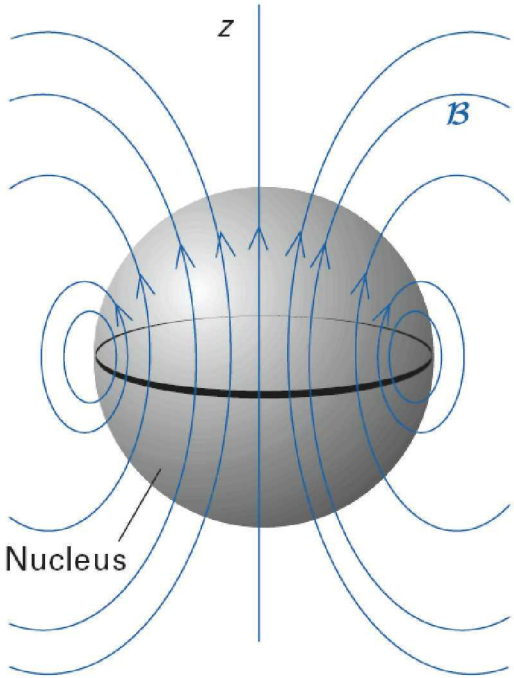
Finally:

$$\Delta\overleftrightarrow{g}_{\mathrm{SO}} = \alpha^2 g' \sum_{S=\pm 1/2} S \int d^3\mathbf{r}'\, \nabla V(\mathbf{r}') \times \overleftrightarrow{j}_{S}^{(1)}(\mathbf{r}')$$

$$\Delta\overleftrightarrow{g}_{\mathrm{SOO}} \simeq \alpha \sum_{S=\pm 1/2} S \int d^3\mathbf{r}'\, \overleftrightarrow{B}_{S}^{(1)}(\mathbf{r}')\rho_S(\mathbf{r}')$$

Hyperfine coupling

$$\overleftrightarrow{A}_R = \left\langle \frac{\partial^2 \mathcal{H}}{\partial \mathbf{S}\, \partial \boldsymbol{I}_R} \right\rangle = A_{\mathrm{iso,R}} \overleftrightarrow{1} + \overleftrightarrow{A}_{\mathrm{dip,R}}$$



Isotropic (Fermi-contact)

$$A_{\mathrm{iso}} = \frac{4\pi}{3} \frac{g_e\, \mu_e\, g_N\, \mu_N}{S} \int d^3\mathbf{r}\, n_s(\mathbf{r}) \delta(\mathbf{r})$$

$$\mathbf{r} \equiv \mathbf{r} - \mathbf{R}$$

Dipolar (traceless)

$$A^{\alpha\beta}_{\mathrm{dip}} = \frac{1}{2} \frac{g_e\, \mu_e\, g_N\, \mu_N}{S} \int d^3\mathbf{r}\, n_s(\mathbf{r}) \frac{3 r_\alpha r_\beta - \delta_{\alpha\beta} r^2}{r^5}$$

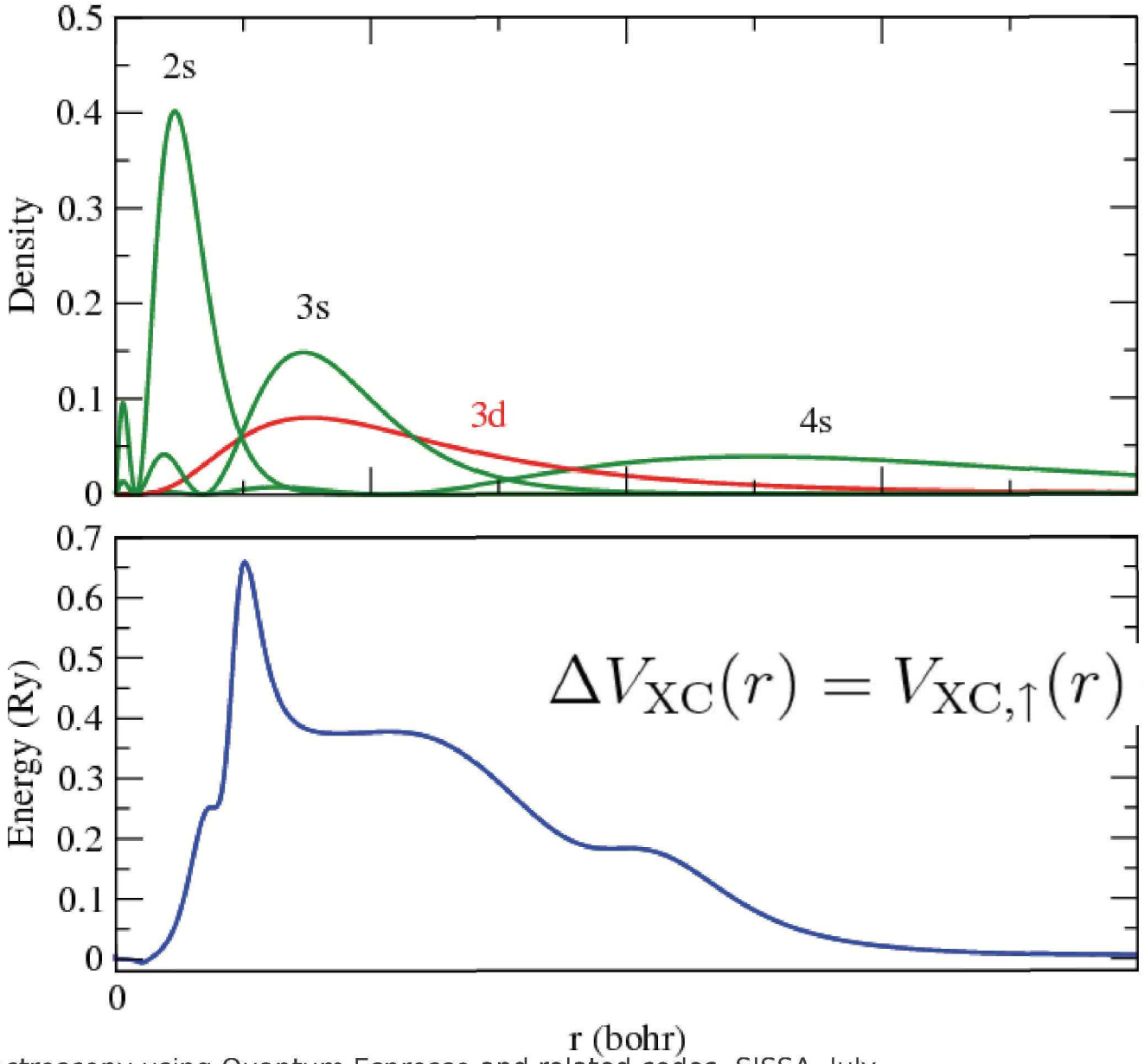
Spin density: $n_s(\mathbf{r}) = n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})$

Spin densities of isolated atoms

Atom	Configuration	1s	2s	3s	4s	Total
Li	$2s(1\uparrow,0\downarrow)$	0.003	0.219			0.222
C	$2s^2\ 2p(2\uparrow,0\downarrow)$	-0.199	0.178			-0.021
N	$2s^2\ 2p(3\uparrow,0\downarrow)$	-0.440	0.429			-0.011
O	$2s^2\ 2p(3\uparrow,1\downarrow)$	-0.417	0.437			0.019
Na	$3s(1\uparrow,0\downarrow)$	0.019	-0.030	0.810		0.799
Si	$3s^2\ 3p(2\uparrow,0\downarrow)$	-0.094	0.056	-0.193		-0.232
Mn	$4s^2\ 3d(5\uparrow,0\downarrow)$	-0.008	-2.203	0.913	1.384	0.086
Mn^{+}	$4s^1\ 3d(5\uparrow,0\downarrow)$	0.040	-2.215	0.833	7.194	5.852
Mn^{2+}	$4s^0\ 3d(5\uparrow,0\downarrow)$	-0.018	-2.294	0.888	0.000	-1.424
Mn^{3+}	$4s^0\ 3d(4\uparrow,0\downarrow)$	-0.018	-2.103	0.942	0.000	-1.179
Mn^{4+}	$4s^0\ 3d(3\uparrow,0\downarrow)$	-0.017	-1.793	0.904	0.000	-0.907

- Calculated with *ld1.x*, extrapolated at the nucleus
- Spin-polarized LDA
- values in elec./bohr^3

Mn orbitals and ΔV_{xc}



$$\Delta V_{\mathrm{XC}}(r) = V_{\mathrm{XC},\uparrow}(r) - V_{\mathrm{XC},\downarrow}(r)$$

Core relaxation

- Project valence density around atoms and add GIPAW reconstruc.

$$n_\sigma(r) = n_{\mathrm{val},\sigma}(r) + n_{\mathrm{rec},\sigma}(r), \qquad r < R_c$$

- Calculate ΔV_{XC} from projected spherical density

$$\Delta V_{\mathrm{XC}} = -\frac{2}{\pi}\frac{n_\uparrow - n_\downarrow}{(n_\uparrow + n_\downarrow)^{2/3}}$$

- Core spin density from Incomplete Perturbation Theory

$$n_{\mathrm{s,core}}(r) = 4\sum_{u\in\mathrm{core}}\sum_{v\neq u}\frac{\langle\phi_{us}|\Delta V_{\mathrm{XC}}|\phi_{vs}\rangle}{\epsilon_{us}-\epsilon_{vs}}\phi_{us}(r)\phi_{vs}(r)$$

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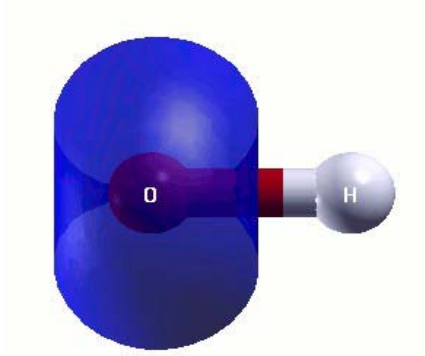
ask Davide Ceresoli,,,

Hyperfine couplings of 2nd row radicals

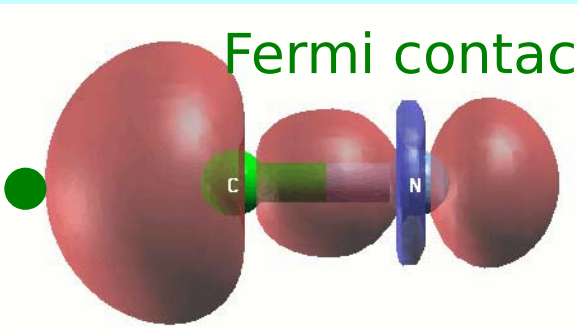
Molecule	Atom	no core relax	core relax	experiment
CH●	C	204	90	47
	H	-50	-50	-58
OH●	O	-142	-61	-45
	H	-56	-56	-73
CH_3●	C	210	122	107
	H	-69	-69	-70
CN●	C	636	581	588
	N	-7	-18	-13
H_2CN●	C	-73	-67	-81
	N	70	34	26
	H	230	230	234

Fermi contact (A_{iso}), values in MHz

OH●



CN●



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Hamiltonians

The simplest Hamiltonian describing all the physics of NMR and EPR is the Dirac-Breit Hamiltonian. The DB Hamiltonian is fully relativistic (four-component) and difficult to solve. In order to make it numerically tractable, it must be reduced to a two-component non-relativistic Hamiltonian by some transformations and approximations.

Physicists apply the Foldy-Wouthuysen transformation to obtain the Pauli Hamiltonian. Chemists prefer the Douglas-Kroll-Hess transformation. Another popular approximation is the ZORA (zeroth-order regular approximation). These transformation lead to different expressions for the Hamiltonian terms, that are numerically very close.

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- I. Souza and D. Vanderbilt, *Dichroic f-sum rule and the orbital magnetization of crystals*, Phys. Rev. B **77**, 054438 (2008)

Online resources: blogs, codes, lectures

- NMR Wiki: http://nmrwiki.org
- Software: http://edunmrsoft.blogsome.com
- NMR periodic table:
  http://www.bruker-nmr.de/guide/eNMR/chem/NMRnuclei.html
- Solid state NMR literature blog: http://ssnmr.blogspot.com
- Other blogs:
  http://nmr-software.blogspot.com
  http://u-of-o-nmr-facility.blogspot.com
  http://scienceblogs.com/scientificactivist/2006/11/nmr_blogs.php

… and of course:
www.quantum-espresso.org
www.gipaw.net
http://qe-forge.org/projects/qe-gipaw