NMR chemical shifts in wien2k

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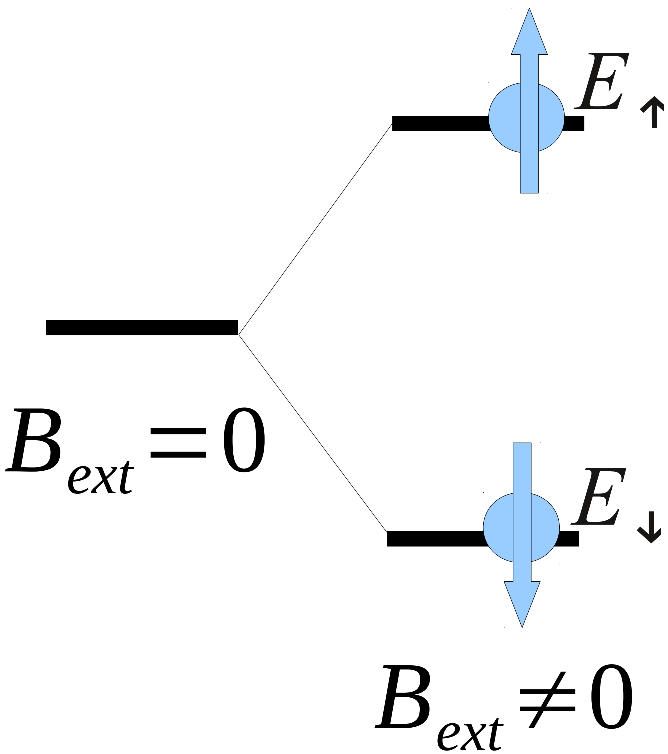
Dipole nucleus



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

induced filed

***B**$_{ext}$**+B**$_{ind}$* is measured at any nucleus by detecting transition energy related to reorientation of its dipole moment

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

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

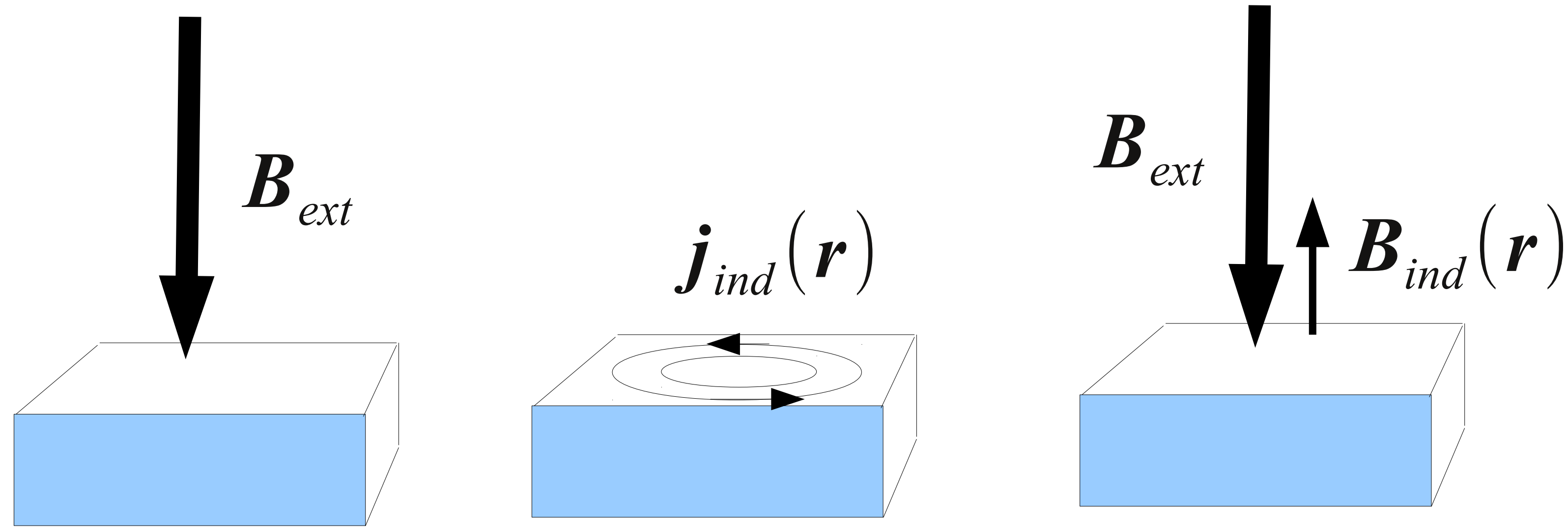
direct dipolar coupling

indirect spin-spin coupling

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

magnetic shielding

NMR shielding



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

$$\boldsymbol{B}_{ind}(\boldsymbol{R}) = -\overline{\sigma}(\boldsymbol{R})\boldsymbol{B}_{ext}$$ shielding tensor at the nucleus ***R***

$$\delta(ppm) = \frac{\sigma_{ref} - \sigma}{1 - \sigma_{ref}} \times 10^6$$ chemical shift

Biot-Savart law:

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

DFT current density:

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

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

symmetric gauge

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

Hamiltonian in the presence of the magnetic field

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

Current operator in the presence of magnetic field

paramagnetic current:

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

diamagnetic current:

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

Linear response formula for induced current

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

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

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

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

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

paramagnetic

diamagnetic

Generalized f-sum rule

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

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

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

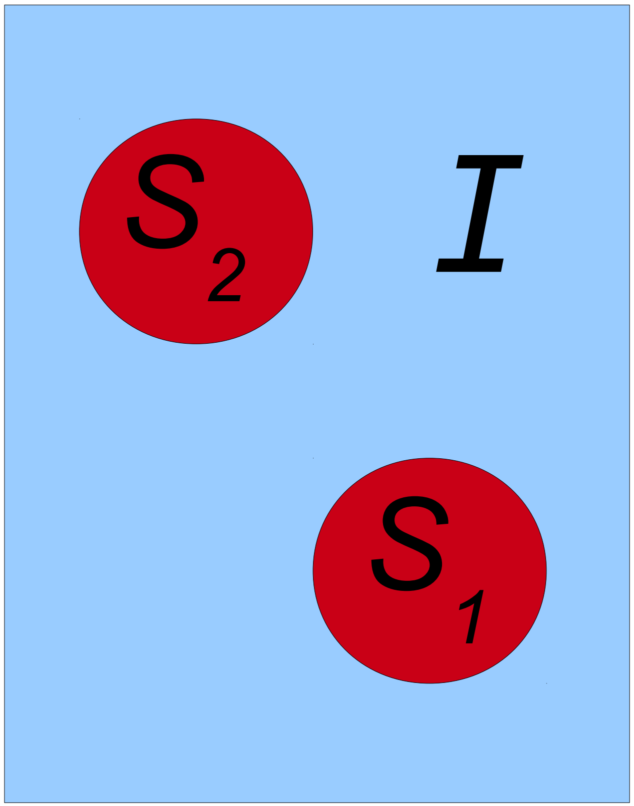
infinite (periodic) structure:

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

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

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

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

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

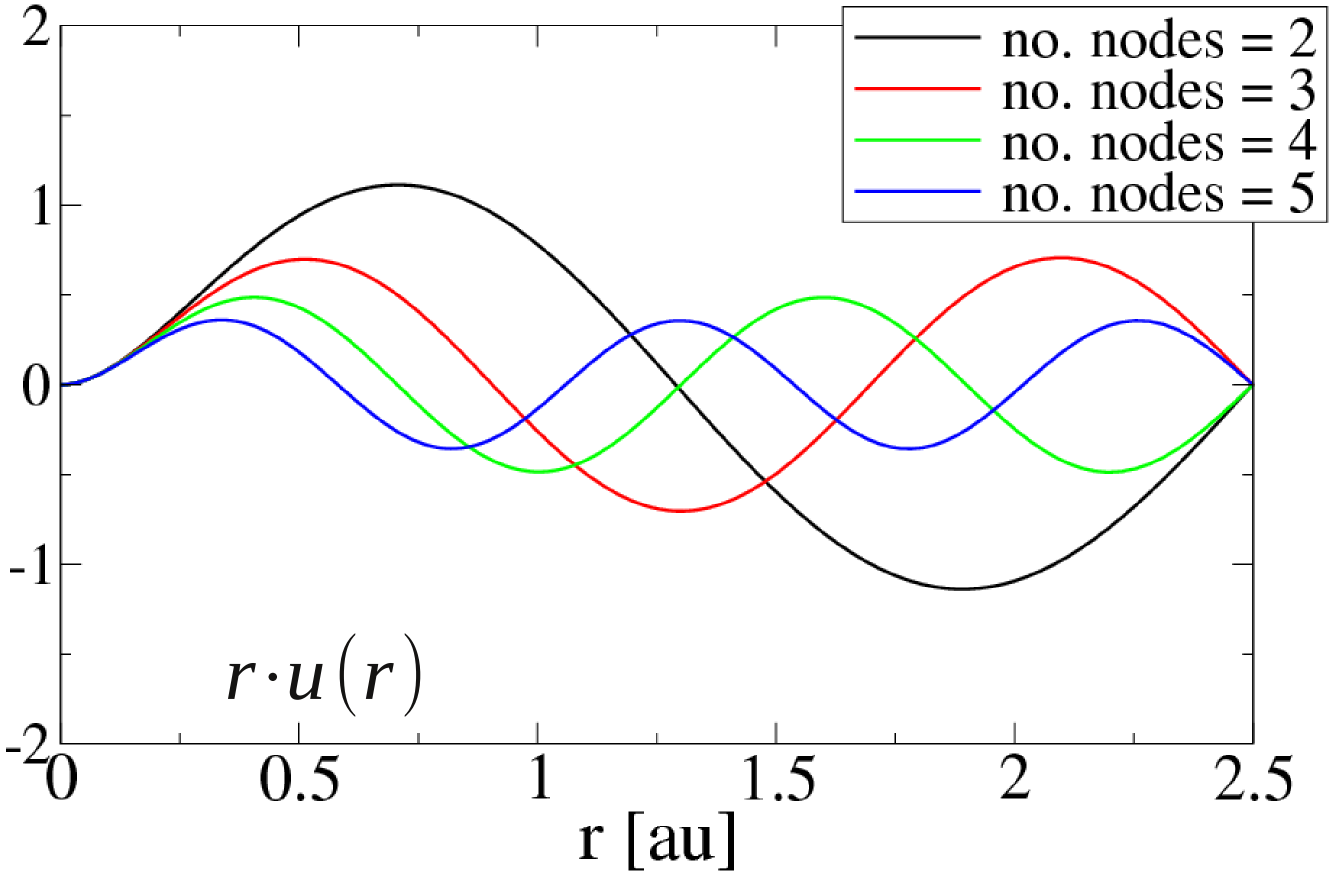
wave function

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

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

$$\phi_{l,m,\mathbf{k}}^{LO,\alpha,i}(\mathbf{r}) = \begin{cases} 0, & \mathbf{r} \in I \\ \Big[A_{l,m}^{i,\alpha,\mathbf{k}} u_l^{\alpha}(r,E_l) + B_{l,m}^{i,\alpha,\mathbf{k}} \dot{u}_l^{\alpha}(r,E_l) & \\ \quad + C_{l,m}^{i,\alpha,\mathbf{k}} u_l^{\alpha,i}(r,E_l^i)\Big] Y_{l,m}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases}$$

- 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
  - r*du/dr radial functions (DUC)

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

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

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

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

PRB 89, 014402 (2014)

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

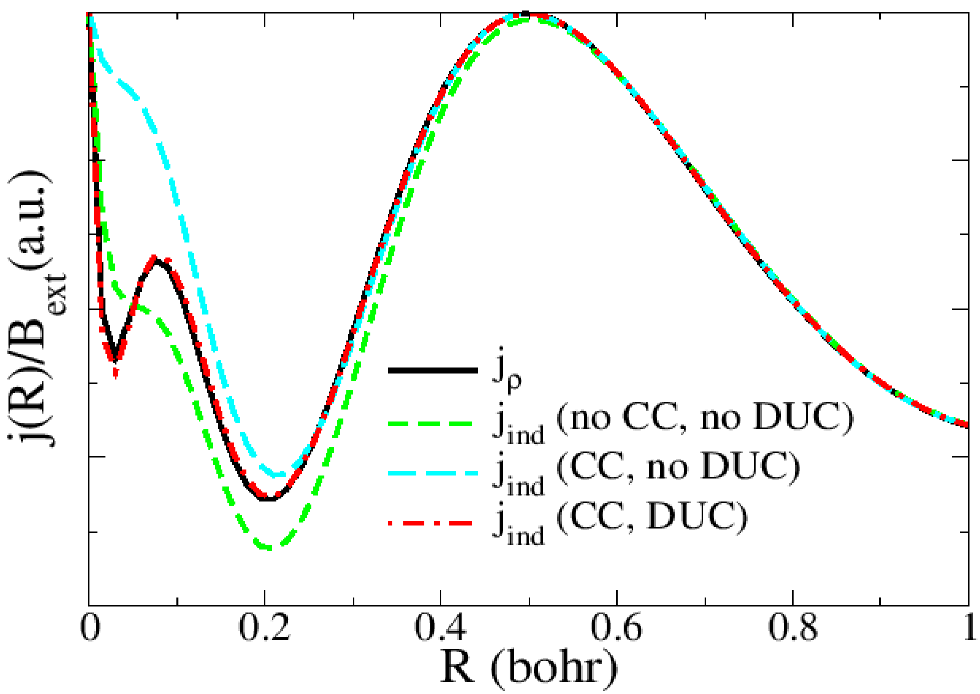
$$\mathbf{j}_{ind}(\mathbf{r}') \;=\; -\frac{1}{2c}\rho_{core}(\mathbf{r}')\mathbf{B}\times\mathbf{r}'$$

- errors corrected by (CC):

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

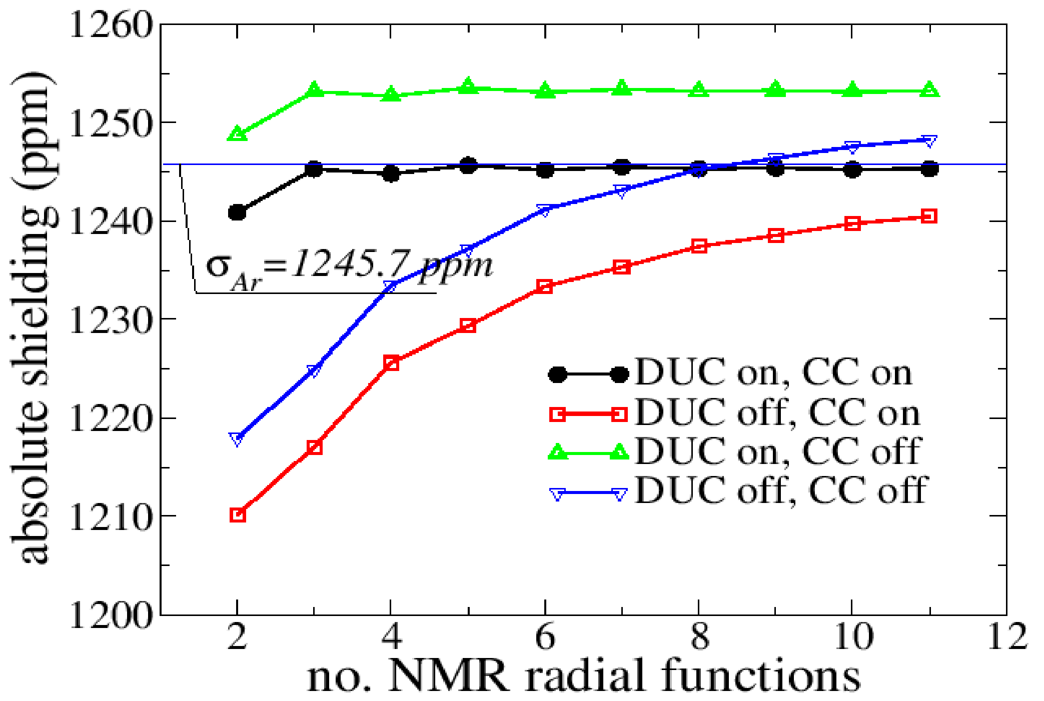
Benchmark: spherical Ar atom

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



effects of DUC and CC

The convergence with respect to number of NMR LO



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)

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.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 -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	

- band wise analysis

  x_nmr -emin *e1* -emax *e2*

- character analysis (s,p,d) of the wave functions of accupied 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_e *atom l*

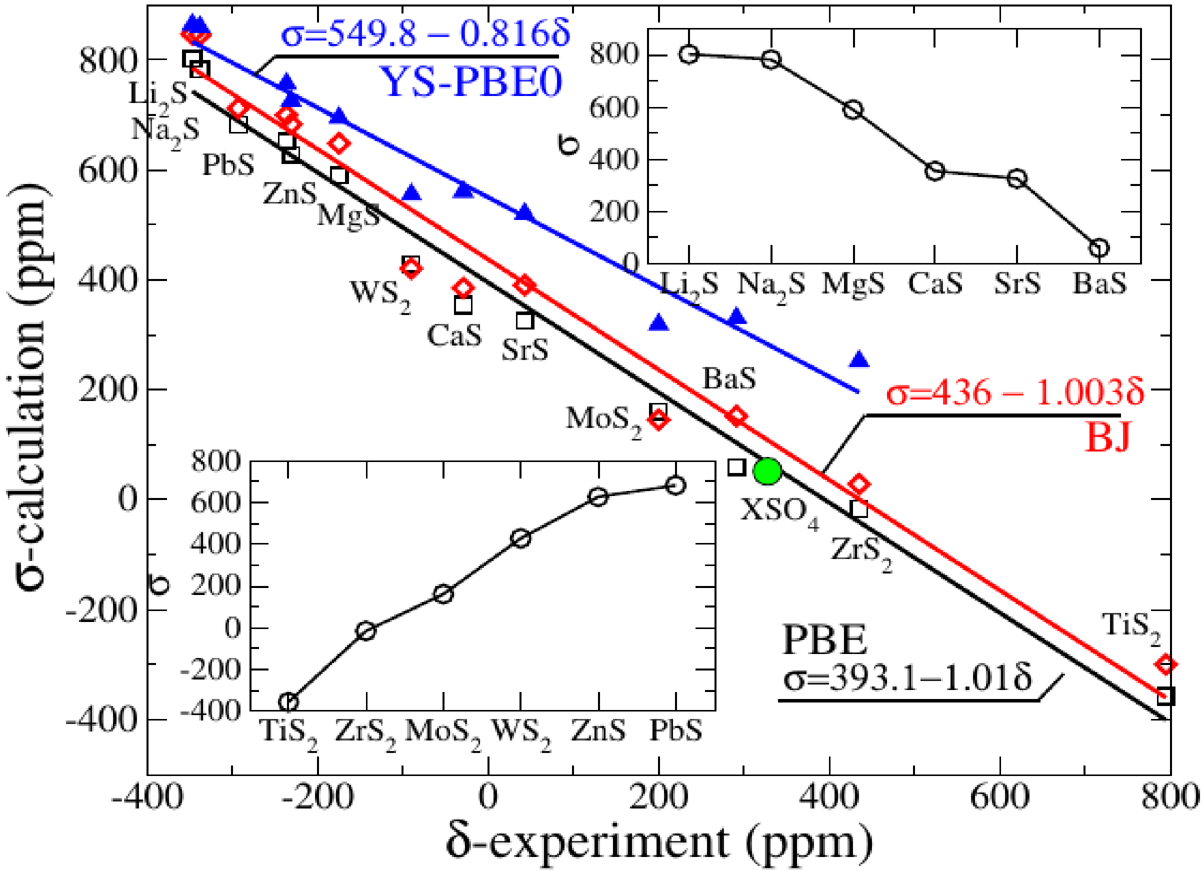
x_nmr -filt_cxyz_o *atom l*

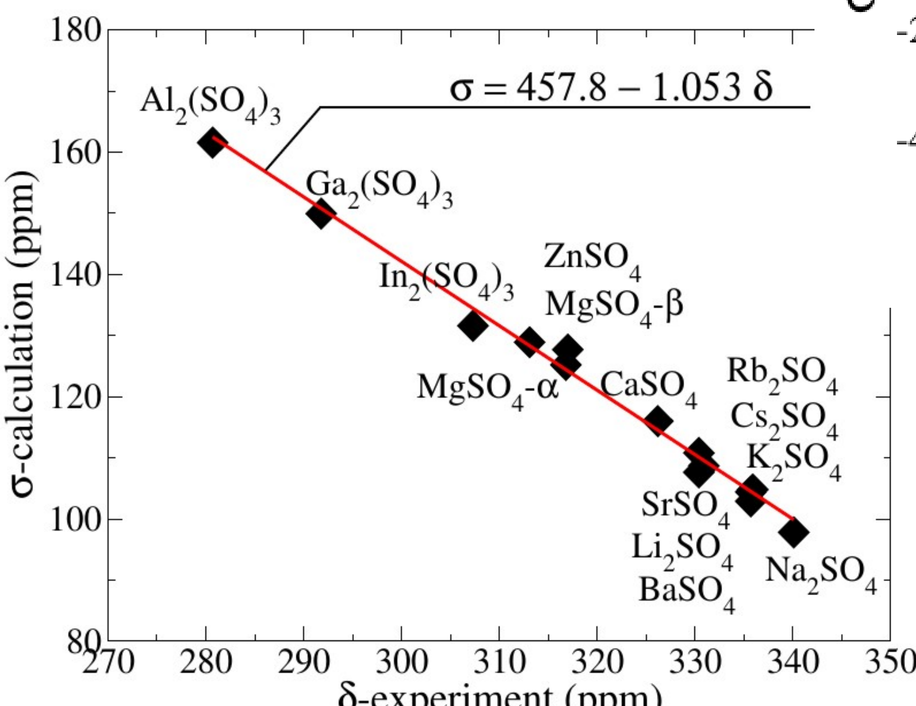
$$|\tilde{\Psi}_o^{(1)}\rangle = \sum_e |\Psi_e^{(0)}\rangle \frac{\langle\Psi_e^{(0)}|\left[(\mathbf{r}-\mathbf{r}')\times\mathbf{p}\cdot\mathbf{B}\right]|\Psi_o^{(0)}\rangle}{\epsilon-\epsilon_e}$$

Shielding ^{33}S, trends, precision

sulfides XS, XS_2

shielding varies within broad range (ppm)





sulfates, XSO_4

Comparing to experiment, slope?