Application of WIEN2k code for computing NMR shielding

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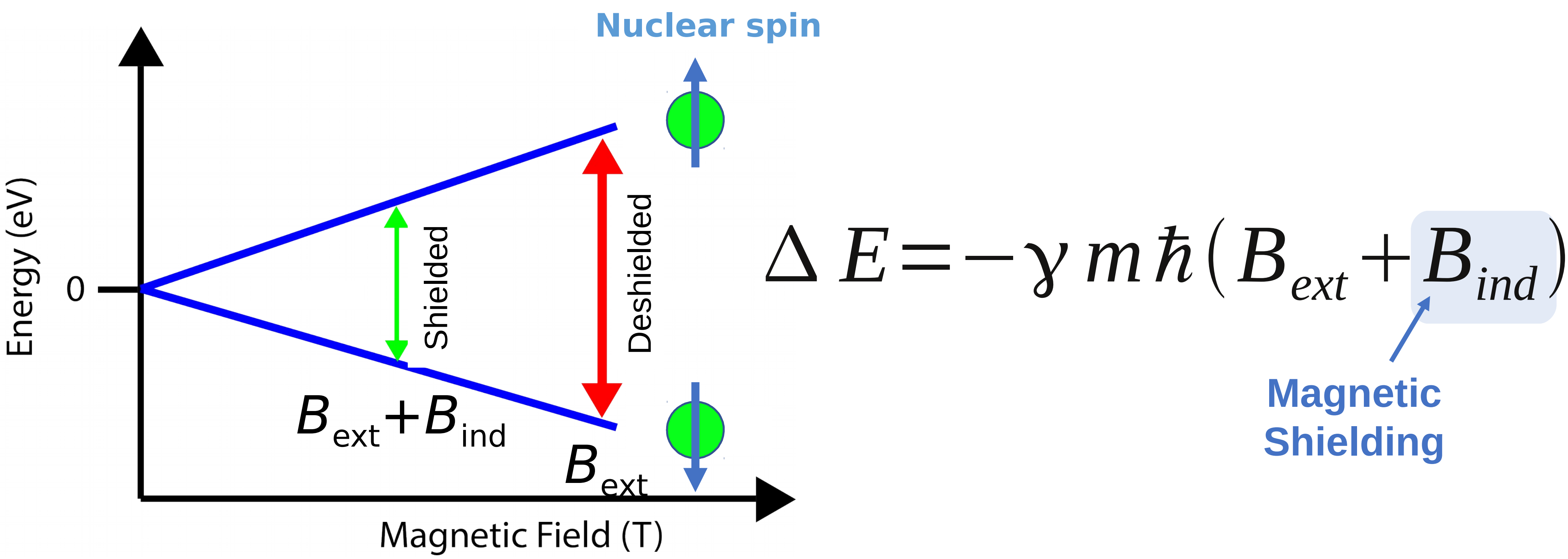
NMR Shielding



$$\Delta E = -\gamma m \hbar (B_{ext} + B_{ind})$$

- Shielding of applied B-field leads to material dependent changes in transition energy

NMR Hamiltonian

perturbation

$$H_{NMR} = H_Z + H_\sigma + H_Q + H_D + H_J + \ldots$$

$$H_Z = -\mu \cdot B_{ext}$$

Zeeman Hamiltonian

electric quadrupole couples to EFG

$$H_Q \approx eQ\Phi / h$$

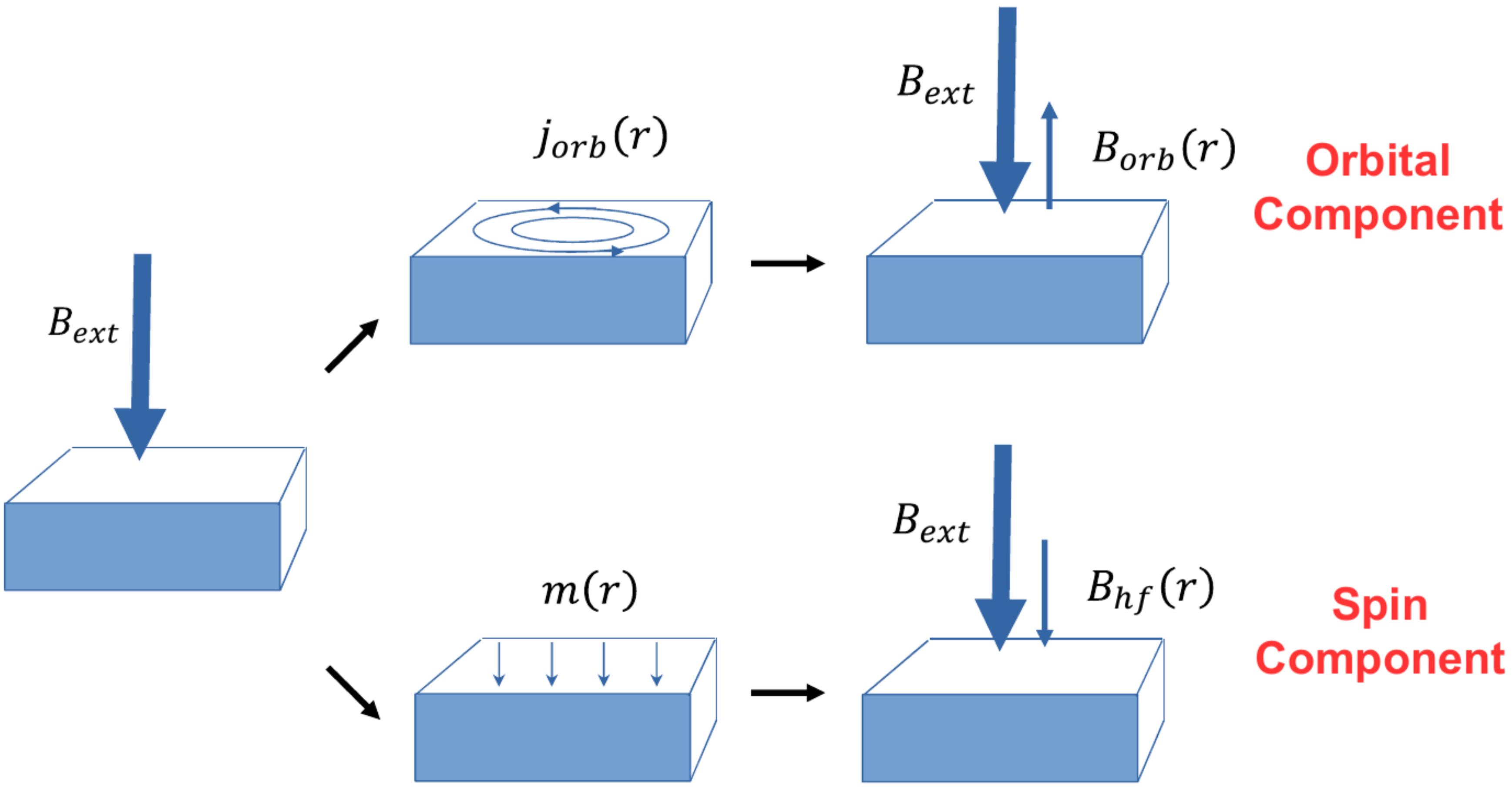
direct dipolar coupling

indirect spin-spin coupling

$$H_\sigma = -\mu \cdot B_{ind}$$

magnetic shielding

Spin and orbital component of NMR shielding

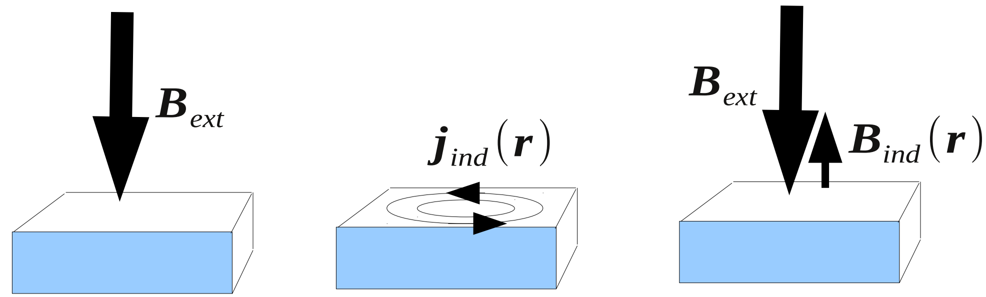


$$B_{ind}(\boldsymbol{R}) = B_{orb} + B_{spn}$$

$$B_{orb} = -\overline{\sigma}_o(\boldsymbol{R})B_{ext}$$

$$B_{spn} = -\overline{\sigma}_s(\boldsymbol{R})B_{ext}$$

Orbital Component of NMR Shielding



$$\boldsymbol{B}_{ext} \rightarrow \boldsymbol{j}_{ind}(\boldsymbol{r}) \rightarrow \boldsymbol{B}_{ind}(\boldsymbol{r})$$

The induced magnetic field ($\boldsymbol{B}_{ind}$) is derived from induced current ($\boldsymbol{j}_{ind}$) using Biot-Savart law:

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

in DFT current density is given by:

$$\boldsymbol{j}(\boldsymbol{r}') = \sum_{o} \langle \Psi_o | \boldsymbol{J}(\boldsymbol{r}') | \Psi_o \rangle$$

Introducing magnetic filed

Replace ***p*** in *H* and ***j(r)*** operators with:

$$\boldsymbol{p} \rightarrow \boldsymbol{p} + \boldsymbol{A}(\boldsymbol{r}')$$

A(***r***) in the symmetric gauge

$$\boldsymbol{A}(\boldsymbol{r}) = \frac{1}{2}\boldsymbol{B} \times (\boldsymbol{r} - \boldsymbol{d})$$

Hamiltonian in the presence of the magnetic field

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

for gauge origin ***d***=0

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

Current operator in the presence of magnetic field

$$\boldsymbol{J}(\boldsymbol{r})=\boldsymbol{J}^{(0)}(\boldsymbol{r})+\boldsymbol{J}^{(1)}(\boldsymbol{r})$$

paramagnetic current operator:

$$\boldsymbol{J}^{(0)}(\boldsymbol{r})=-\frac{\boldsymbol{p}|\boldsymbol{r}\rangle\langle\boldsymbol{r}|+|\boldsymbol{r}\rangle\langle\boldsymbol{r}|\boldsymbol{p}}{2}$$

diamagnetic current operator:

$$\boldsymbol{J}^{(1)}(\boldsymbol{r})=-\frac{\boldsymbol{B}\times\boldsymbol{r}}{2c}|\boldsymbol{r}\rangle\langle\boldsymbol{r}|$$

Linear response formula for induced current

$$|\Psi_o\rangle = |\Psi_o^{(0)}\rangle + |\Psi_o^{(1)}\rangle$$

first order perturbation of the occupied states

$$|\Psi_o^{(1)}\rangle = \sum_e |\Psi_e^{(0)}\rangle \frac{\langle\Psi_e^{(0)}|H^{(1)}|\Psi_o^{(0)}\rangle}{\epsilon - \epsilon_e}$$

A(***r***) in the symmetric gauge

$$H^{(1)} = \frac{1}{2c}\boldsymbol{L}\cdot\boldsymbol{B}$$

$$\boldsymbol{j}(\boldsymbol{r}') = \sum_o \langle\Psi_o|\boldsymbol{J}(\boldsymbol{r}')|\Psi_o\rangle$$

$$\boldsymbol{j}_{ind}(\boldsymbol{r}') = \underbrace{\sum_o \Re\left[\langle\Psi_o^{(1)}|\boldsymbol{J}^{(0)}(\boldsymbol{r}')|\Psi_o^{(0)}\rangle\right]}_{\text{paramagnetic}} - \underbrace{\frac{\boldsymbol{B}\times\boldsymbol{r}'}{2c}\rho(\boldsymbol{r}')}_{\text{diamagnetic}}$$

paramagnetic

diamagnetic

Generalized f-sum rule

$$\rho(\mathbf{r}')\mathbf{B} \times \mathbf{r}' = -\sum_{o} \langle \Psi_o^{(0)} | \frac{1}{i} [\mathbf{B} \times \mathbf{r}' \cdot \mathbf{r}, \mathbf{J}^{(0)}(\mathbf{r}')] | \Psi_o^{(0)} \rangle]$$

$$\boldsymbol{j}_{ind}(\boldsymbol{r}') = \sum_{o} \Re\left[\left\langle \Psi_o^{(0)} \middle| \boldsymbol{J}^{(0)}(\boldsymbol{r}') \middle| \widetilde{\Psi}_o^{(1)} \right\rangle\right]$$

$$|\tilde{\Psi}_o^{(1)}\rangle = \sum_{e} |\Psi_e^{(0)}\rangle \frac{\langle \Psi_e^{(0)} | \left[(\mathbf{r} - \mathbf{r}') \times \mathbf{p} \cdot \mathbf{B} \right] | \Psi_o^{(0)} \rangle}{\epsilon_o - \epsilon_e}$$

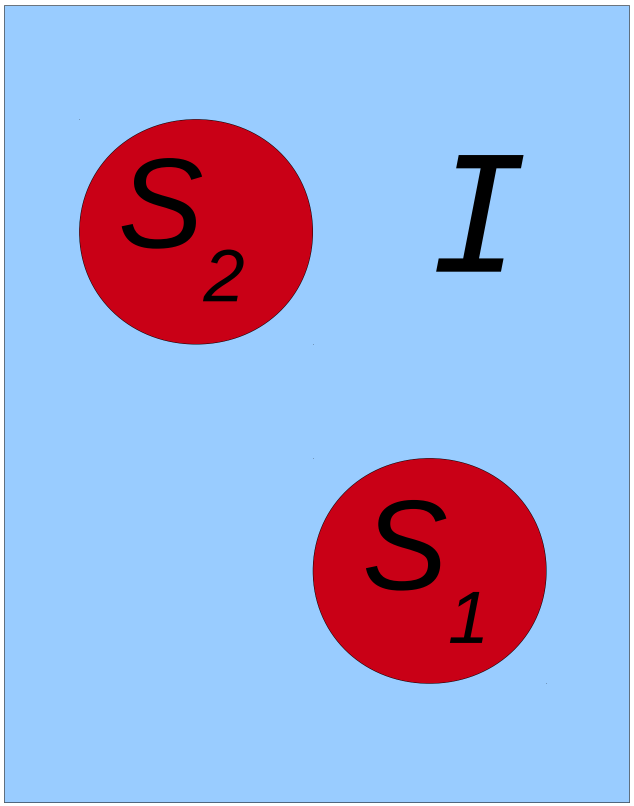
Considering infinite periodic structure

$$\mathbf{r}\cdot\hat{\mathbf{u}}_i = \lim_{q\to 0} \frac{1}{2q}\left(e^{iq\hat{\mathbf{u}}_i\cdot\mathbf{r}} - e^{-iq\hat{\mathbf{u}}_i\cdot\mathbf{r}}\right)$$

- Calculations are done using small q vector
- Eigenfunctions have to be computed on k-meshes shifted by +/- q

Details in: PRB 85, 035132 (2012)

APW (wien2k) basis



LAPW plane waves

$$\phi^{LAPW}_{\mathbf{k},\mathbf{G}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \mathbf{r} \in I \\ \sum_{l,m} \left[A^{\alpha,\mathbf{k}+\mathbf{G}}_{l,m} u^{\alpha}_{l}(r, E_l) \right. & \\ \quad \left. + B^{\alpha,\mathbf{k}+\mathbf{G}}_{l,m} \dot{u}^{\alpha}_{l}(r, E_l) \right] Y_{l,m}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases}$$

local orbitals

$$\phi^{LO,\alpha,i}_{l,m,\mathbf{k}}(\mathbf{r}) = \begin{cases} 0, & \mathbf{r} \in I \\ \left[A^{i,\alpha,\mathbf{k}}_{l,m} u^{\alpha}_{l}(r, E_l) + B^{i,\alpha,\mathbf{k}}_{l,m} \dot{u}^{\alpha}_{l}(r, E_l) \right. & \\ \quad \left. + C^{i,\alpha,\mathbf{k}}_{l,m} u^{\alpha,i}_{l}(r, E^{i}_{l}) \right] Y_{l,m}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases}$$

wave function

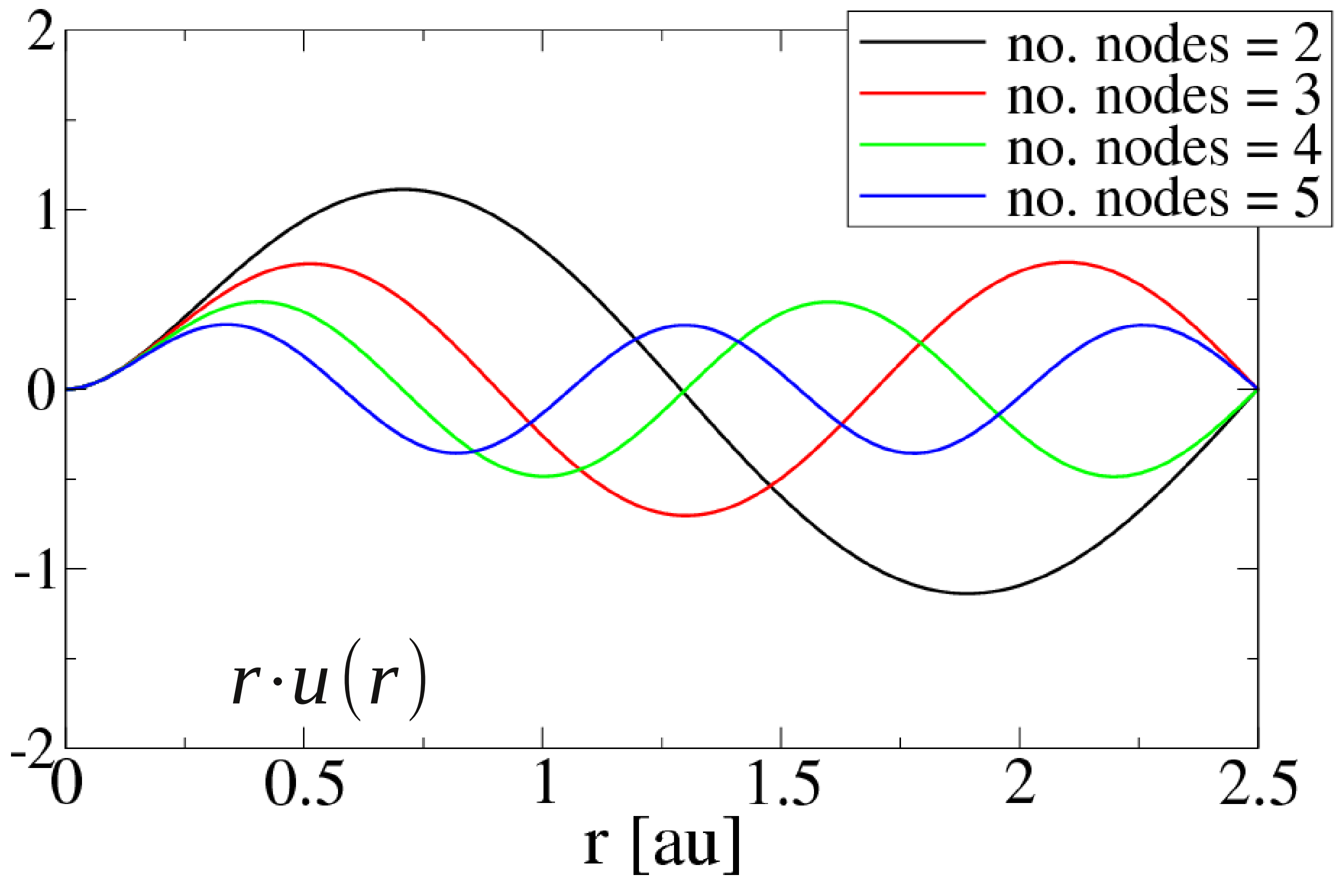
$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C^{n}_{G} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \mathbf{r} \in I \\ \sum_{l,m} W^{n,\alpha,\mathbf{k}}_{l,m}(r) Y_{l,m}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases}$$

APW, fine tuning

- APW basis is perfect only for states with eigen energy close to the linearization energy
  - to remedy this we include extended set of local orbitals (NMR LO)

$$\phi^{LO,\alpha,i}_{l,m,\mathbf{k}}(\mathbf{r}) = \begin{cases} 0, & \mathbf{r} \in I \\ \Big[A^{i,\alpha,\mathbf{k}}_{l,m} u^{\alpha}_{l}(r, E_l) + B^{i,\alpha,\mathbf{k}}_{l,m} \dot{u}^{\alpha}_{l}(r, E_l) & \\ \quad + C^{i,\alpha,\mathbf{k}}_{l,m} u^{\alpha,i}_{l}(r, E^{i}_{l})\Big] Y_{l,m}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases}$$

- NMR LO has node at the sphere boundary
- number of nodes increase by one in subsequent LO



p LOs in atomic Be

- APW does not include directly radial derivative of u(r), which results in slow convergence with respect of number of NMR LO
  - Adding to the basis r*du/dr radial functions helps (**DUC**)

$$\xi_{l,k}(r,\tilde{\epsilon}) = \begin{cases} r\frac{d}{dr}u_{l+1}(r,\tilde{\epsilon}) + (l+2)u_{l+1}(r,\tilde{\epsilon}), & k=1 \\ r\frac{d}{dr}u_{l-1}(r,\tilde{\epsilon}) - (l-1)u_{l-1}(r,\tilde{\epsilon}), & k=2 \end{cases}$$

$$\tilde{u}_{l,k}(r) = \xi_{l,k}(r,\tilde{\epsilon}) - \sum_i b_{l,k,i}u_{l,i}(r).$$

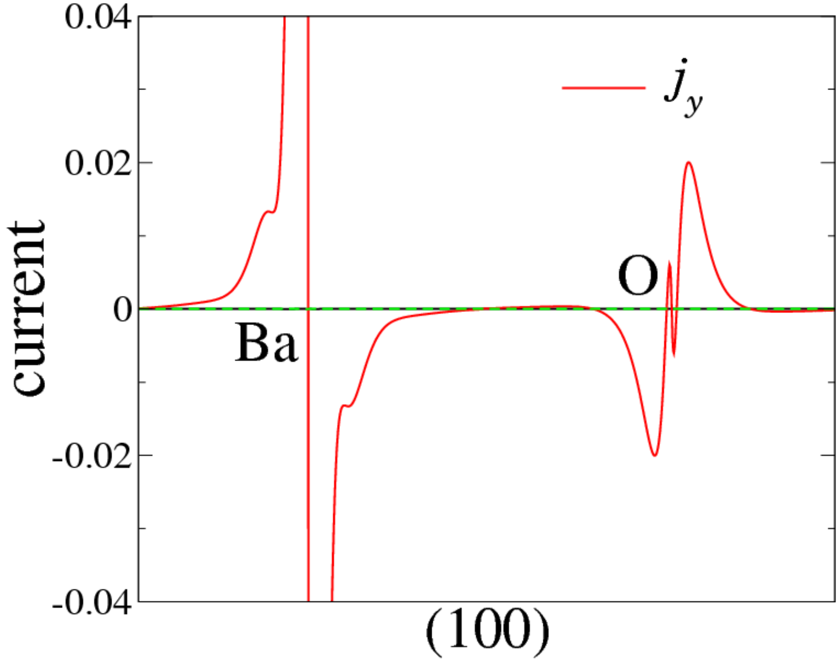
$$|\phi_{lm,k}\rangle = \tilde{u}_{l,k}(r)Y_{lm}$$

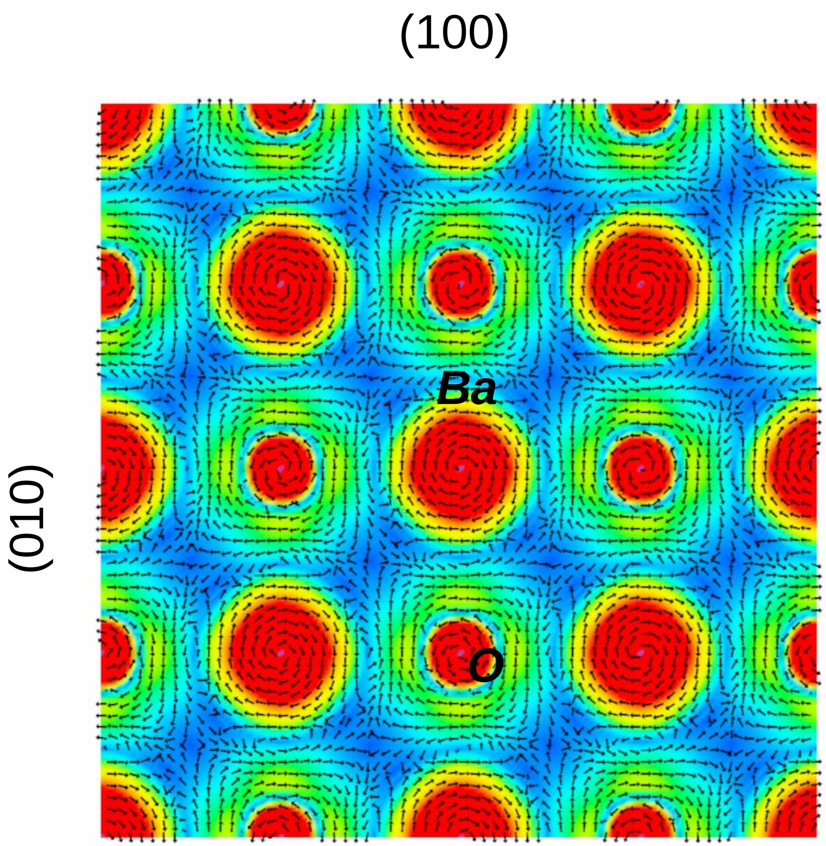
$$\mathcal{G}(\epsilon_i) = \sum_e \frac{|\Psi_e^{(0)}\rangle\langle\Psi_e^{(0)}|}{\epsilon_i - \epsilon_e} + \sum_k \frac{|\phi_k\rangle\langle\phi_k|}{\langle\phi_k|\,(\epsilon_i - H)\,|\phi_k\rangle}$$

Details in: PRB 89, 014402 (2014)

Induced current in LAPW

$$\mathbf{j}_{ind}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} \mathbf{j}_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, & \mathbf{r} \in I \\ \sum_{l,m} \mathbf{j}^{\alpha}_{l,m}(r) Y_{l,m}(\hat{r}). & \mathbf{r} \in S_\alpha \end{cases}$$





BaO (fcc) , $\boldsymbol{B}_{ext}$ in *(001)*

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

Integration of the induced current

- modification of Weinert (M. Weinert, J. Math. Phys. 22, 11 (1981).) method is used to integrate the induced current

$$\mathbf{j}_{\mathrm{ind}}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} \left(\mathbf{j}_{\mathbf{G}} + \tilde{\mathbf{j}}^{s}_{\mathbf{G}}\right) e^{i\mathbf{G}\cdot\mathbf{r}}, & \mathbf{r} \in \Omega \\ \sum_{lm} \left[\mathbf{j}^{\alpha,c}_{lm}(r) - \tilde{\mathbf{j}}_{\alpha}(\mathbf{r})\right] Y_{lm}(\hat{r}), & \mathbf{r} \in S_{\alpha} \end{cases}$$

$$\tilde{\mathbf{j}}^{s}_{\alpha}(\mathbf{r}) = \sum_{lm} \mathbf{Q}^{\alpha}_{lm} Y_{lm}(\hat{\mathbf{r}}) \sum_{\eta}^{n} a_{\eta} r^{\nu_{\eta}}, \quad \mathbf{r} \in S_{\alpha}$$

$$\tilde{\mathbf{j}}^{s}_{\mathbf{G}} = \frac{4\pi}{\Omega} \sum_{lm,\alpha} \frac{(-i)^{l}(2l+2n+3)!!}{(2l+1)!!} \times \frac{j_{l+n+1}(GR_{\alpha})}{(GR_{\alpha})^{n+1}} \mathbf{q}^{\alpha}_{lm} e^{-i\mathbf{G}\xi_{\alpha}} Y_{lm}(\hat{\mathbf{G}})$$

Integration of the induced current

Sphere centered on nucleus shielding is computed

$$\mathbf{B}_{\mathrm{ind}}^{S,\alpha}(0) = -\frac{1}{c}\int_{\alpha} d^3r\,\mathbf{j}_{\mathrm{ind}}(\mathbf{r}) \times \frac{\hat{\mathbf{r}}}{|\mathbf{r}|^2}$$

$$\mathbf{B}_{\mathrm{ind}}^{S,\alpha}(0) = \frac{1}{c}\sqrt{\frac{4\pi}{3}}\sum_{lm}\left[\int_0^R dr\ \mathbf{j}_{\mathrm{ind}}^{q}(\mathbf{r})\right]\left[\frac{1}{\sqrt{2}}\left(G_{l01}^{m01} - G_{l01}^{m0-1}\right)\right. \\ \left.\frac{i}{\sqrt{2}}\left(G_{l01}^{m01} + G_{l01}^{m0-1}\right), G_{l01}^{m00}\right].$$

Whole unit-cell volume

$$\mathbf{B}_{\mathrm{ind}}^{\mathrm{PW}}(\mathbf{G}) = \frac{4\pi}{c}\,\frac{i\mathbf{G} \times \left(\mathbf{j}_{\mathbf{G}} + \tilde{\mathbf{j}}_{\mathbf{G}}^{s}\right)}{G^2} \qquad \mathbf{B}_{\mathrm{ind}}^{\mathrm{PW}}(\mathbf{G}=0) = \frac{8\pi}{3}\overleftrightarrow{\chi}\,\mathbf{B}$$

Core contribution

- Core states are covered by a separate eigenvalue problem, contribution accounts for spherical charge:

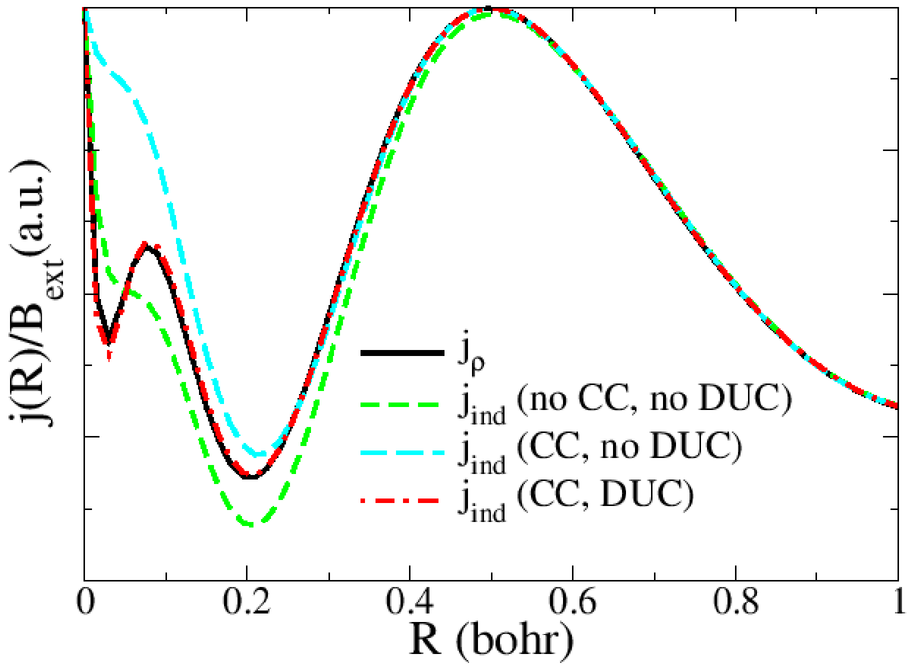
$$\mathbf{j}_{\mathrm{ind}}(\mathbf{r}') = -\frac{1}{2c}\rho_{\mathrm{core}}(\mathbf{r}')\mathbf{B} \times \mathbf{r}'$$

- Due to the separation, correction is needed (**CC**):

$$\left|\Psi_o^{(1)}\right\rangle = \sum_e \left|\Psi_e^{(0)}\right\rangle \frac{\left\langle\Psi_e^{(0)}\middle|H^{(1)}\middle|\Psi_o^{(0)}\right\rangle}{\epsilon_o - \epsilon_e} + \sum_{\mathrm{core}} \left|\Psi_{\mathrm{core}}^{(0)}\right\rangle \frac{\left\langle\Psi_{\mathrm{core}}^{(0)}\middle|H^{(1)}\middle|\Psi_o^{(0)}\right\rangle}{\epsilon_o - \epsilon_{\mathrm{core}}}$$

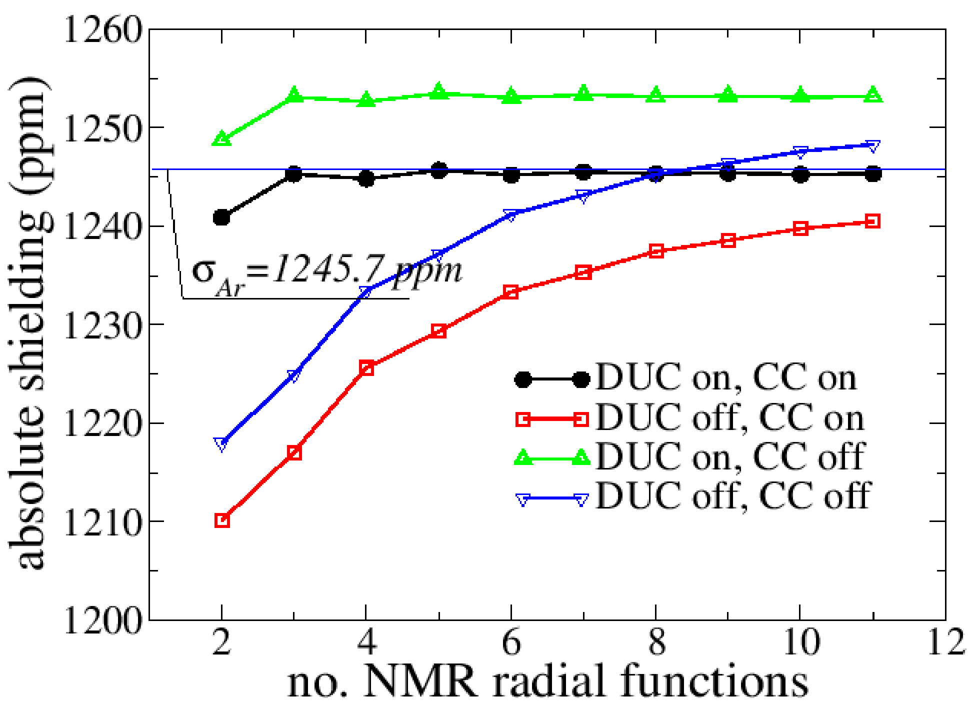
Benchmark: spherical Ar atom

Test of the solution for spherically symmetric Ar atom



$$\boldsymbol{j}_{\rho}(\boldsymbol{r}')=\frac{-\boldsymbol{B}\times\boldsymbol{r}'}{2c}\rho(\boldsymbol{r}')$$

The convergence with respect to number of NMR LO, with and without basis extension



How to run the code

1) run SCF calculation
2) prepare *case.in1_nmr* (add NMR LO): *x_nmr -mode in1*
3) run *x_nmr*

Master script: *x_nmr [options]*

x_nmr -h	prints help
x_nmr -p	run parallel using .machines

case.in1_nmr

```
WFFIL  EF=.533144859350   (WFFIL, WFPRI, ENFIL, SUPWF)
  7.00       10    4 (R-MT*K-MAX; MAX L IN WF, V-NMT
 0.30   19  0      (GLOBAL E-PARAMETER WITH n ….
 0  -0.58576    0.002 CONT 1
 0   4.80000    0.000 CONT 1
 0  36.60000    0.000 CONT 1
 0  66.66000    0.000 CONT 1
 0 104.26000    0.000 CONT 1
 0 149.26000    0.000 CONT 1
 0 201.50000    0.000 CONT 1
 …
```

NMR LO's

x_nmr (work flow)

1) computes eigenvectors using shifted and non-shifted meshes, the results are stored in: ./nmr_q0, ./nmr_mqx, ./nmr_pqx, ./nmr_mqy, ./nmr_pqy, ./nmr_mqz, ./nmr_pqz (mode lapw1)

   x_nmr -mode lapw1

2) computes weights for each k-mesh, (mode lapw2)

   x_nmr -mode lapw2

3) computes core wave-functions

   x_nmr -mode lcore

4) computes induced current

   x_nmr -mode current

5) integrates the current

   x_nmr -mode integ

output

- case.output_"*mode*"
- final results (shielding tensor, trace, anisotropy ..)

case.output_integ

```
:NMRTOT001  ATOM:     Ba1   1  NMR(total/ppm) Sigma-ISO =   5384.00    Sigma_xx =   5474.82   Sigma_yy =   5385.93   Sigma_zz =   5291.24
:NMRASY001  ATOM:     Ba1   1  NMR(total/ppm) ANISO (delta-sigma) =   -139.13    ASYM (eta) = 0.958    SPAN =    183.57    SKEW =-0.032

:NMRTOT002  ATOM:     S 1   2  NMR(total/ppm) Sigma-ISO =    111.31    Sigma_xx =     85.34   Sigma_yy =    107.93   Sigma_zz =    140.67
:NMRASY002  ATOM:     S 1   2  NMR(total/ppm) ANISO (delta-sigma) =     44.03    ASYM (eta) = 0.770    SPAN =     55.33    SKEW = 0.183
```

x_nmr - important options

x_nmr -mode *mode _id*	executes particular mode
x_nmr -initonly	only lapw1, lapw2, lcore
x_nmr -noinit	only current, integ
x_nmr -p	
x_nmr -scratch *scratch*	
x_nmr -h	

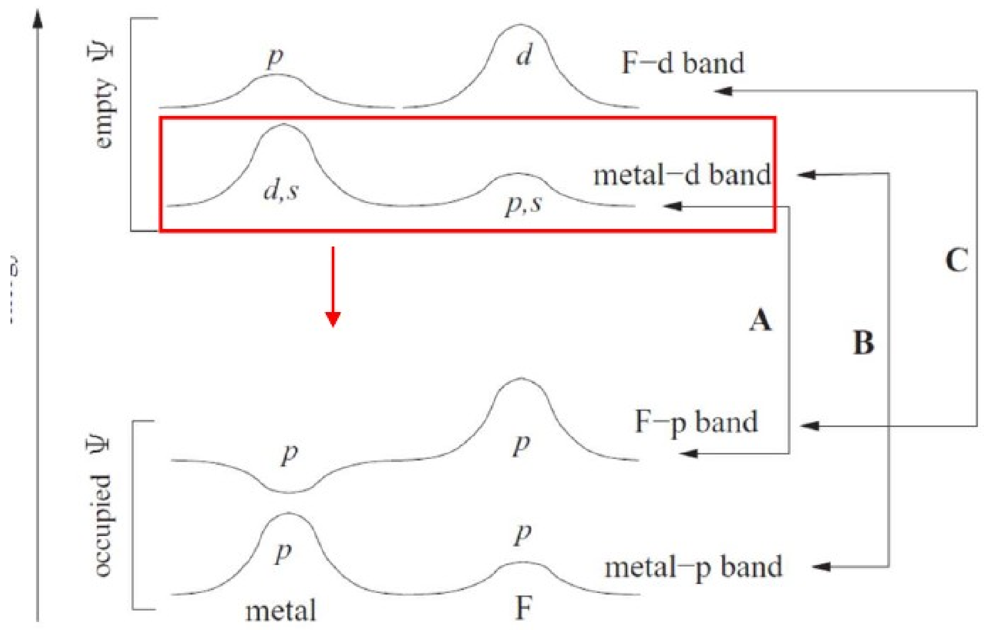
Where does it come from? - orbital part

$$|\Psi_o^{(1)}\rangle = \sum_e |\Psi_e^{(0)}\rangle \frac{\langle\Psi_e^{(0)}|H^{(1)}|\Psi_o^{(0)}\rangle}{\epsilon_o - \epsilon_e}$$

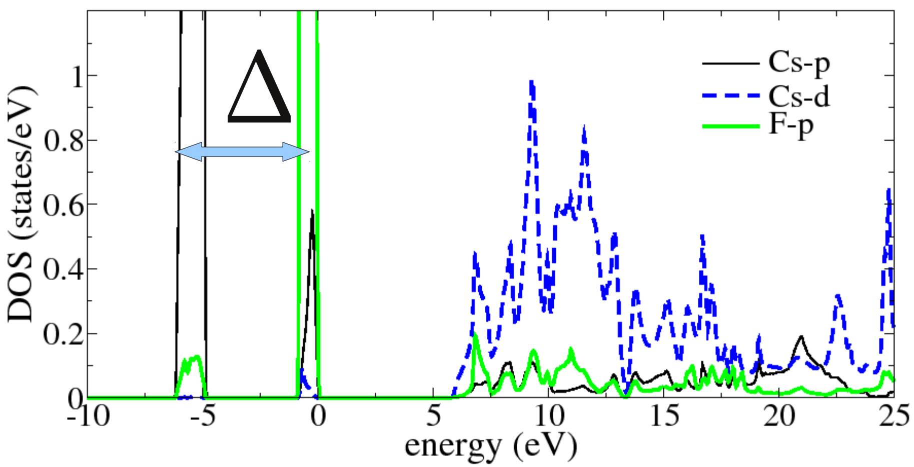
$$H^{(1)} = \frac{1}{2c}\boldsymbol{L}\cdot\boldsymbol{B}$$

- Coupling between occupied and empty band
- Directly related to bands character and the band gap

Shielding in Fluorides



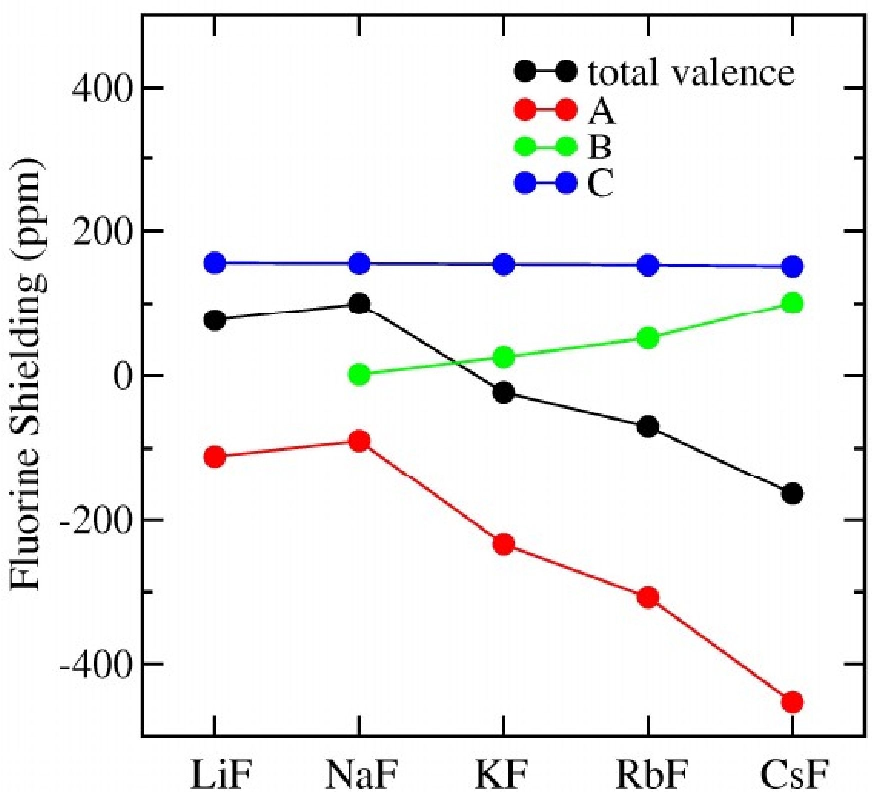
Schematic diagram representing major couplings contributing to NMR shielding



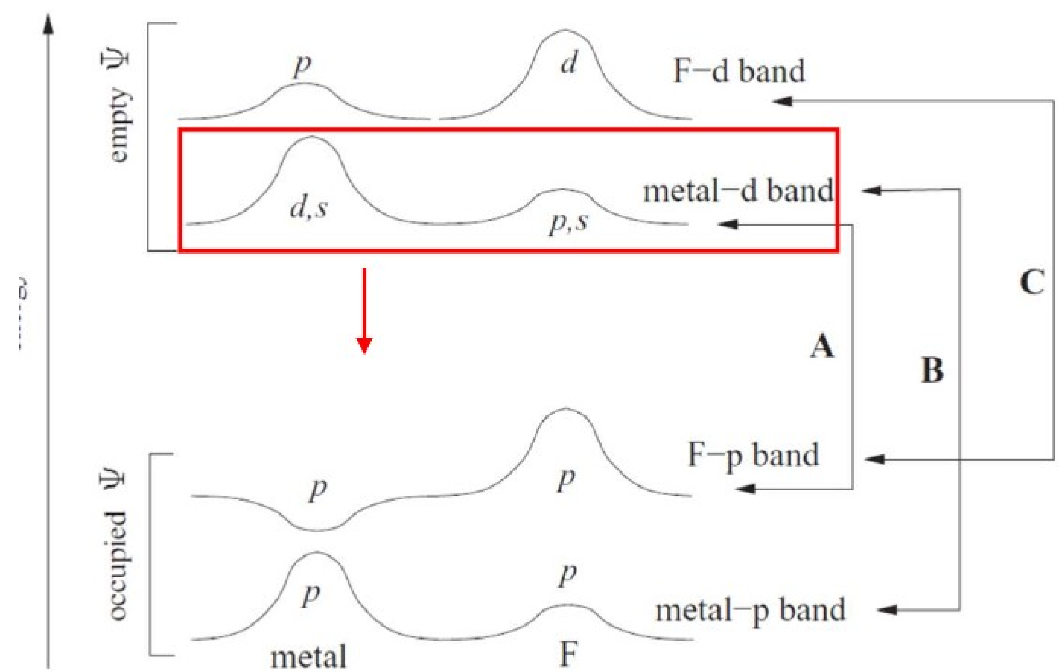
Δ varies between 5 eV for CsF to 20 eV for NaF

PRB 85, 245117 (2012)

Shielding in Fluorides



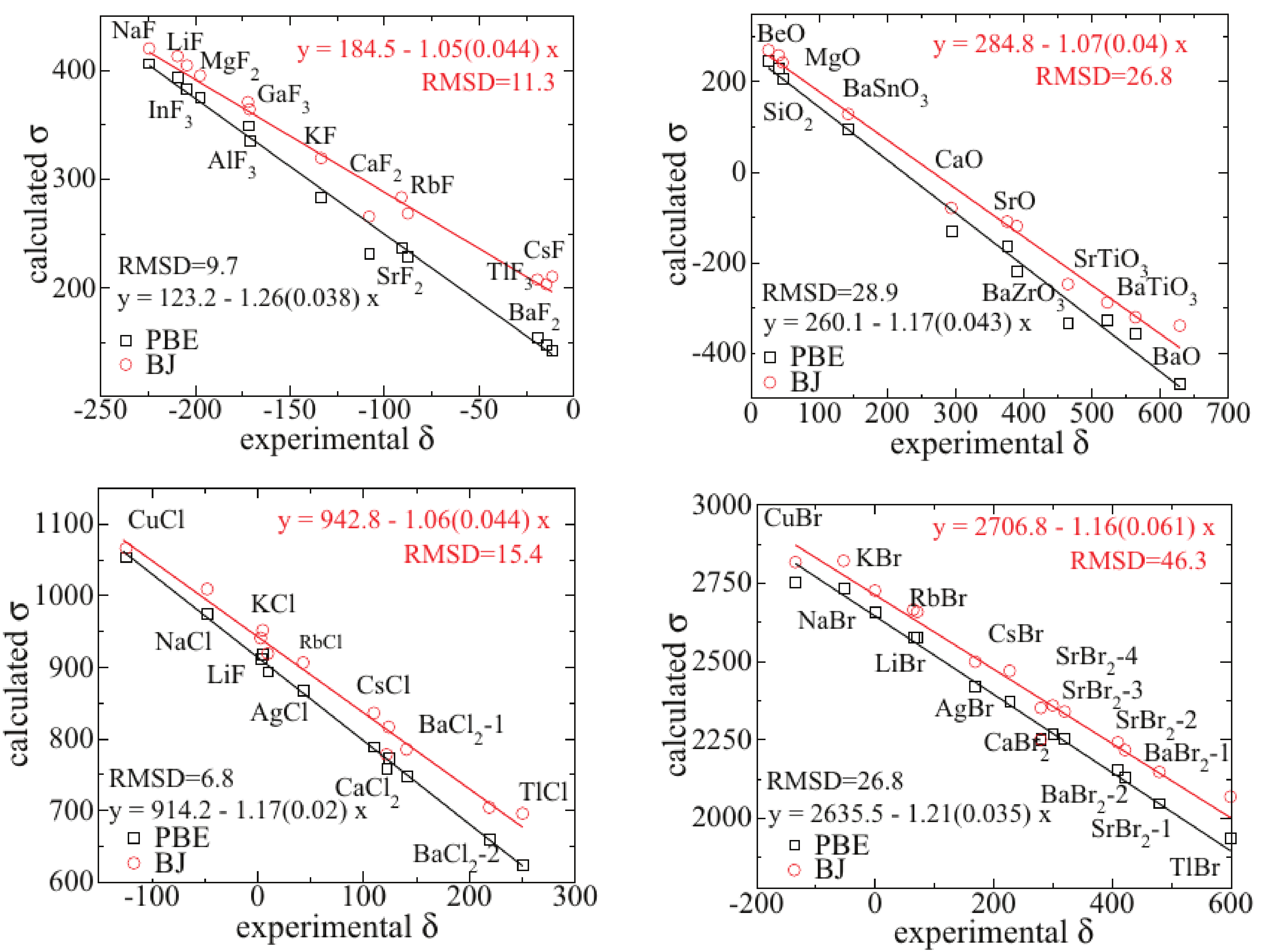
NMR shielding at fluorine nucleus in alkali fluoride series for different couplings



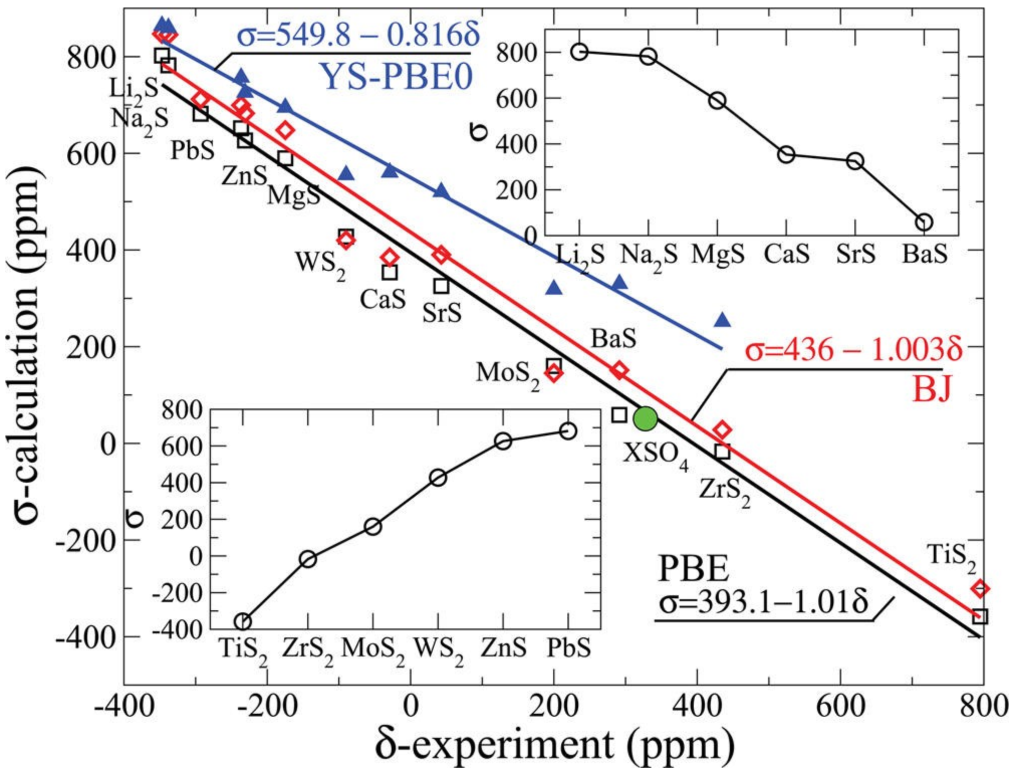
Schematic diagram representing major couplings contributing to NMR shielding

PRB 85, 245117 (2012)

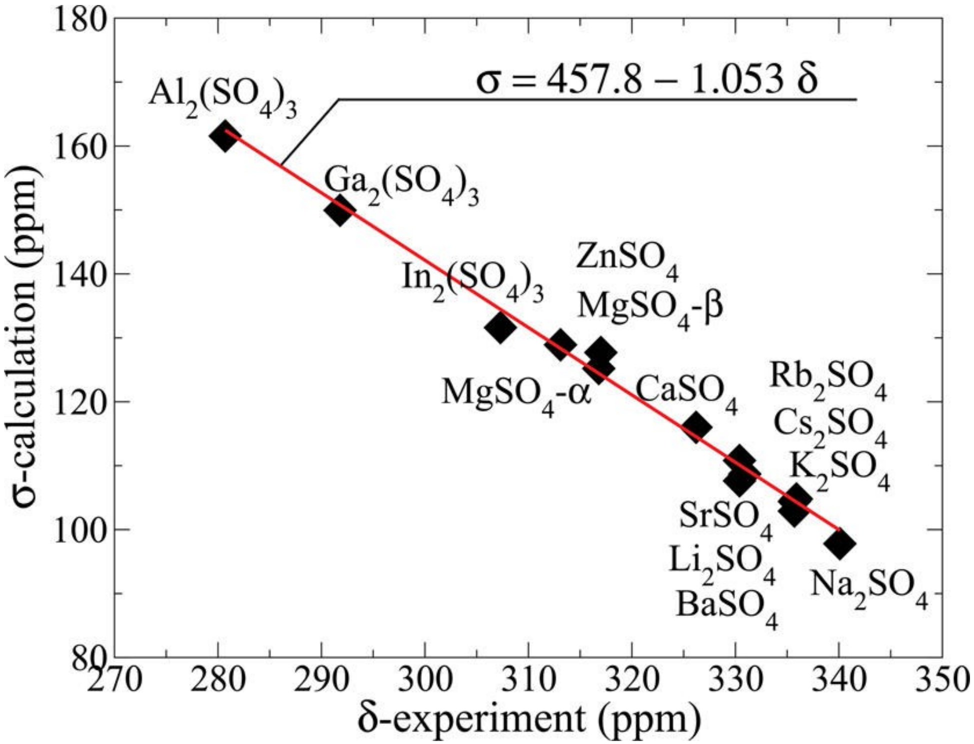
Slope problem



inorganic sulfides

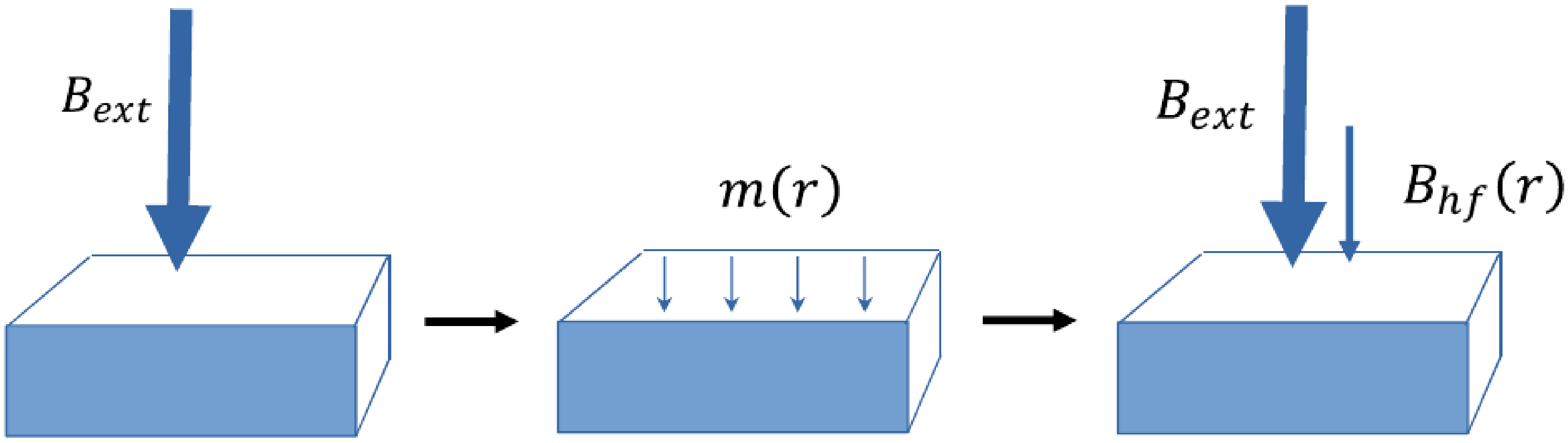


inorganic sulfates



Spin Component of NMR Shielding

NMR, spin component



contact term

$$\mathbf{B}_{\mathrm{hf}} = \underbrace{\frac{8\pi}{3}\mathbf{m}_{\mathrm{av}}}_{\text{contact term}} + \underbrace{\int \frac{S(r)}{r^3}\left[3(\mathbf{m}(r)\hat{r})\hat{r} - \mathbf{m}(r)\right] d^3r}_{\text{dipole term}}$$

dipole term

Workflow

- converge regular SCF (spin polarized)

```
runsp_lapw -cc 0.0001 -p ….
save_lapw -f -d ….
```

- converge SCF with magnetic field applied to spin only, use large number of k-points

```
3  1  0
PRATT  1.0
1 1 0
100
0 0 1
```

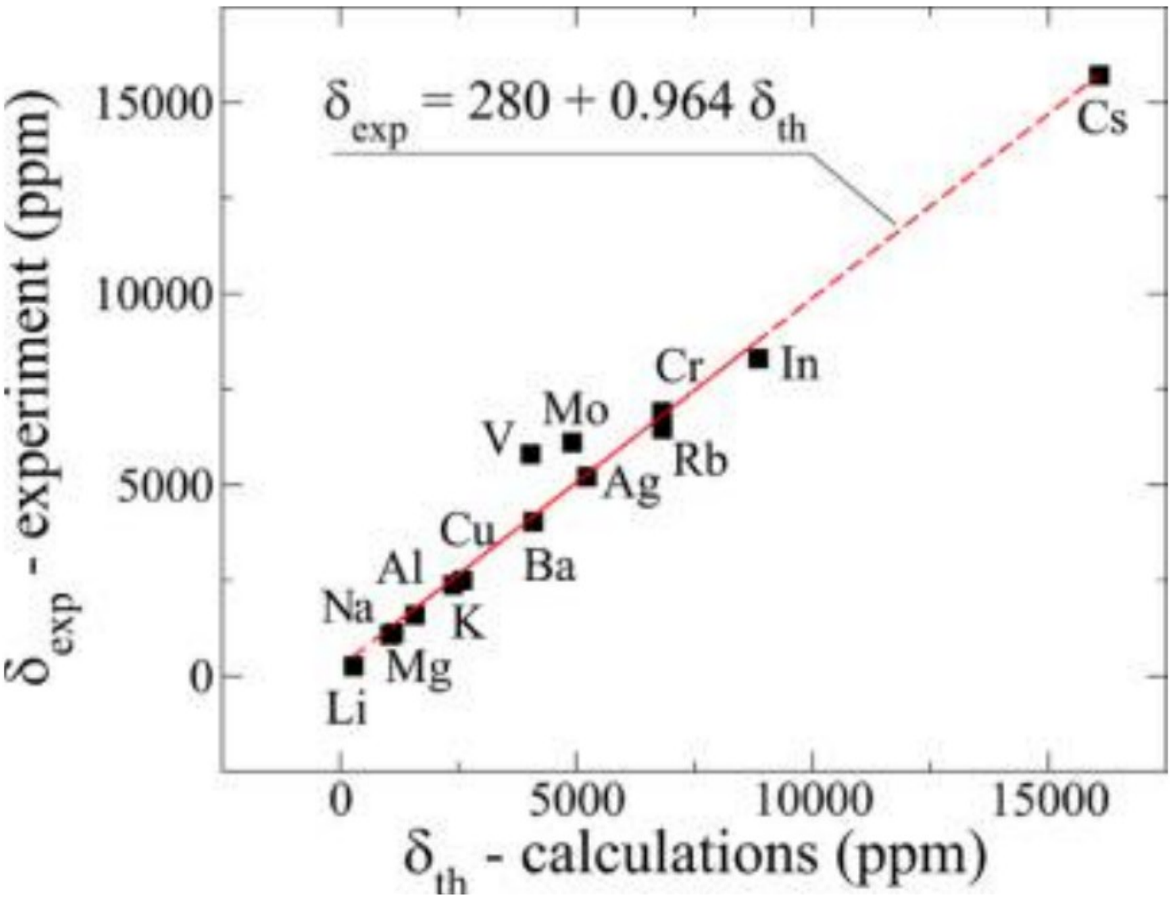
B_{ext}[T] (points to the value 100)

case.inorb

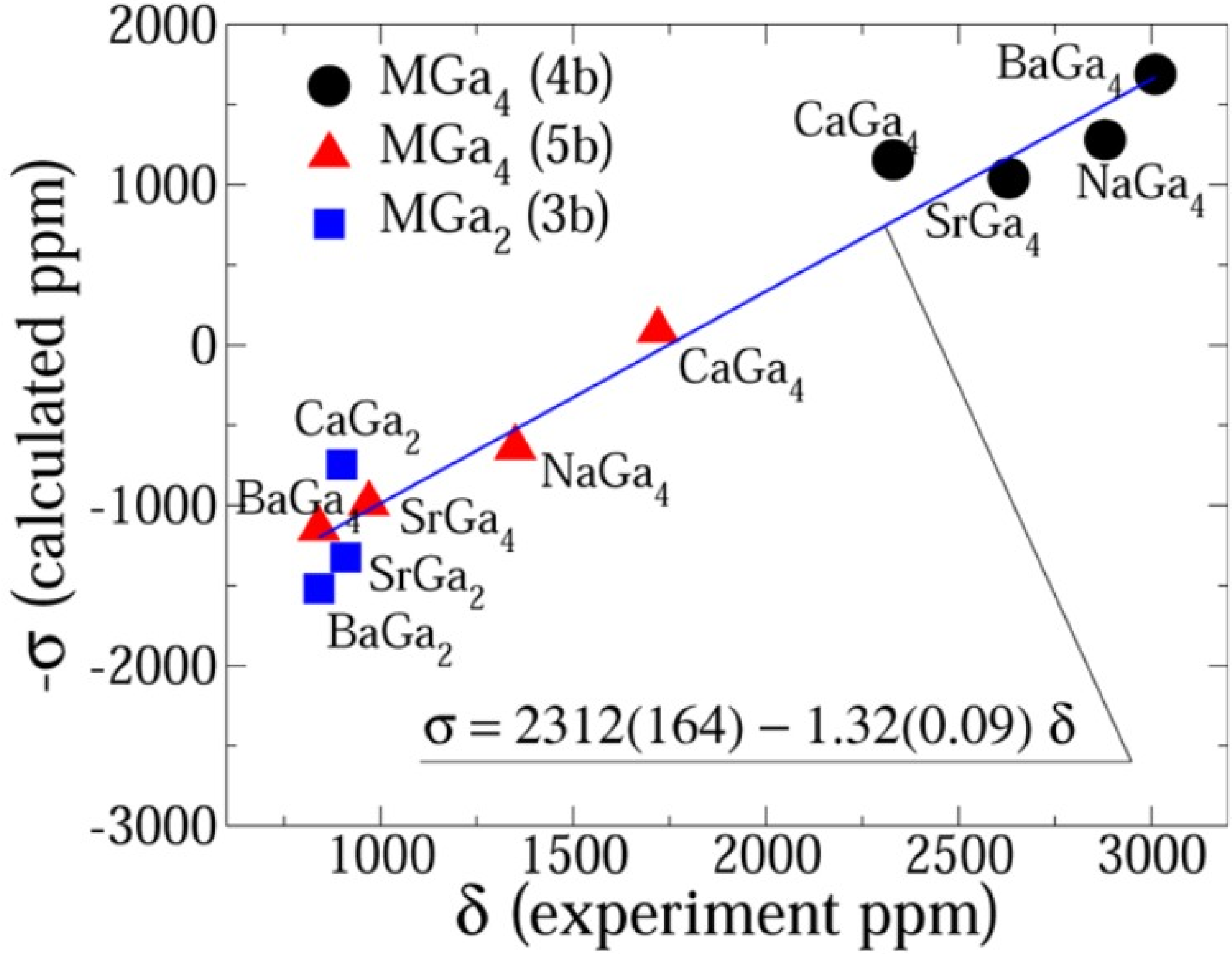
```
x_lapw orb -up
x_lapw kgen
runsp_lapw -cc 0.000001 -p
x_lapw lapwdm
```

- look in case.scf for :HFF (multiply by $10^5/B_{ext}$) for shielding in ppm
- case.scfdm for dipolar contribution

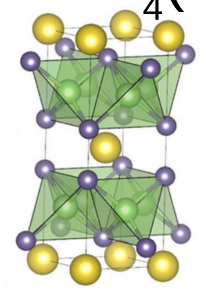
NMR shielding in simple metals



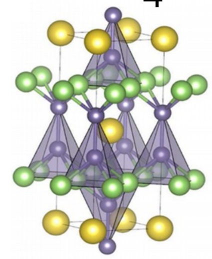
Gallides, theory vs. experiment



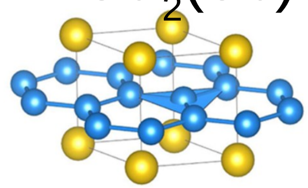
MGa$_4$(4b)



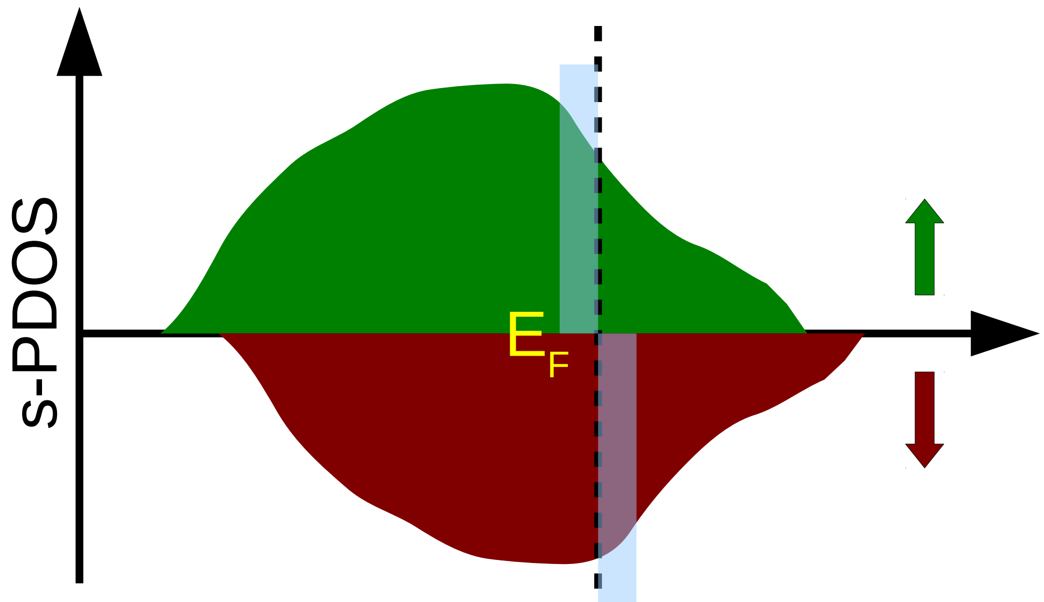
MGa$_4$(5b)



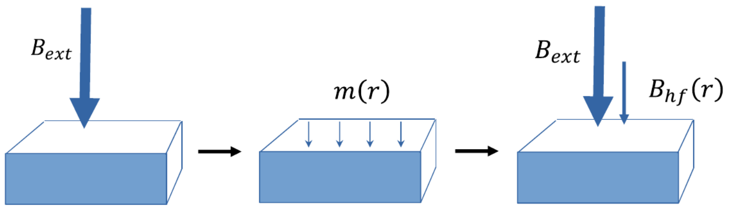
MGa$_2$(3b)



Where does it come from? - spin part

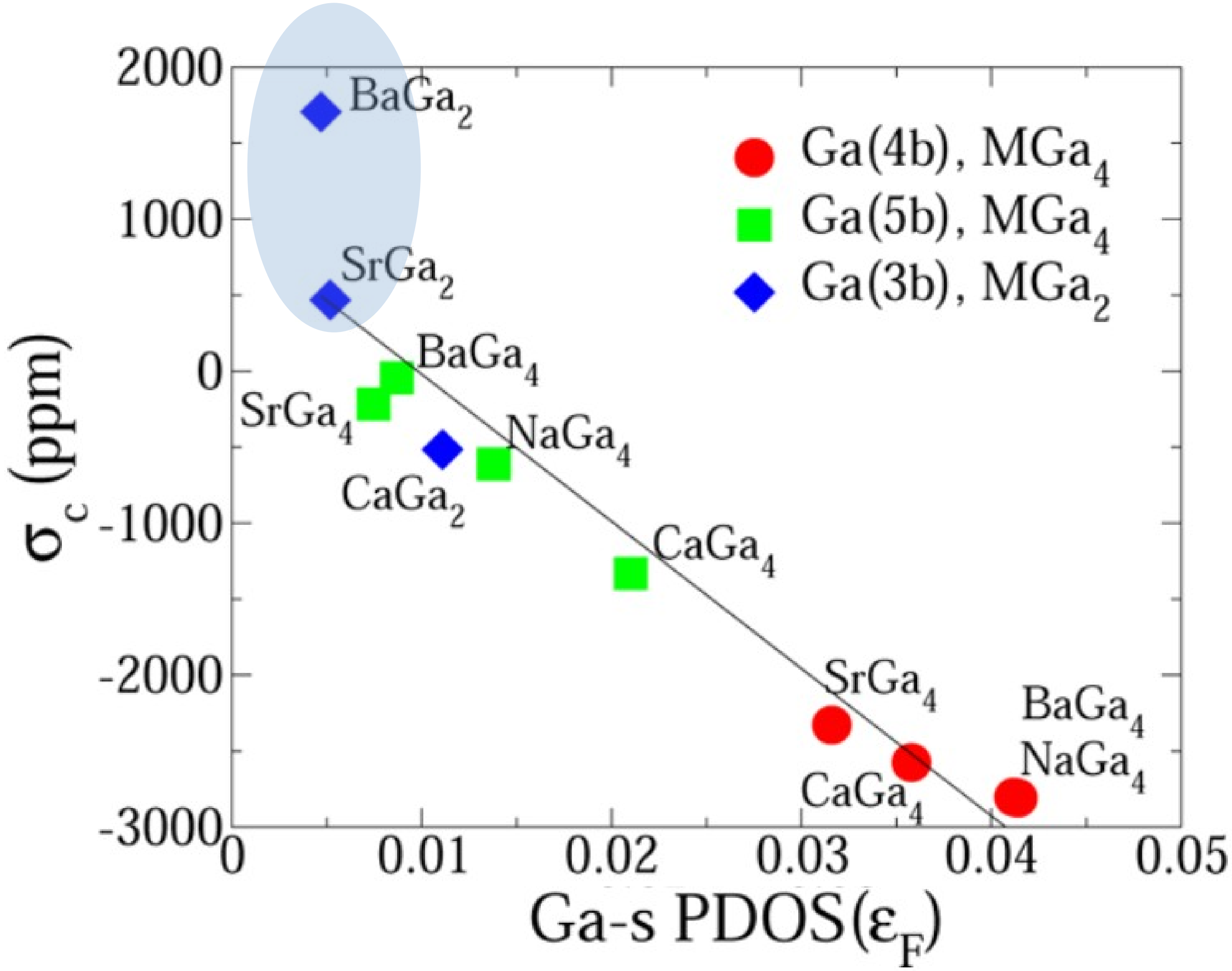


Contact term



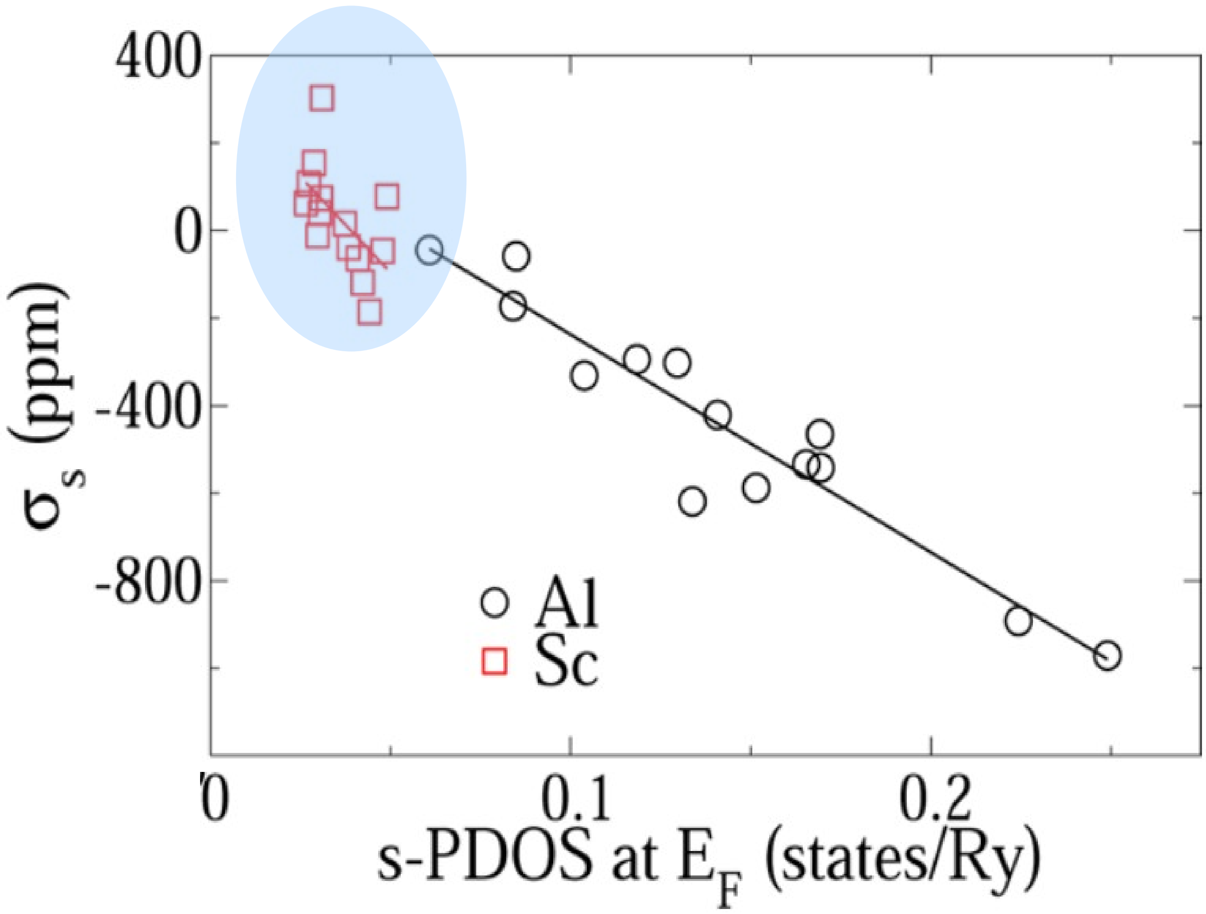
- common sense interpretation leads to paramagnetic response (negative)
- S-PDOS at Fermi level matters

Gallides, contact term



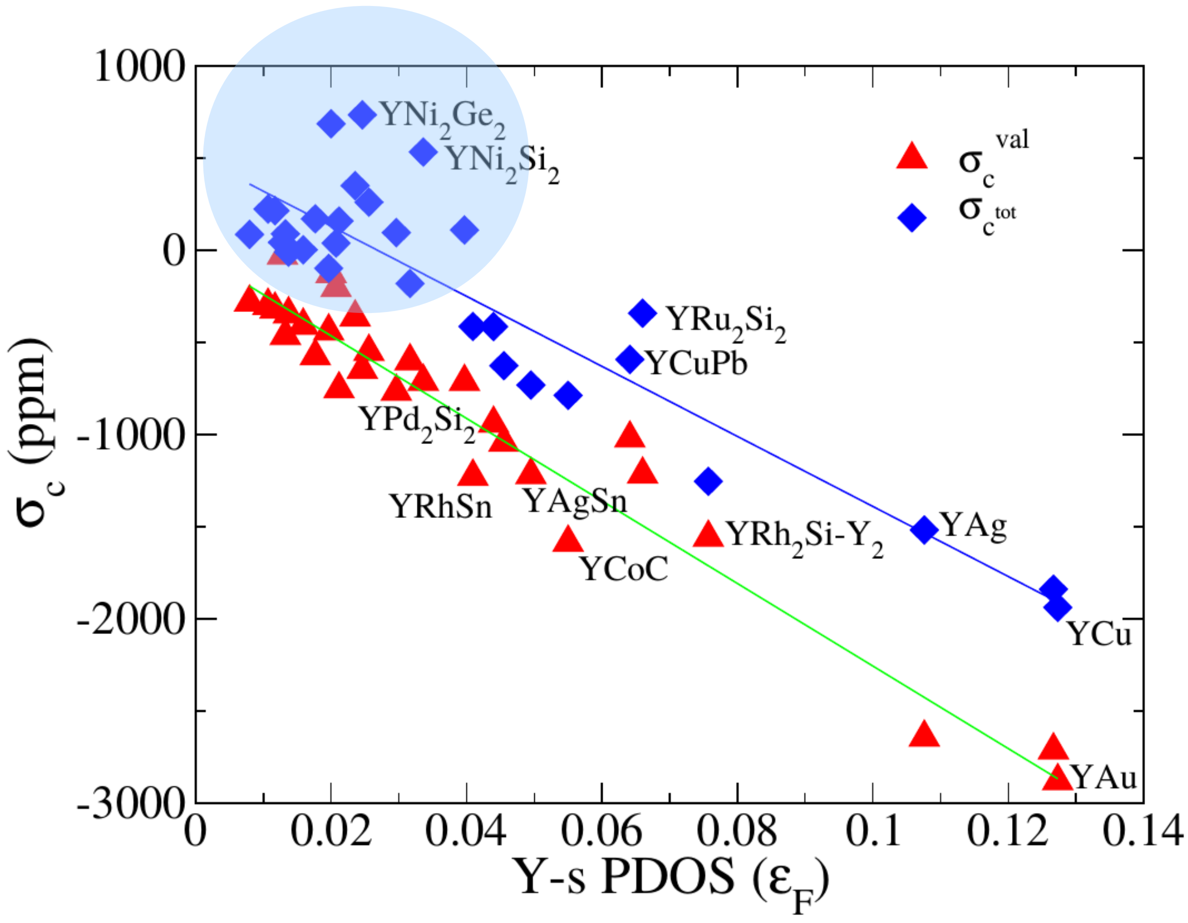
- $BaGa_2$ and $SrGa_2$ show positive contact term !!!

Al and Sc shielding in ScTT′Al



J. Phys. Chem. C 121, 12398 (2017)

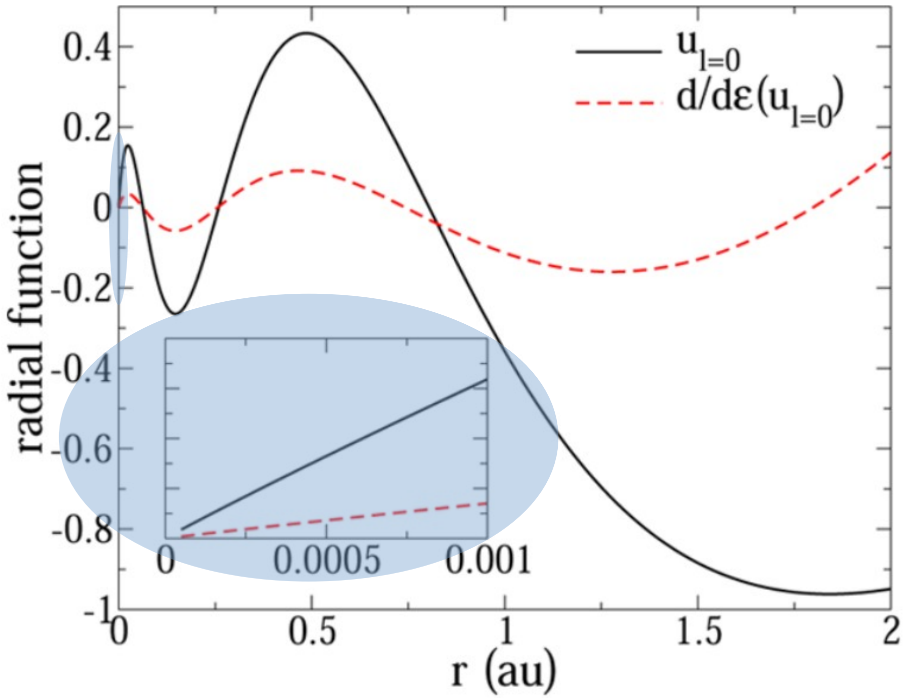
Y NMR shielding in intermetallic Yttrium compounds



Why contact term is sometimes positive?

- It happens for low s-PDOS end of the diagrams
- Wave-function around nucleus is different for spin up and down states

Radial function changes with energy



$$m(\mathbf{r}) = \psi_\uparrow(\mathbf{r})\psi_\uparrow^*(\mathbf{r}) - \psi_\downarrow(\mathbf{r})\psi_\downarrow^*(\mathbf{r})$$

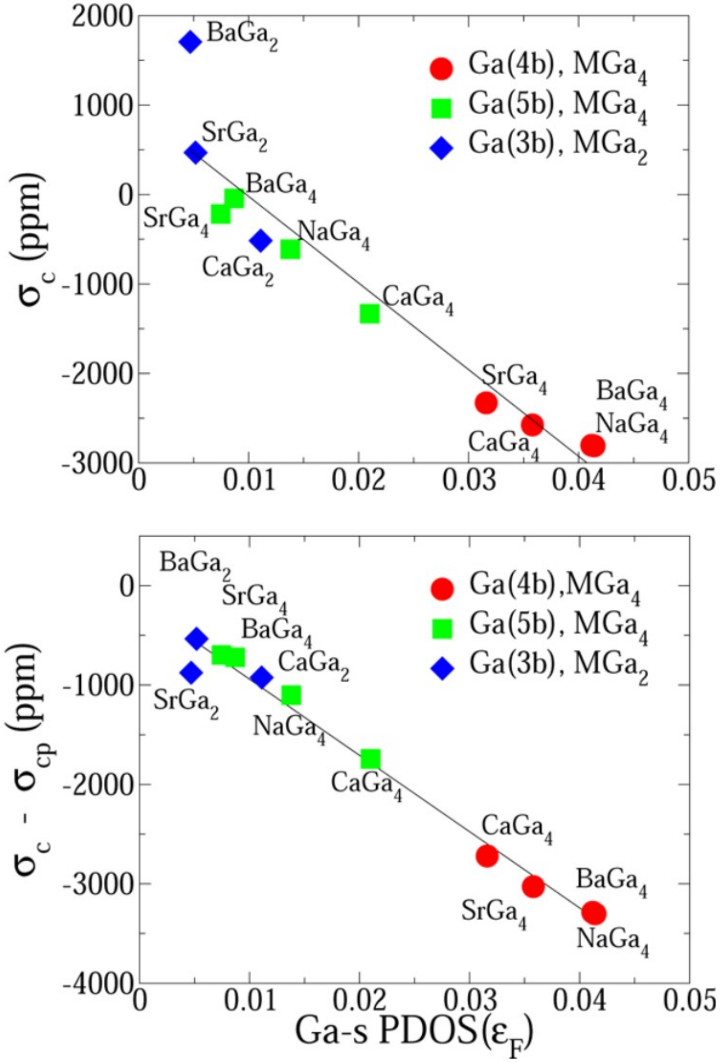
$$u_\sigma(B_{ext}, r) = u^0(r) + \dot{u}^0(r)\Delta\epsilon_\sigma(B_{ext})$$

$$\mathbf{m}(r) = -\mu_B B[u^0(r)\dot{u}^0(r)]$$

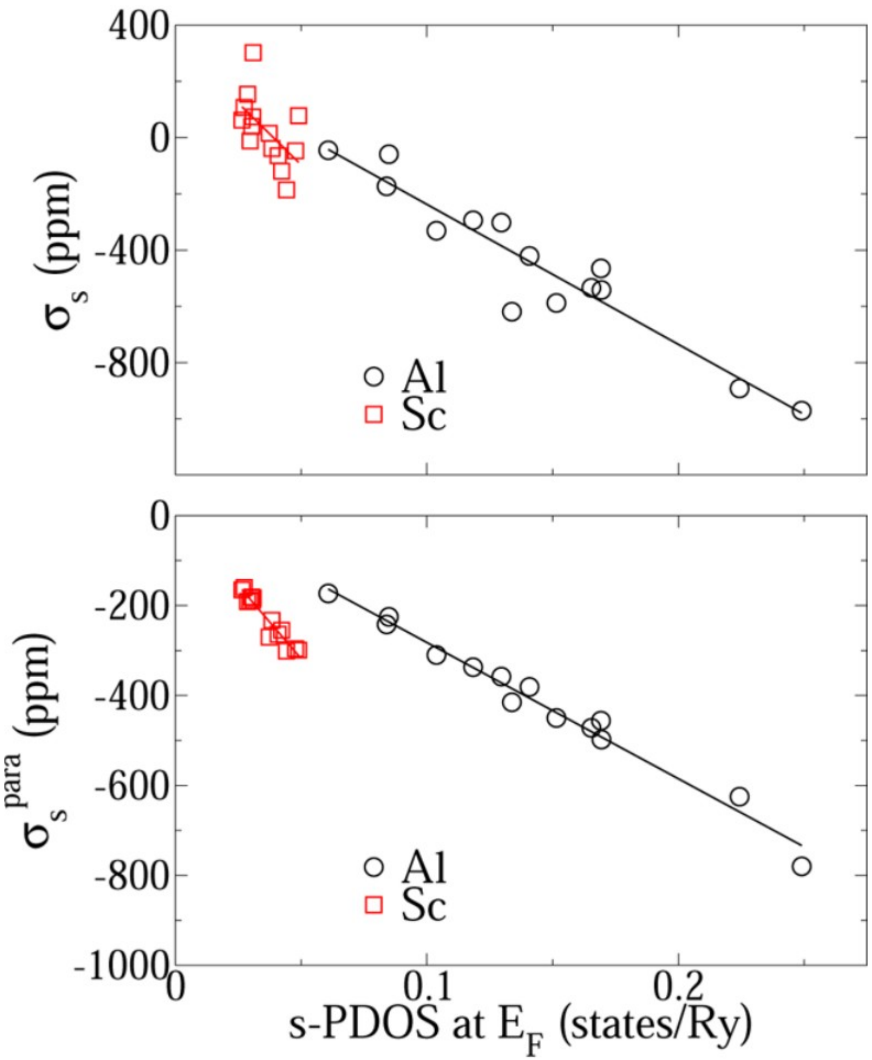
- Both u(r) and du/dr are positive close to nucleus leads to diamagnetic contribution to contact term
- it is small, up to 100ppm
- **Also seen for non-zero band gap**

Only paramagnetic polarization

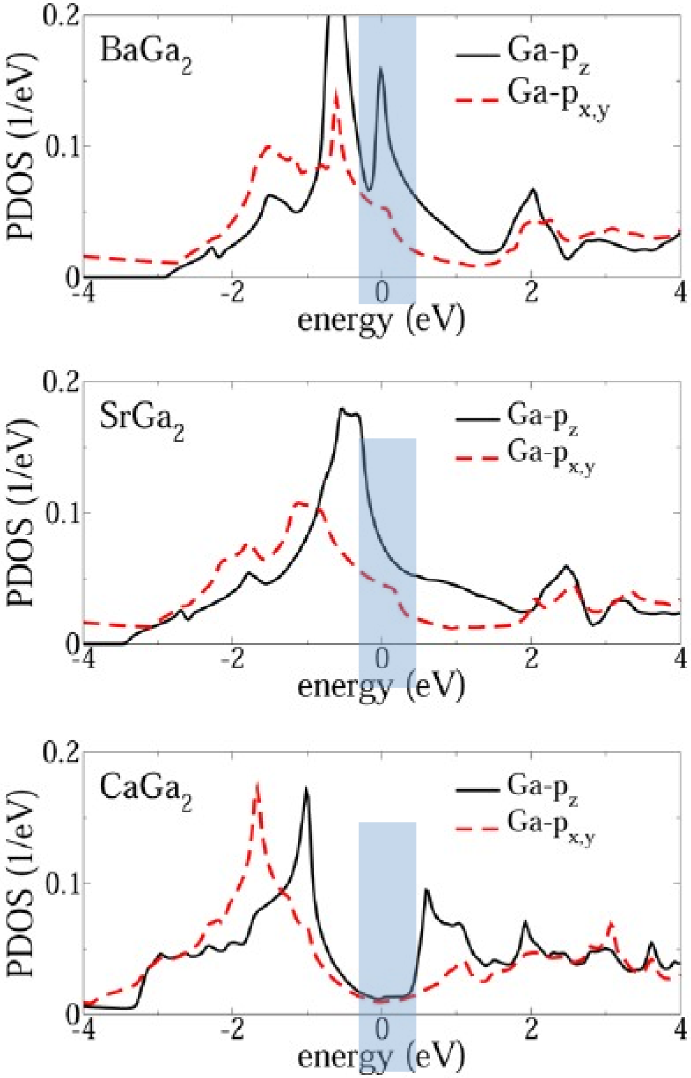
MGa$_x$



ScTT′Al



SCF effects, MGa_x



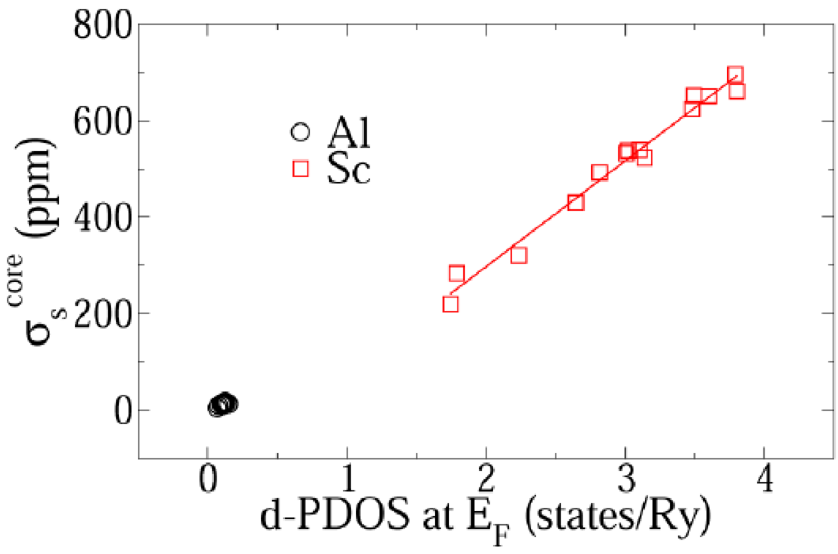
$$\sigma_{c,SCF} = 2622\ ppm$$

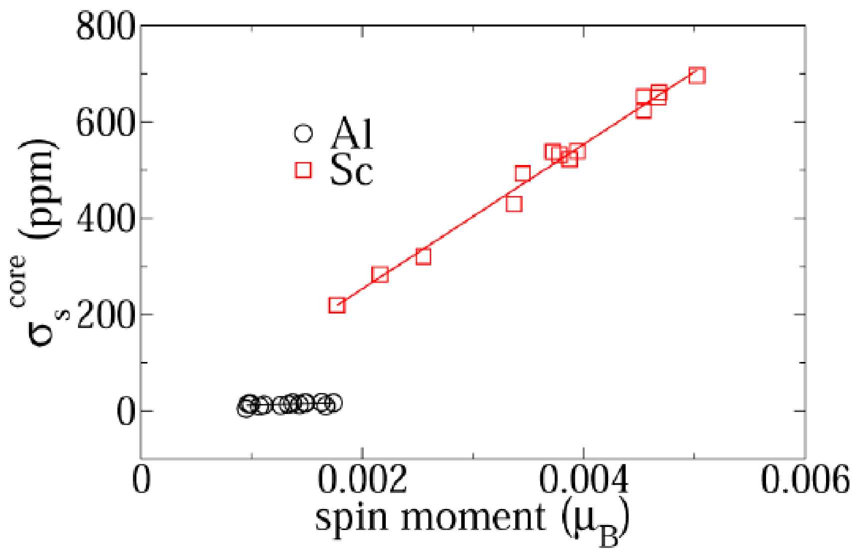
- Also large SCF effects coming from the spike

$$\sigma_{c,SCF} = 1010\ ppm$$

$$\sigma_{c,SCF} = 415\ ppm$$

SCF effects, ScTT'Al





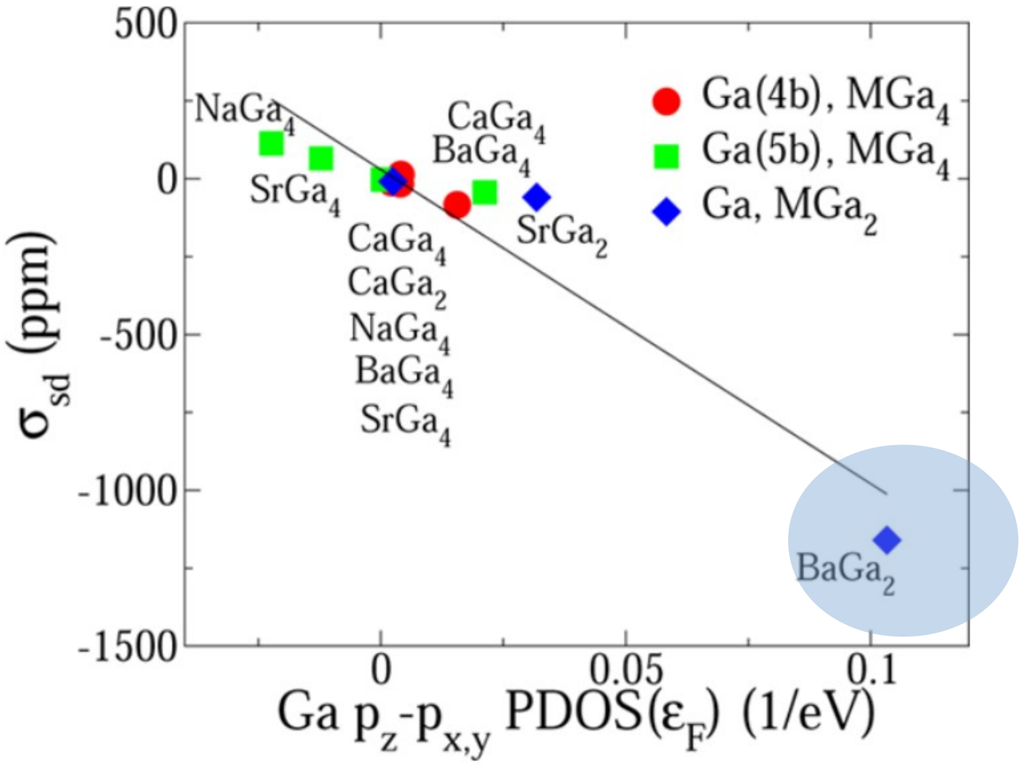
100 T external magnetic field

- Contact term contribution from core and semicore states !!!

Spin component - dipolar term

$$\mathbf{B}_{\mathrm{hf}} = \frac{8\pi}{3}\mathbf{m}_{\mathrm{av}} + \underbrace{\int \frac{S(r)}{r^3}[3(\mathbf{m}(r)\hat{r})\hat{r} - \mathbf{m}(r)]\, d^3r}_{\text{dipole term}}$$

dipole term



- BaGa2, huge dipole term, p-PDOS ?

$$B^z_{\mathrm{sd}} \sim -\frac{3}{2}\sum_o \langle o|\frac{S(r)}{r^3}(l_x^2 + l_y^2 - 2l_z^2)|o\rangle$$

Thank you for your attention