Calculations of NMR Shielding in Solids

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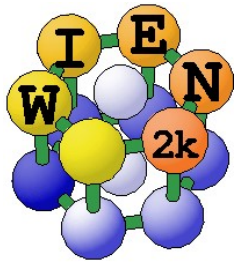
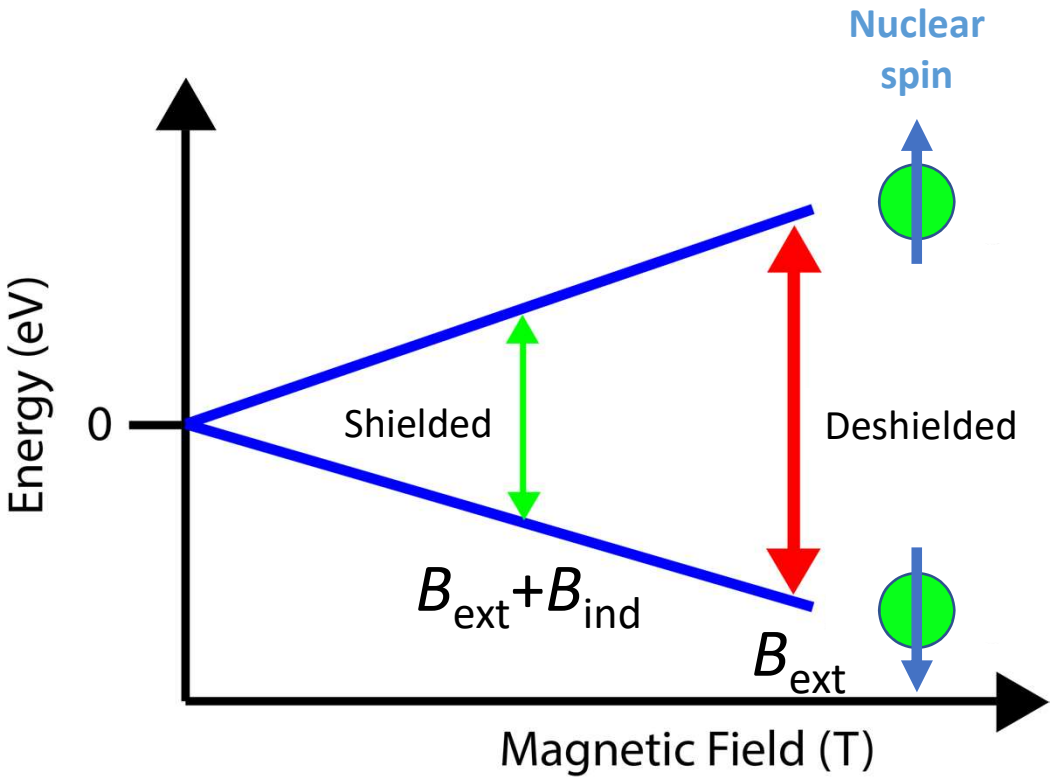


NMR Shielding

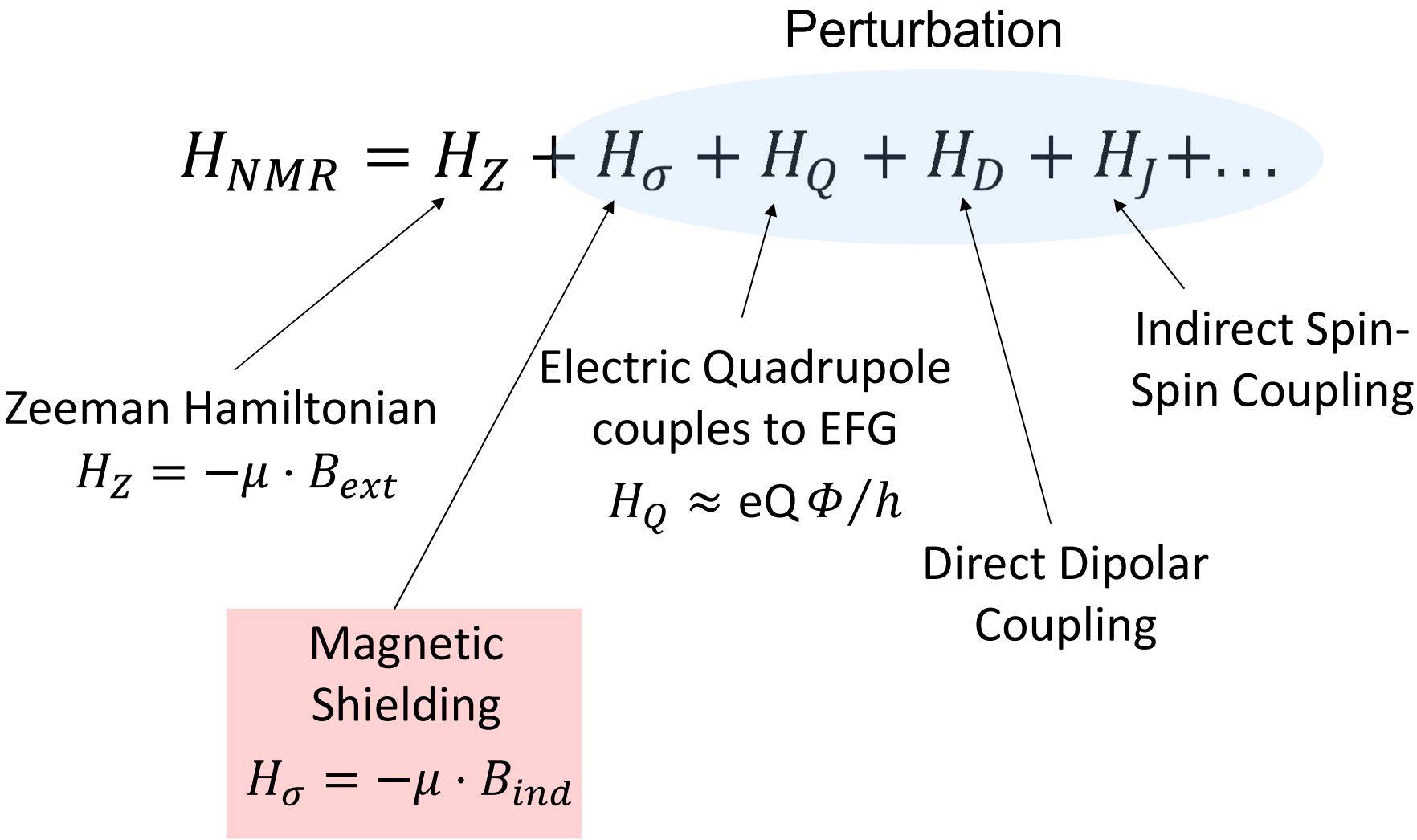


$$\Delta E = -\gamma m \hbar (B_{ext} + B_{ind})$$

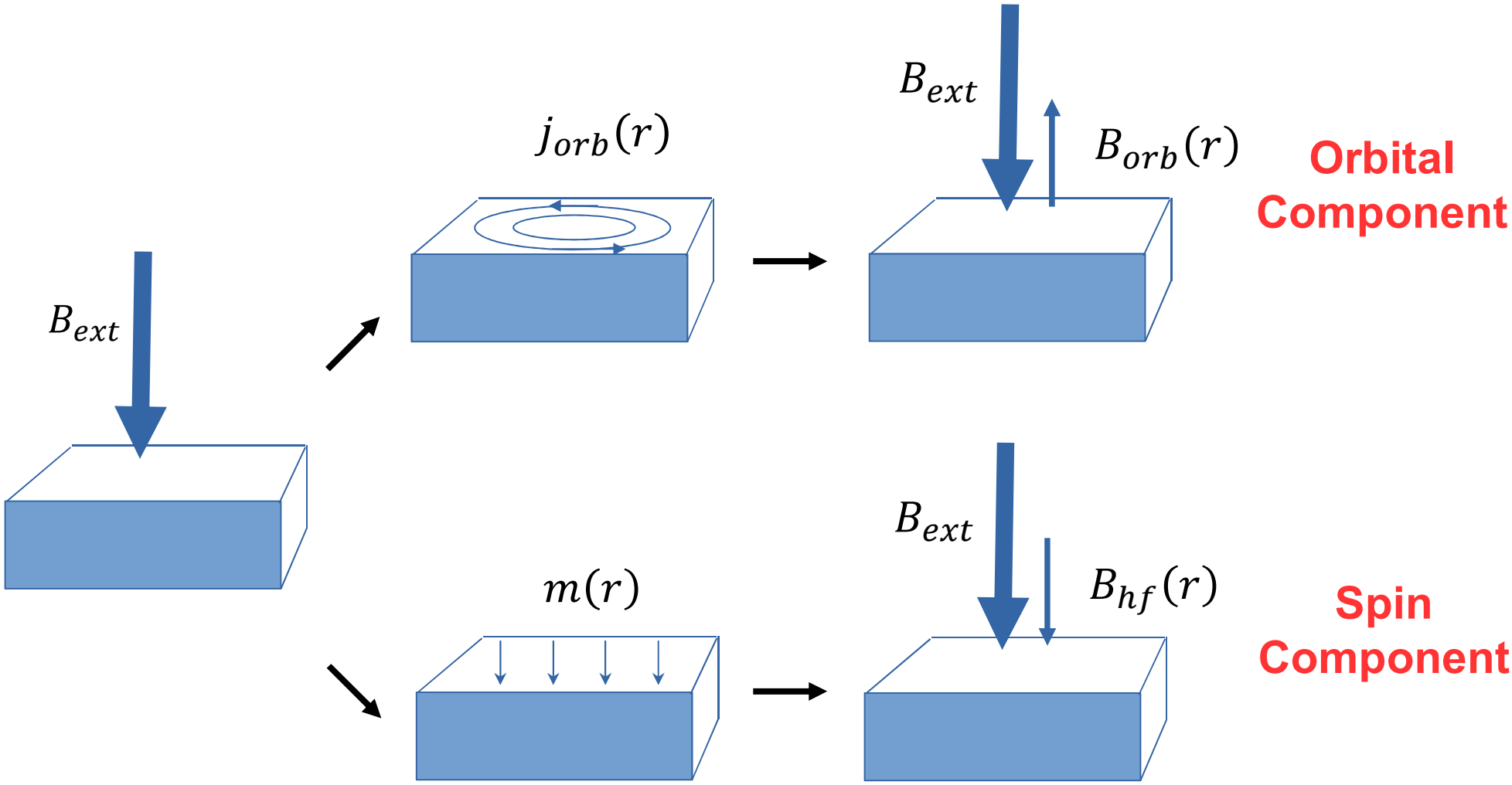
Magnetic Shielding

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

NMR Hamiltonian



Sources of Magnetic Shielding



Isotropic Shift

$$B_{ind}(\boldsymbol{R}) = B_{orb} + B_{spn}$$ where $$B_{orb} = -\overline{\sigma}_o(\boldsymbol{R})B_{ext}$$ $$B_{spn} = -\overline{\sigma}_s(\boldsymbol{R})B_{ext}$$

$$\overline{\sigma}(\boldsymbol{R}) = \overline{\sigma_o}(\boldsymbol{R}) + \overline{\sigma_s}(\boldsymbol{R})$$ shielding tensor at nucleus ***R***

$$\sigma(\boldsymbol{R}) = \frac{1}{3}Tr[\overline{\sigma}(\boldsymbol{R})]$$ isotropic shielding

$$\delta(ppm) = (\sigma_{ref} - \sigma) \times 10^6$$ isotropic shift

Orbital Component of NMR Shielding

Orbital Shielding

- The induced magnetic field $\boldsymbol{B_{orb}}$ is derived from induced current ***j*** using the Biot-Savart law

$$B_{orb}(r) = \frac{1}{c}\int j(r') \times \frac{r - r'}{|r - r'|^3}\, d^3r'$$

- Current *j*(*r*) comes from DFT:

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

- Eigenstates $|\Psi_o\rangle$ are obtained in presence of B-field

$$\boldsymbol{p} \rightarrow \boldsymbol{p} + \boldsymbol{A}(\boldsymbol{r}') \quad \text{where} \quad \boldsymbol{A}(\boldsymbol{r}) = \frac{1}{2}\boldsymbol{B} \times (\boldsymbol{r} - \boldsymbol{d}) \quad \text{(symmetric gauge)}$$

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

ill defined for extended systems

- **Linear response theory**
- Wavefunction in **first-order perturbation**

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

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

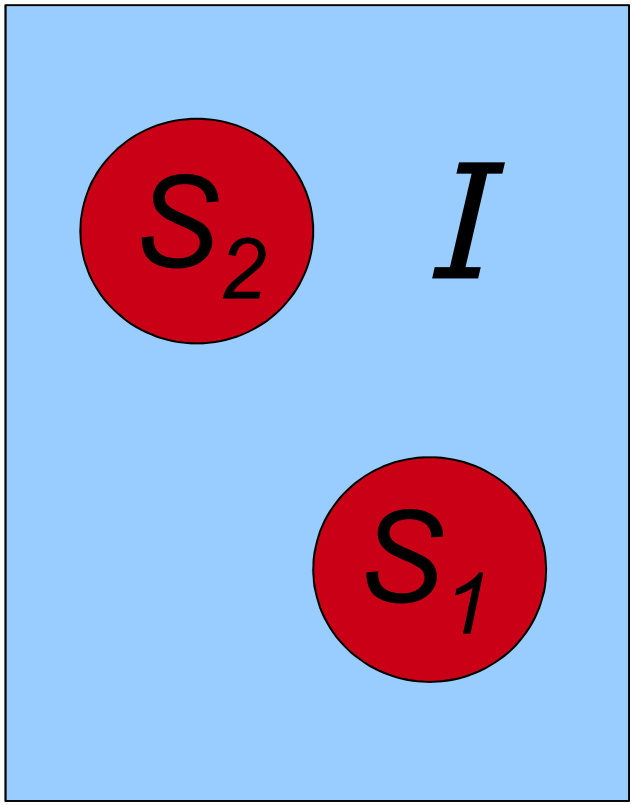
Periodic Symmetry

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

- $H^{(1)}$ couples $\boldsymbol{k}$ and $\boldsymbol{k}\pm\boldsymbol{q}$ states
- Eigenfunctions have to be computed on k-meshes shifted by $\pm\boldsymbol{q}$ for small q

PRB **85**, 035132 (2012), PRB **89**, 014402 (2014)

APW (WIEN2k) Basis Set



LAPW plane waves

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

Local orbitals

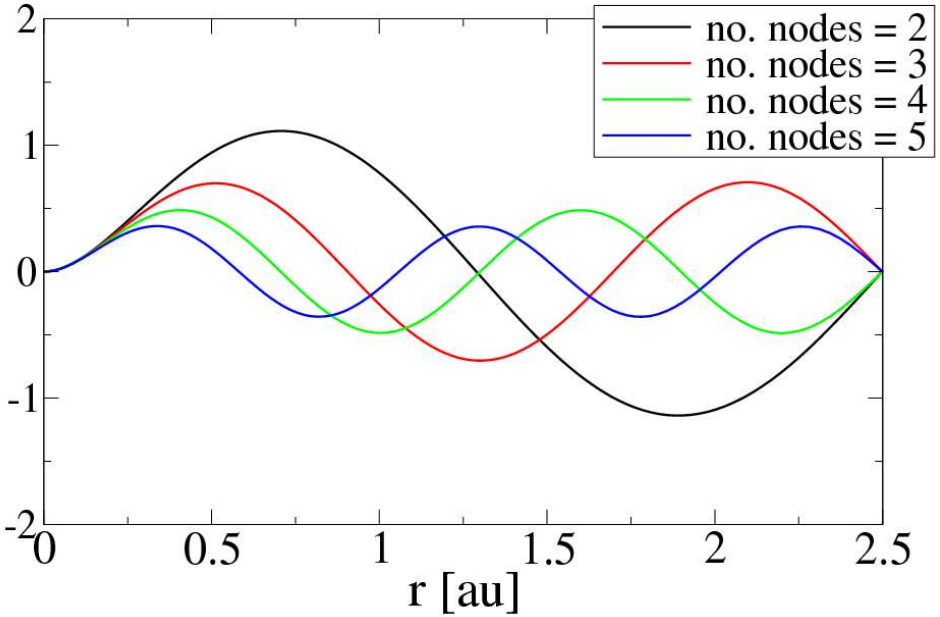
$$\phi^{LO,\alpha,i}_{l,m,\mathbf{k}}(\mathbf{r}) = \begin{cases} 0, & \mathbf{r} \in I \\ \left[A^{i,\alpha,\mathbf{k}}_{l,m} u^{\alpha}_{l}(r, E_l) + B^{i,\alpha,\mathbf{k}}_{l,m} \dot{u}^{\alpha}_{l}(r, E_l) \right. & \\ \left. \quad + C^{i,\alpha,\mathbf{k}}_{l,m} u^{\alpha,i}_{l}(r, E^i_l) \right]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

Wave function

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

Augmenting the APW Basis Set

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



p LOs in atomic Be

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

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

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

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

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

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

Core Contributions

- Core states are covered by a separate eigenvalue problem, contribution is purely diamagnetic:

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

- Separate treatment of core and valence orbitals introduces some errors, corrected by:

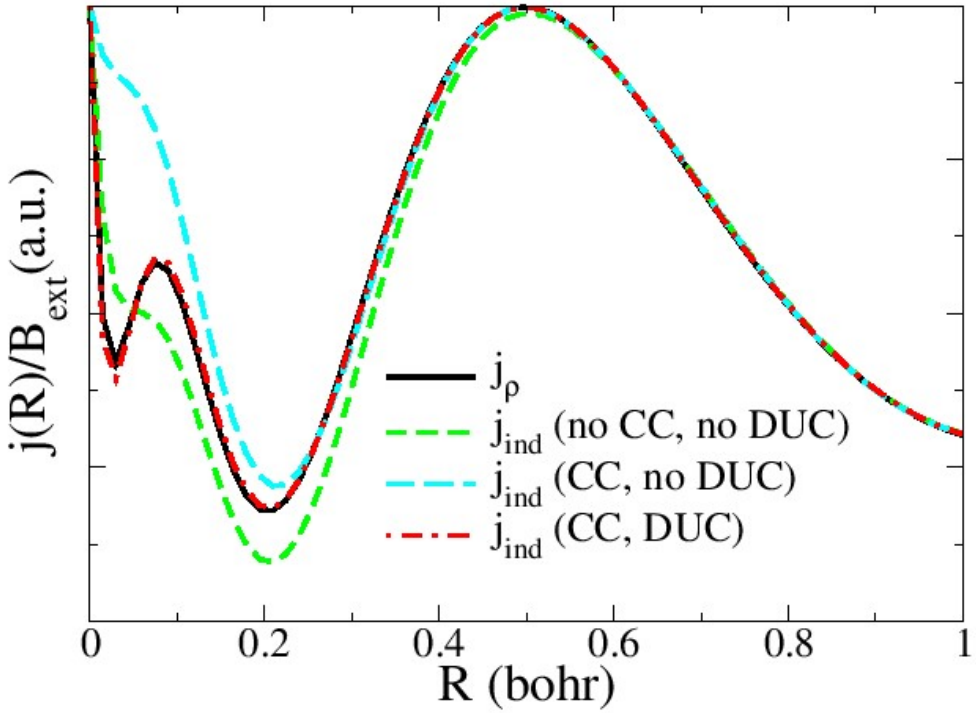
$$|\Psi_o^{(1)}\rangle = \sum_e |\Psi_e^{(0)}\rangle \frac{\langle \Psi_e^{(0)}|H^{(1)}|\Psi_o^{(0)}\rangle}{\epsilon_o - \epsilon_e} + \sum_{core} |\Psi_{core}^{(0)}\rangle \frac{\langle \Psi_{core}^{(0)}|H^{(1)}|\Psi_o^{(0)}\rangle}{\epsilon_o - \epsilon_{core}}$$

← **Correction**

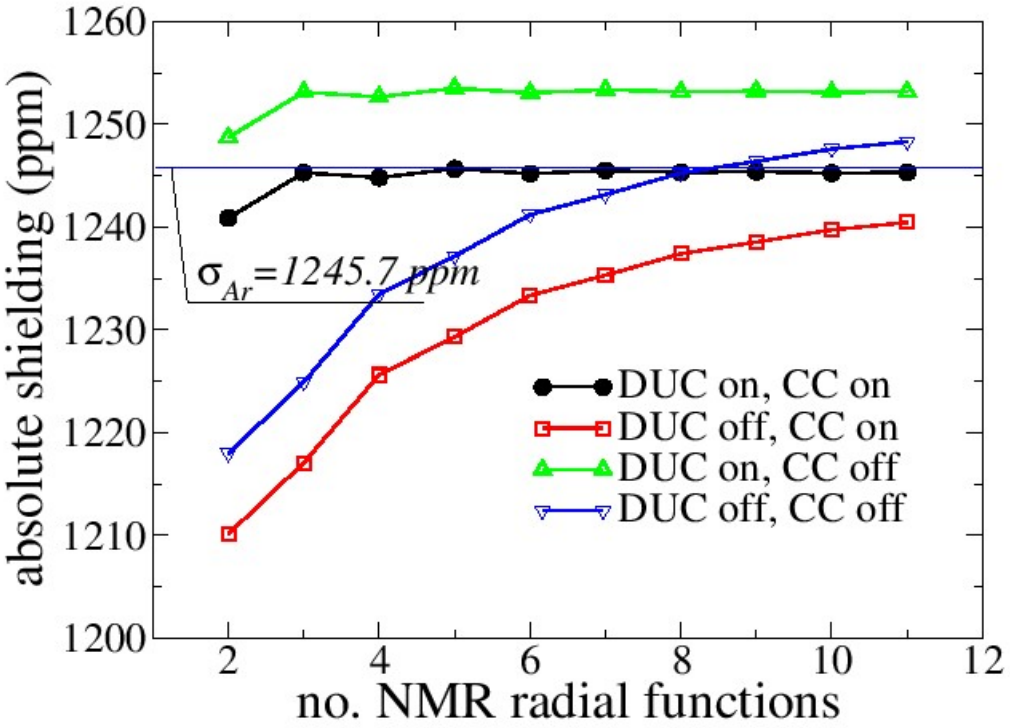
PRB **89**, 014402 (2014)

Benchmark: Spherical Ar Atom

Test of the solution for spherically symmetric Ar atom



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



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

Running the Code

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

   (-focus, -nodes)
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
- …

x_nmr (work flow)

prepare case.in1

x_nmr -mode in1

executes:

lapw1 at +/- **q**

results in:

`./nmr_q0, ./nmr_mqx, ./nmr_pqx`
`./nmr_mqy, ./nmr_pqy./nmr_mqz,`
`./nmr_pqz`

x_nmr -mode lapw1

executes *x lapw2* -fermi in `./nmr_xxx` (weights)

x_nmr -mode lapw2

executes *x lcore* (core wave-functions)

x_nmr -mode lcore

computes induced current

x_nmr -mode current

integrates the Biot-Savart law and computes the shielding

x_nmr -mode integ

output

- case.outputnmr_”*mode*”
- Final results (shielding tensor, trace, anisotropy, …)

case.outputnmr_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 -h	
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 *dir*	scratch
x_nmr -quota *numk*	

- band wise analysis

  x_nmr -emin *e1* -emax *e2*

- character analysis (s,p,d) of the wave functions of occupied and empty states

x_nmr -filt_curr_o *atom l*

x_nmr -filt_curr_fop *atom l*

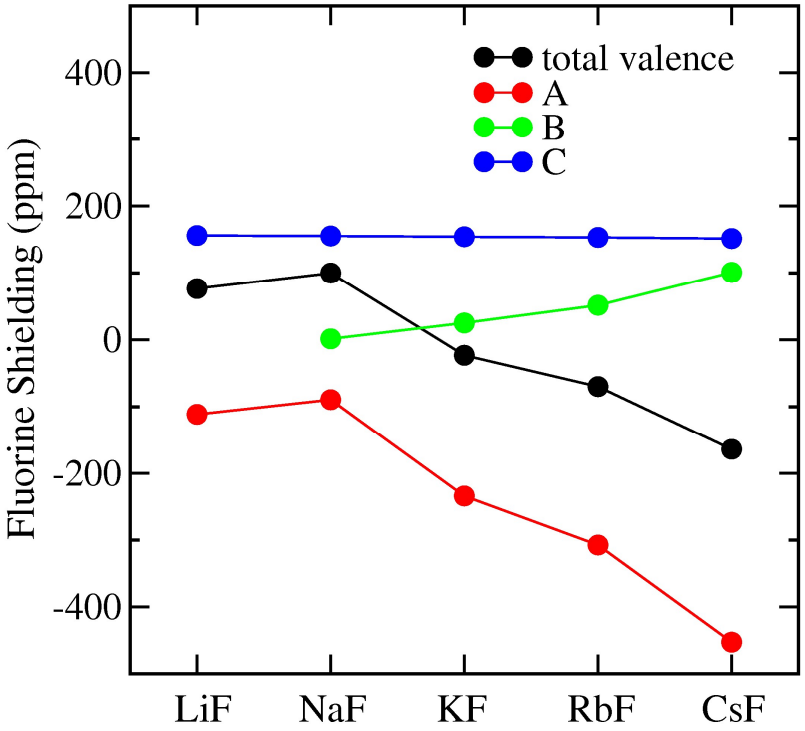
$$\mathbf{j}_{ind}(\mathbf{r}') = \frac{1}{c}\sum_{o} Re\left[\langle\Psi_o^{(0)}|\mathbf{J}^0(\mathbf{r}')|\tilde{\Psi}_o^{(1)}\rangle\right]$$

x_nmr -filt_cxyz_q *atom l*

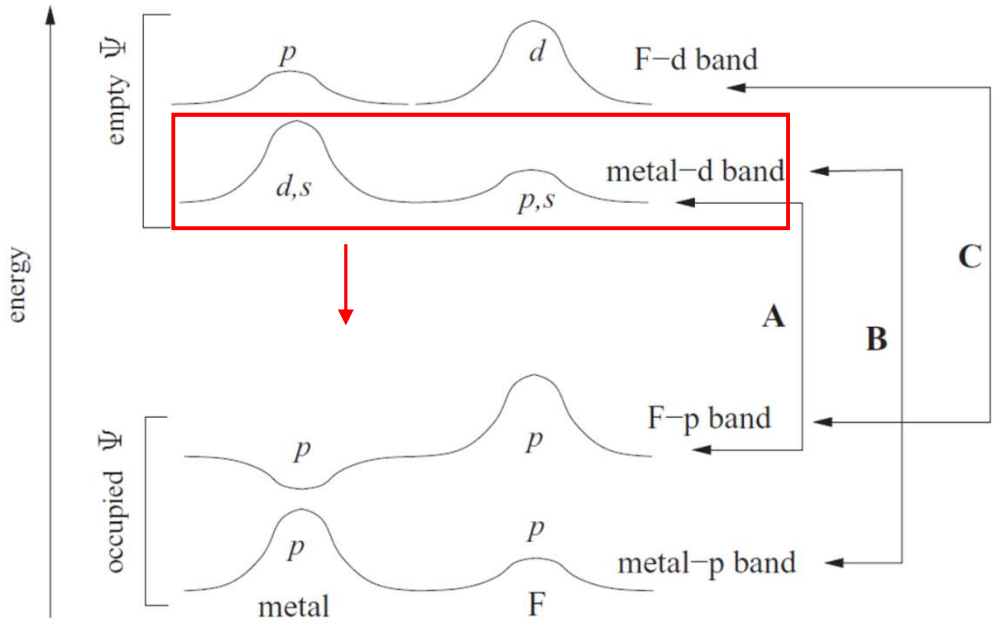
x_nmr -filt_cxyz_o *atom l*

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

Origin of Shielding in Fluorides



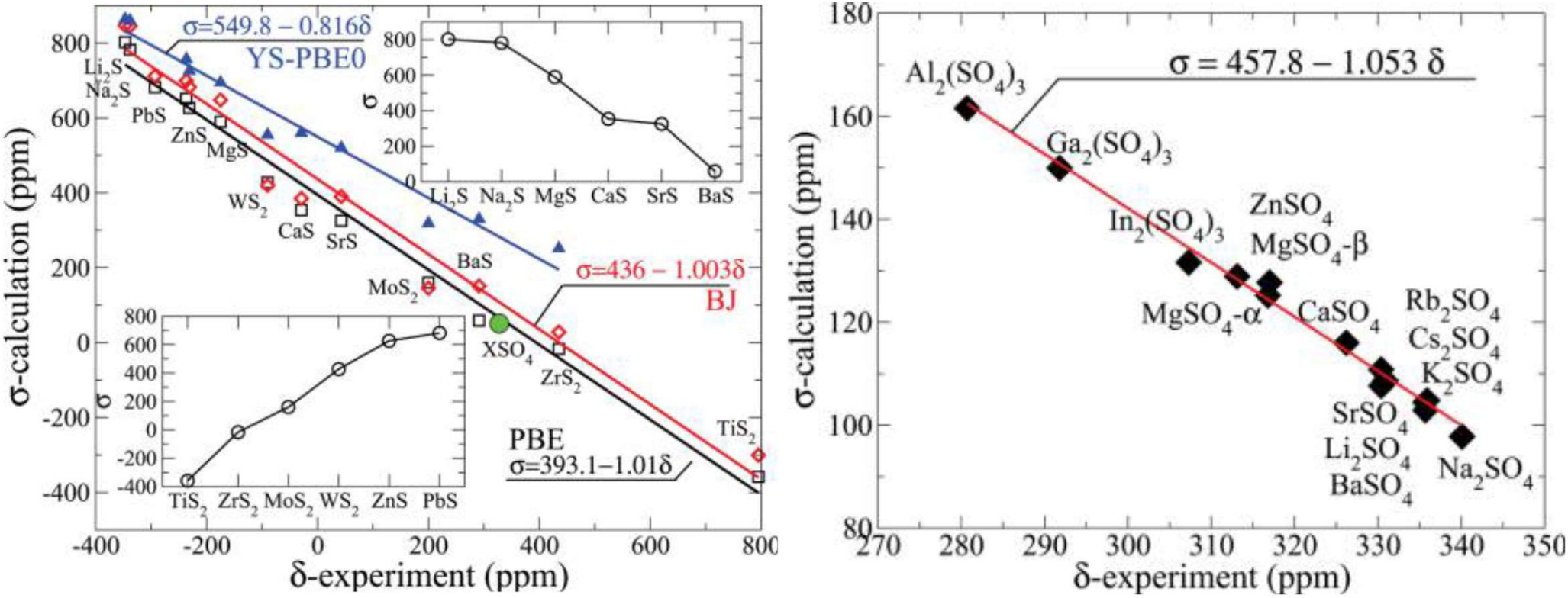
NMR shielding at fluorine nucleus in alkali fluoride series for different couplings



Schematic diagram representing major couplings contributing to NMR shielding

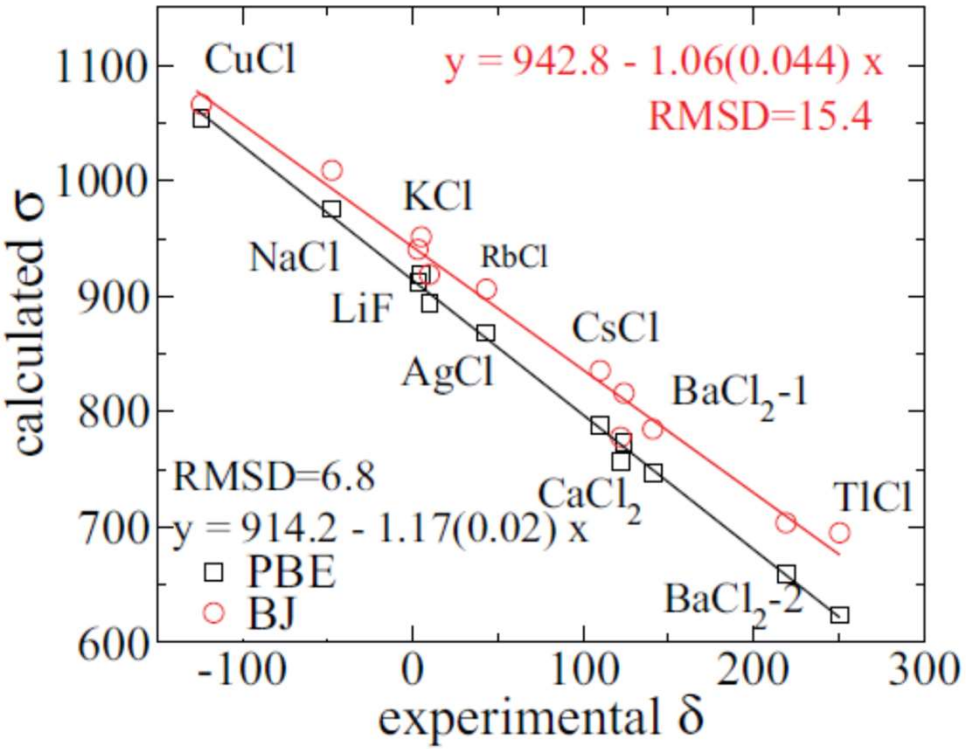
PRB **85**, 245117 (2012)

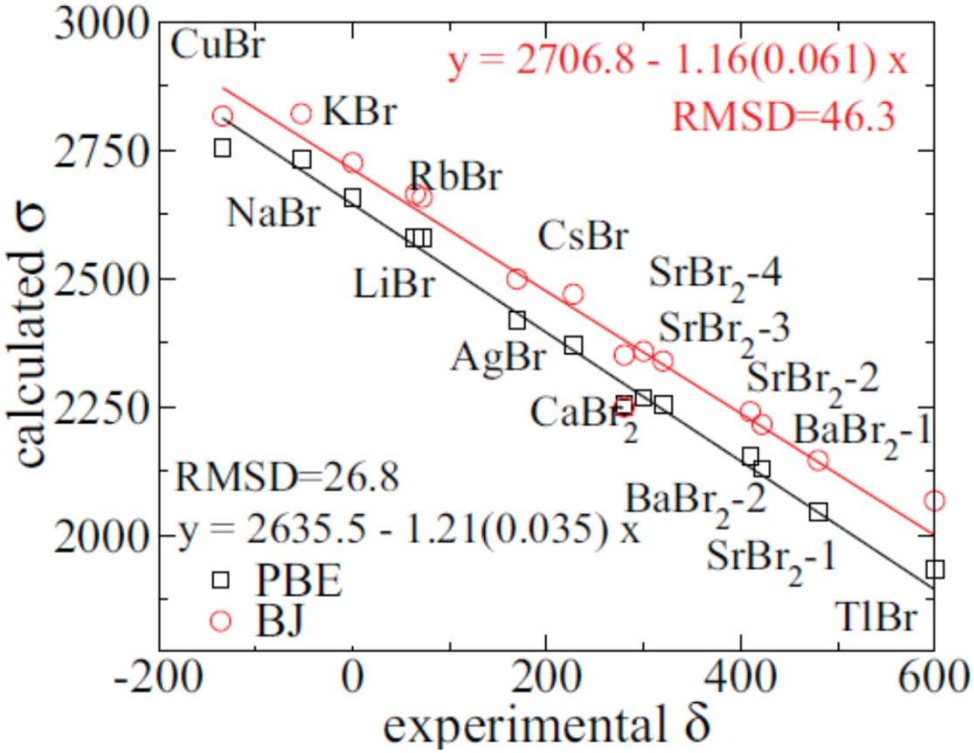
Results



Correlation of calculated NMR shielding vs measured chemical shifts for inorganic sulphides (left) and sulphates (right)

JPCC **119**, 731 (2015)

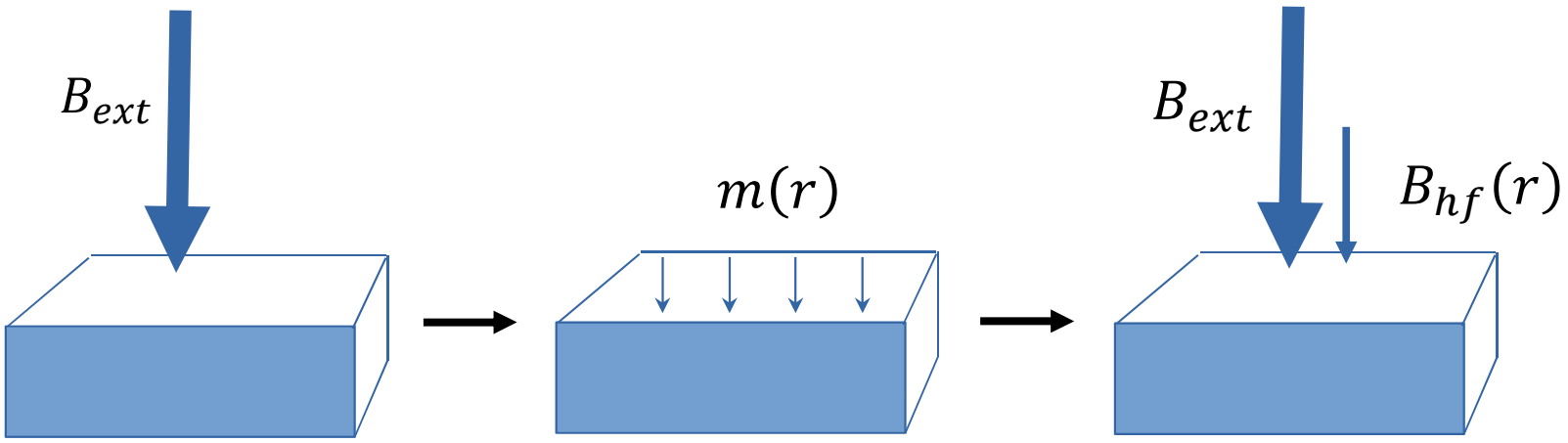




PRB **87**, 19130 (2013)

Spin Component of NMR Shielding

Spin Shielding (Knight Shifts)



- $\boldsymbol{B_{ext}}$ cast as potential acting only on spins
- Compute $\boldsymbol{m}(\boldsymbol{r})$ from **self-consistent** DFT

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

contact term **dipole term**

JPCC **119**, 19390 (2015)

Calculation for Contact Term

1) Spin-polarized calculation with **zero** moment

- *instgen -nm* # generate nonmagnetic atomic configurations
- *init_lapw -sp -fermit 0.004 -numk XXX ...* # initialization
- *runsp_c_lapw -c 0.00001 [-p] ...* # run scf with zero moment

2) Copy input file specifying 100T field

- *cp $WIENROOT/SRC templates/case.vorbup(dn)_100T case.vorbup(dn)*

3) SCF calculation with external magnetic field

- *runsp_lapw -orbc -cc 0.000001 [-p] ...* # scf calculation
- *grepline :HFF0XX case.scf* # get the hyperfine field

:HFF0XX is contact hyperfine field in kGauss

$$\sigma_c[ppm] = -HFF * 1000$$ for B_{ext} = 100T

HYPERFINE FIELDS FOR THOMSON RADIUS

:HFF001:	0.659	0.000	-0.040	0.619 (KGAUSS)
:HFF002:	4.445	0.000	-2.205	2.239 (KGAUSS)
:HFF003:	0.146	0.000	-0.161	-0.015 (KGAUSS)

valence **semicore** **core**

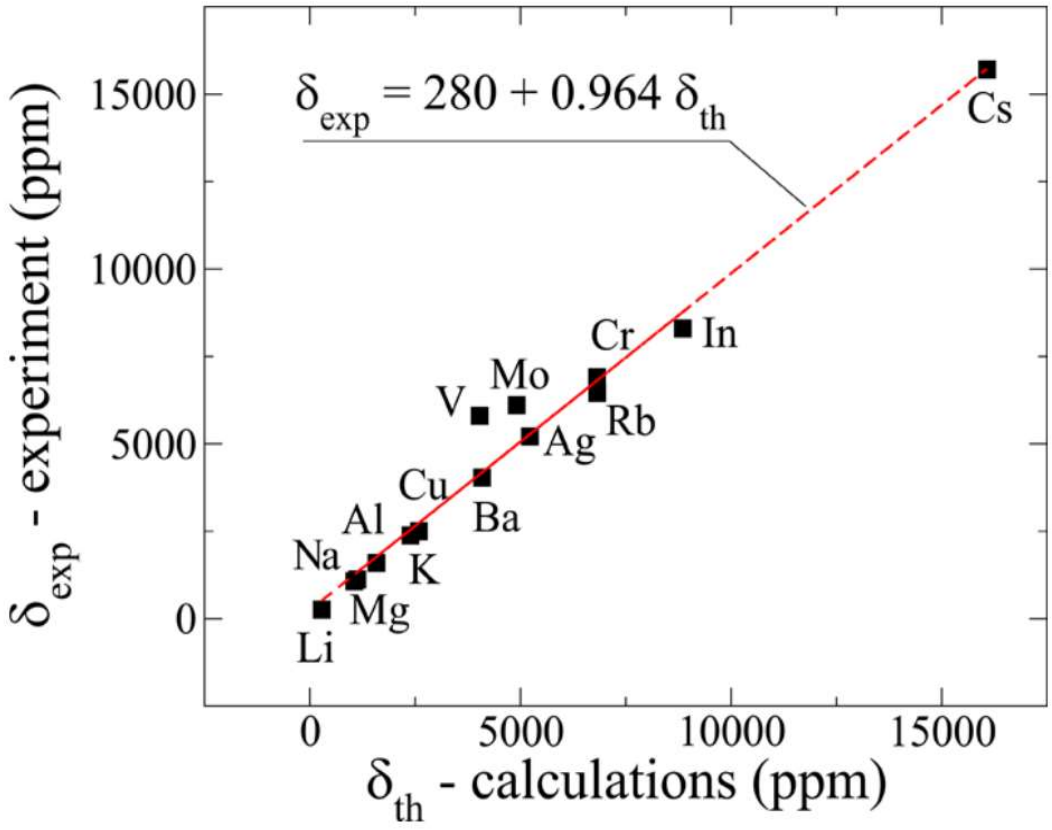
Calculation for Spin Dipolar Term

After getting self-consistent density in B-field:

- *cp $WIENROOT/SRC templates/case.indm case.indm*
- Set last line of *case.indm* (r-index, (l,s)index) to “3 5”
- *x lapwdm -up/dn ...*
- Find difference of total :XOP0xx values in *case.scfdmup/dn* files

$$\sigma_{sd}[ppm] = -(XOP_{up} - XOP_{dn}) * 10000$$ for B_{ext} = 100T

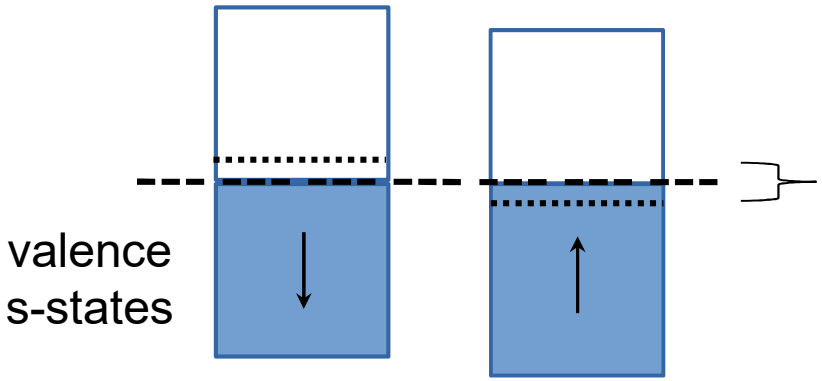
Results



Correlation of measured vs calculated NMR shifts for various metallic elements

JPCC **119**, 19390 (2015)

Conventional Wisdom on Spin Shielding



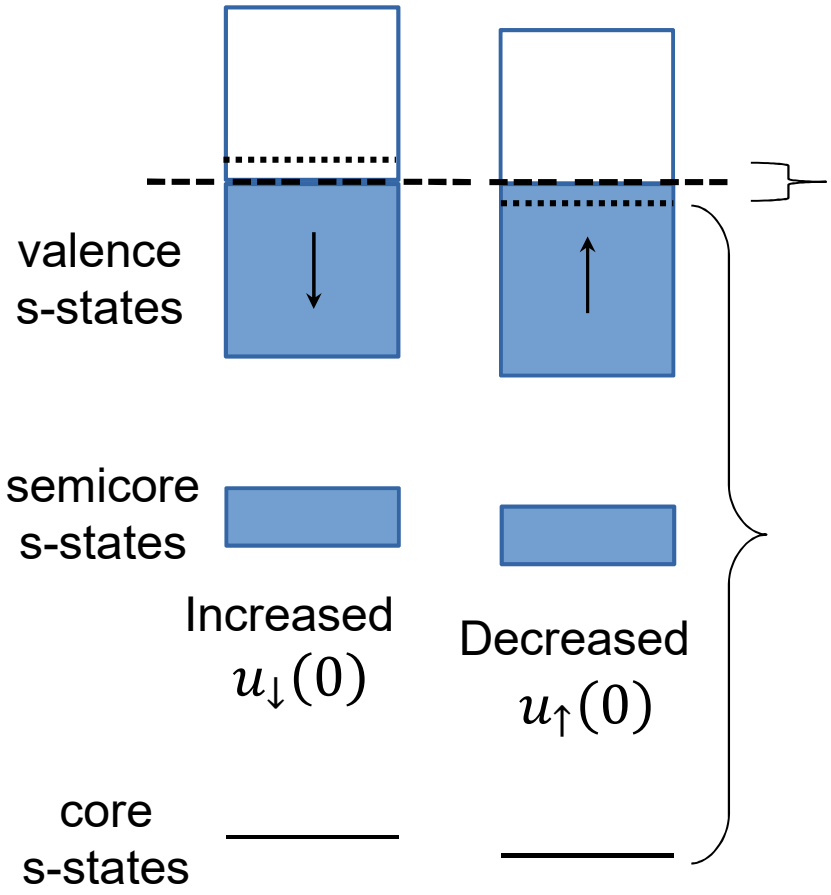
Paramagnetic

$$m(r=0) = N_{l=0}(\epsilon_F)\left(\Delta\epsilon_{\downarrow}(B_{ext}) - \Delta\epsilon_{\uparrow}(B_{ext})\right)u_{l=0}(0)^2$$

- Spin Shielding is thought to be:
  - ***Only paramagnetic***
  - ***Only valence contributions (frozen core)***
  - ***Absent in insulators***
  - ***Linear response is sufficient***

Our work shows above assumptions are not always true (however good for sp-metals)

Core Polarization Effects



Paramagnetic

$$m(r=0) = N_{l=0}(\epsilon_F)\left(\Delta\epsilon_\downarrow(B_{ext}) - \Delta\epsilon_\uparrow(B_{ext})\right)u_{l=0}(0)^2$$

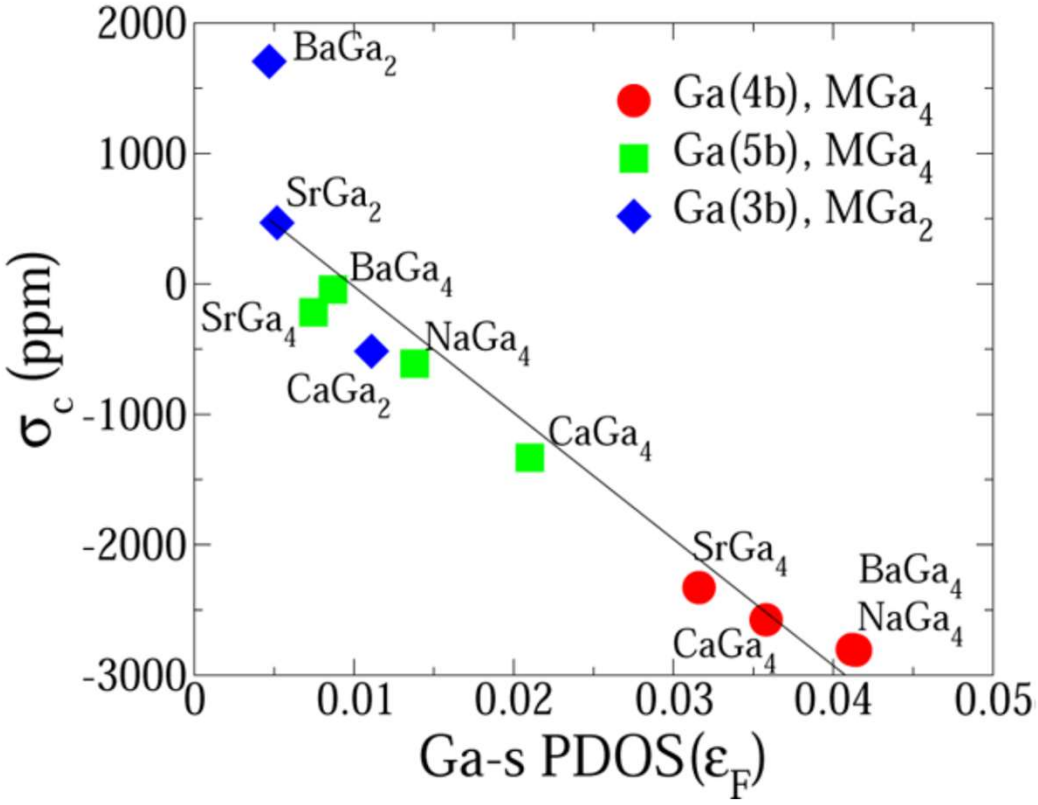
Diamagnetic

$$\Delta u_\sigma(0) = \dot{u}_{l=0}(0)\Delta\epsilon_\sigma(B_{ext})$$

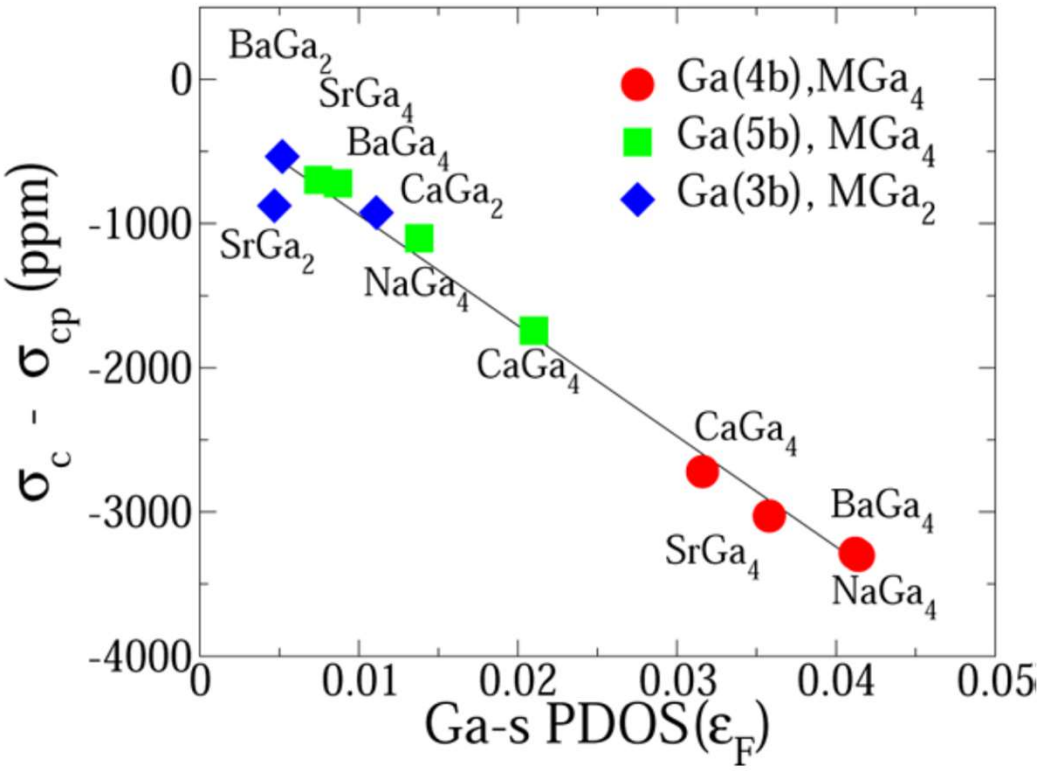
$u_\uparrow(0)$ decreases and $u_\downarrow(0)$ increases

- Fully occupied states (including semicore and core) also contribute to σ_c
- σ_c can also have diamagnetic contributions

Contact Contribution for MGa_n



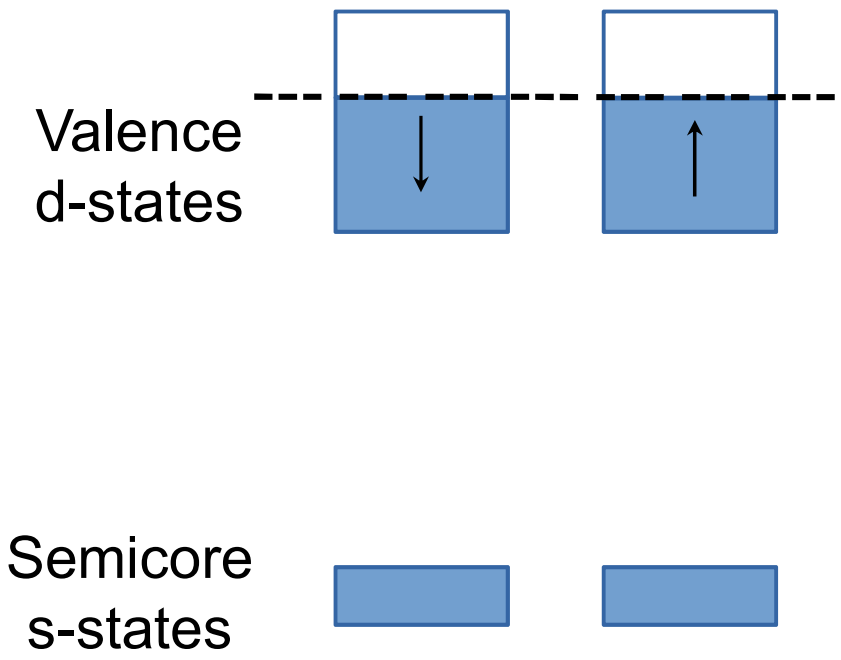
σ_c vs s-partial DOS at ε_F for MGa_n



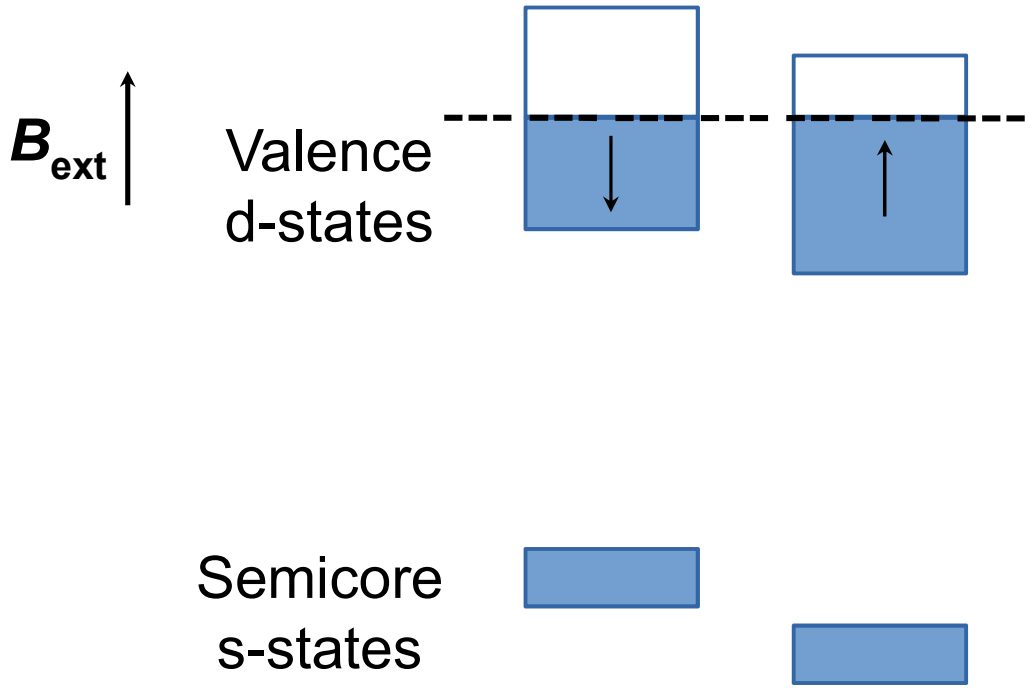
Paramagnetic σ_c^{para} from reoccupation of spin up and down states vs s-partial DOS at ε_F for MGa_n

JPCC **121**, 753 (2017)

Self-Consistency Effects



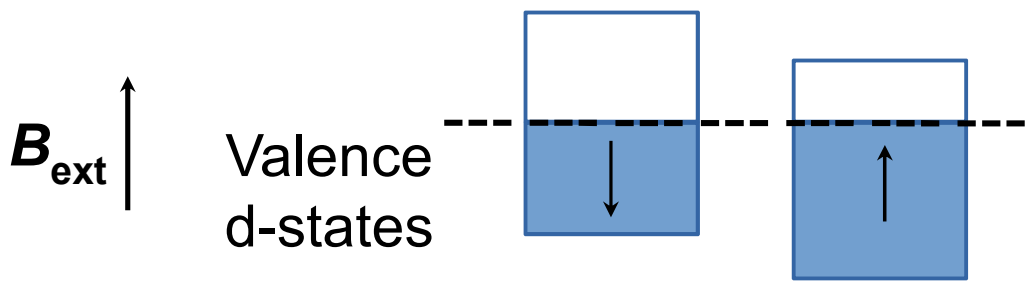
Self-Consistency Effects



Linear response

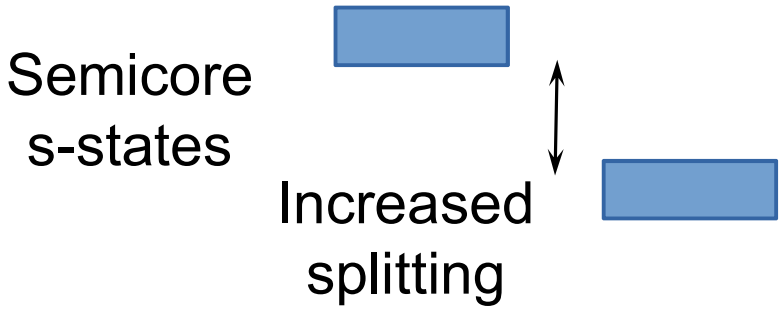
B_{ext} induces $m_d(r)$

Self-Consistency Effects



Linear response

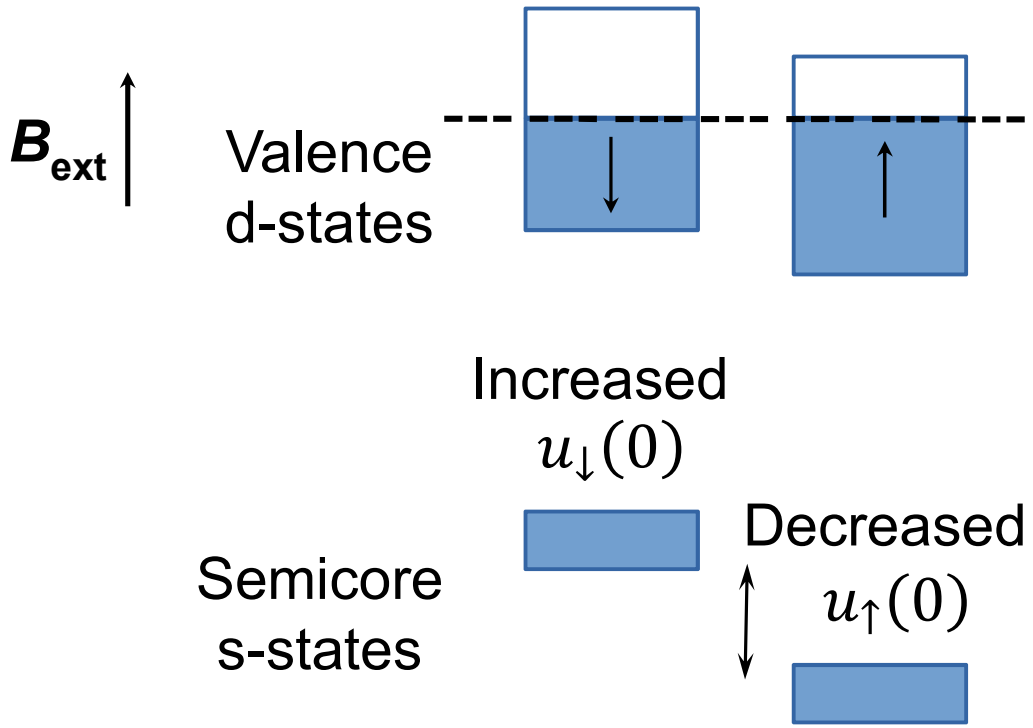
B_{ext} induces $m_d(r)$



Self-consistency

Exchange field due to $m_d(r)$ further splits semicore s-states

Self-Consistency Effects



Linear response

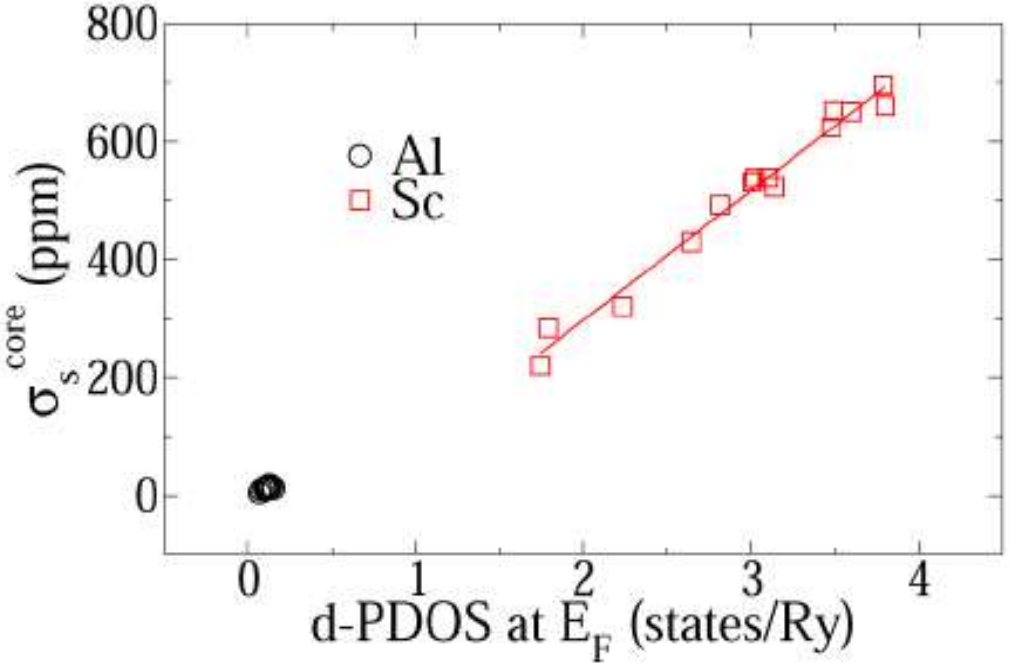
B_{ext} induces $m_d(r)$

Self-consistency

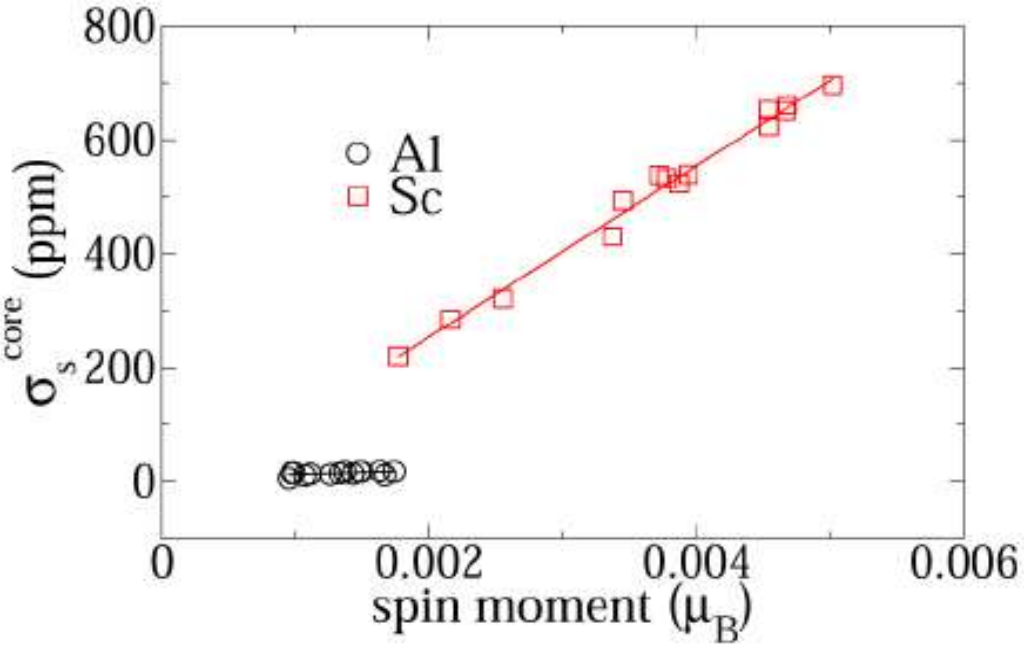
Exchange field due to $m_d(r)$ further splits semicore s-states

- Diamagnetic contribution of semicore states to σ_c increased after self-consistency
- Core/semicore contribution to σ_c scales with *d*-partial DOS at ε_F

Core Spin Shielding for ScTT'Al Heusler Alloys



σ_c^{core} vs Sc/Al *d*-PDOS at ε_F (B_{ext} = 100 T)



σ_c^{core} vs induced spin moment at ε_F (B_{ext} = 100 T)

JPCC **121**, 12398 (2017)

Thank you for your attention !!