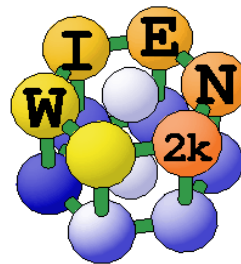


NMR chemical shifts in wien2k

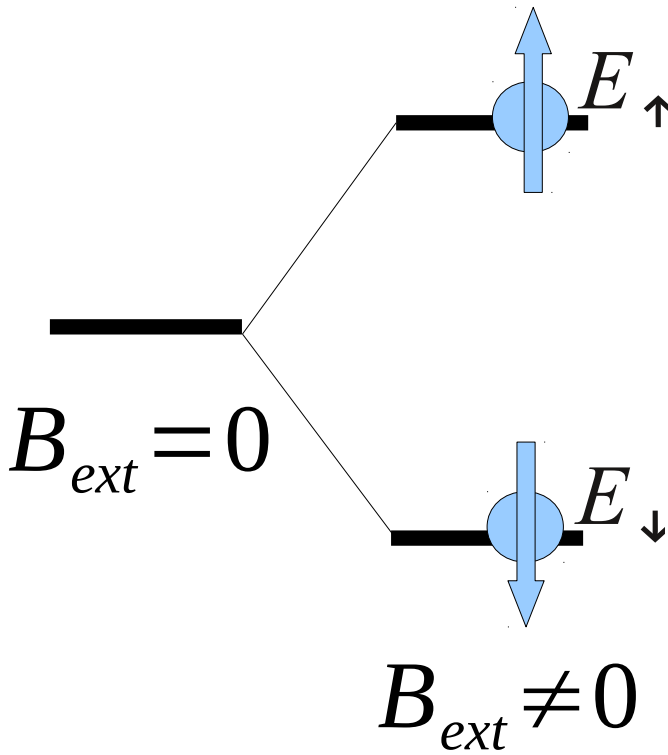
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Dipole nucleus



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

↓
induced field

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

NMR Hamiltonian

perturbation

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

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

Zeeman Hamiltonian

electric quadrupole
couples to EFG

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

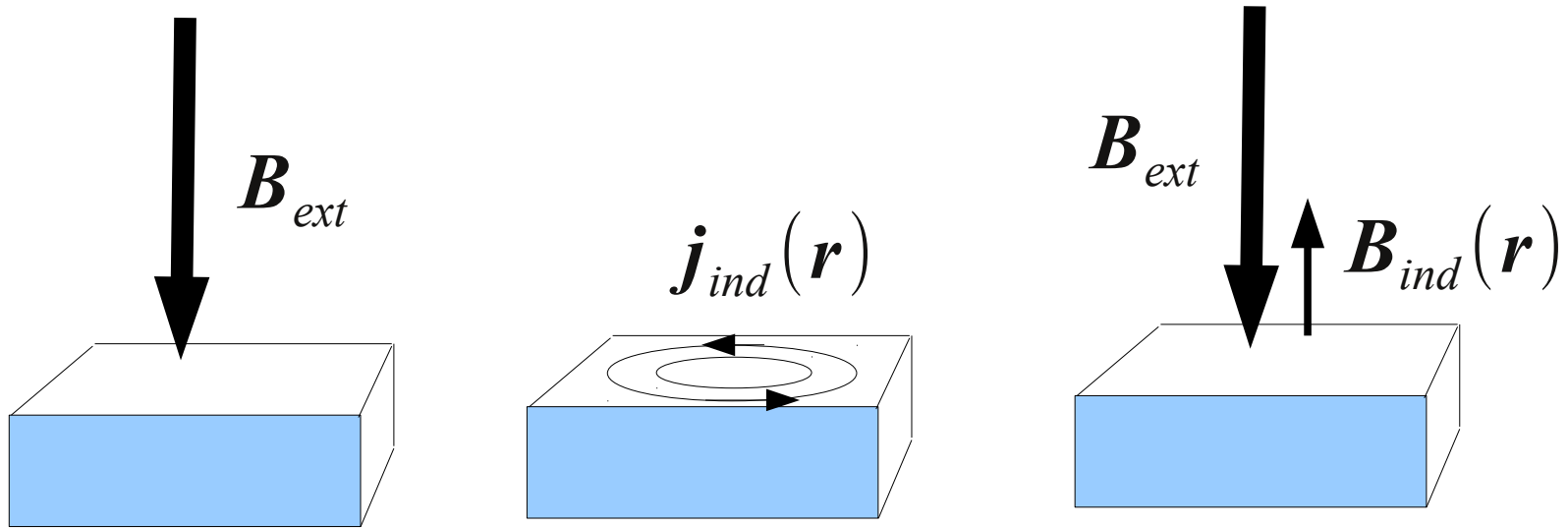
direct dipolar
coupling

indirect spin-spin
coupling

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

magnetic shielding

NMR shielding



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

$$\mathbf{B}_{ind}(\mathbf{R}) = -\bar{\sigma}(\mathbf{R}) \mathbf{B}_{ext} \quad \text{shielding tensor at the nucleus } \mathbf{R}$$

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

Biot-Savart law:

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

DFT current density:

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

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

symmetric gauge

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

Hamiltonian in the presence of the magnetic field

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

Current operator in the presence of magnetic field

paramagnetic current: $\mathbf{J}^{(0)}(\mathbf{r}') = -\frac{\mathbf{p} |\mathbf{r}'\rangle \langle \mathbf{r}'| + |\mathbf{r}'\rangle \langle \mathbf{r}'| \mathbf{p}}{2}$

diamagnetic current: $\mathbf{J}^{(1)}(\mathbf{r}') = -\frac{\mathbf{B} \times \mathbf{r}}{2c} |\mathbf{r}'\rangle \langle \mathbf{r}'|$

Linear response formula for induced current

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

first order perturbation of the occupied states

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

$\mathbf{A}(\mathbf{r})$ in the symmetric gauge

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

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



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

paramagnetic

diamagnetic

Generalized f-sum rule

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

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

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

infinite (periodic) structure:

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

- 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

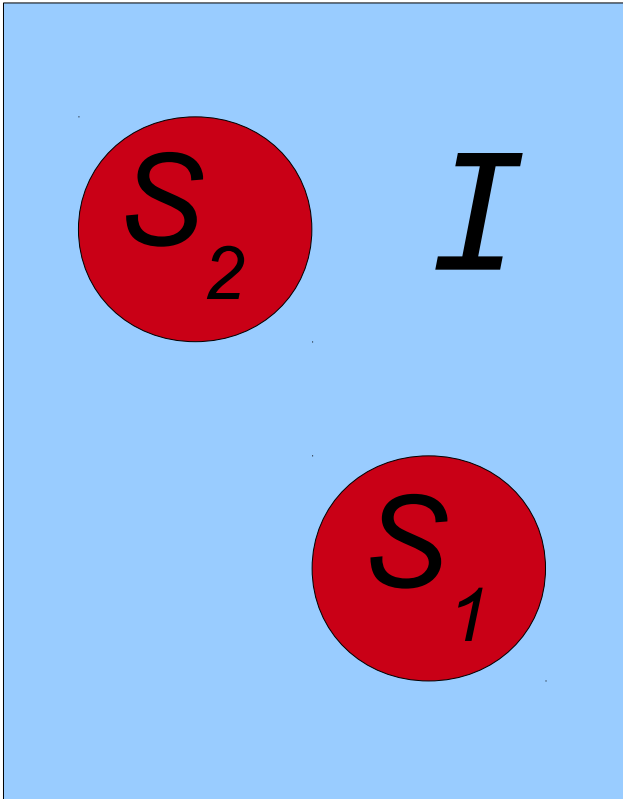
$$\phi_{\mathbf{k},\mathbf{G}}^{LAPW}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \mathbf{r} \in I \\ \sum_{l,m} \left[A_{l,m}^{\alpha,\mathbf{k}+\mathbf{G}} u_l^\alpha(r, E_l) + B_{l,m}^{\alpha,\mathbf{k}+\mathbf{G}} \dot{u}_l^\alpha(r, E_l) \right] Y_{l,m}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases}$$

local orbitals

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

wave function

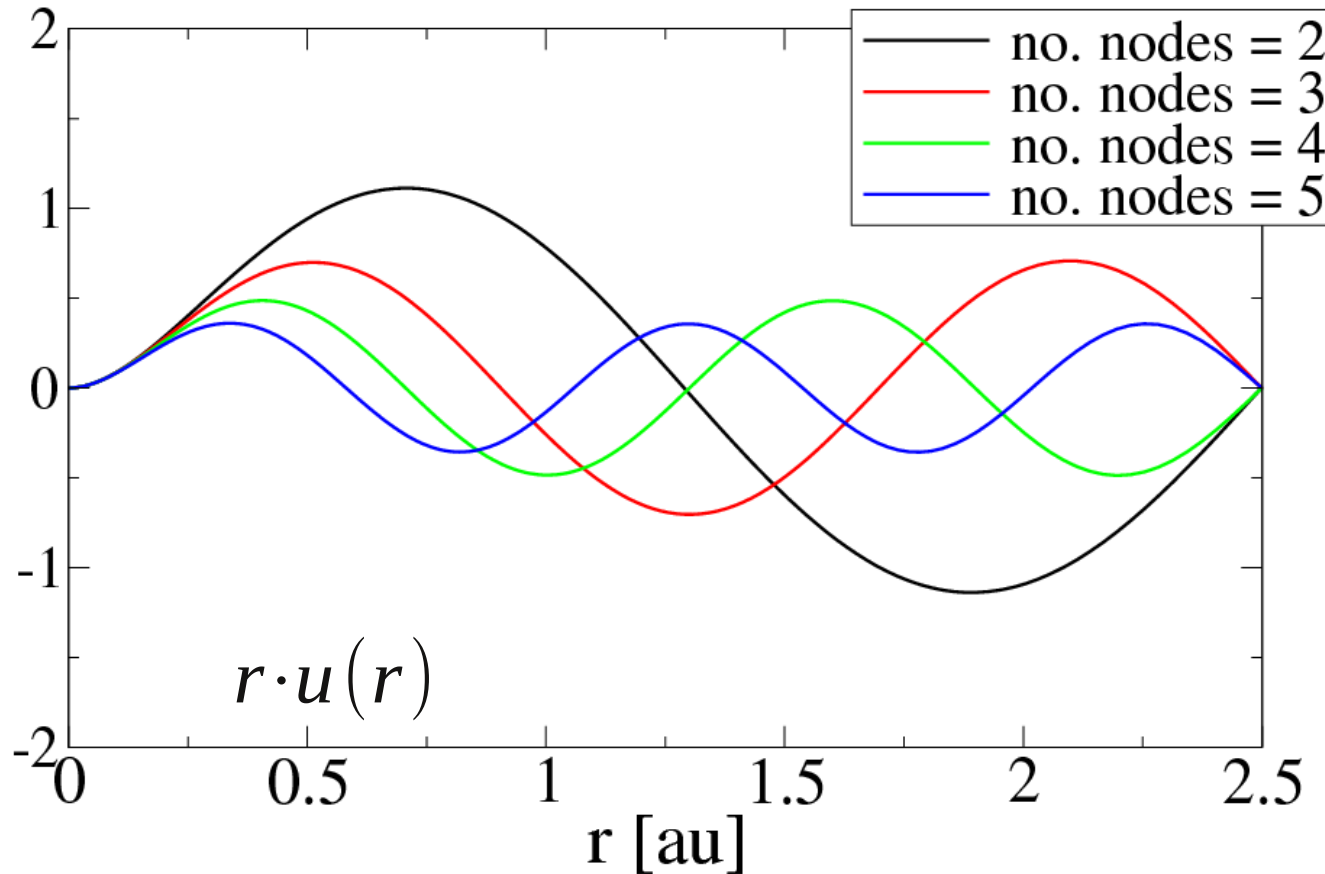
$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_{\mathbf{G}}^n e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \mathbf{r} \in I \\ \sum_{l,m} W_{l,m}^{n,\alpha,\mathbf{k}}(r) Y_{l,m}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases}$$



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

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

- 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)

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

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

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

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

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

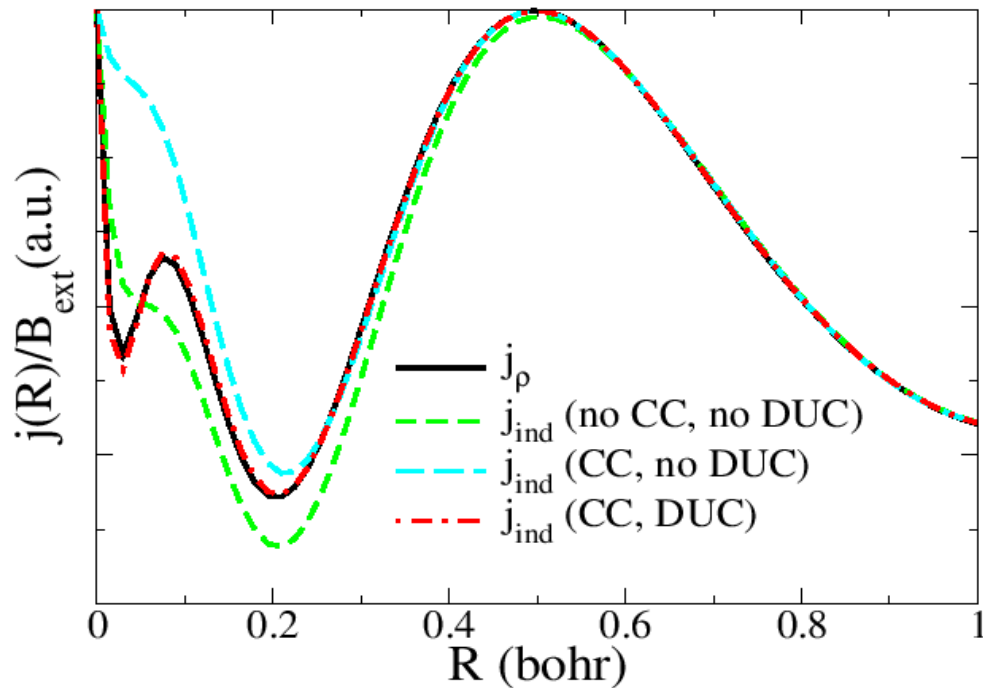
$$\mathbf{j}_{ind}(\mathbf{r}') = -\frac{1}{2c}\rho_{core}(\mathbf{r}')\mathbf{B} \times \mathbf{r}'$$

- errors corrected by (CC):

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

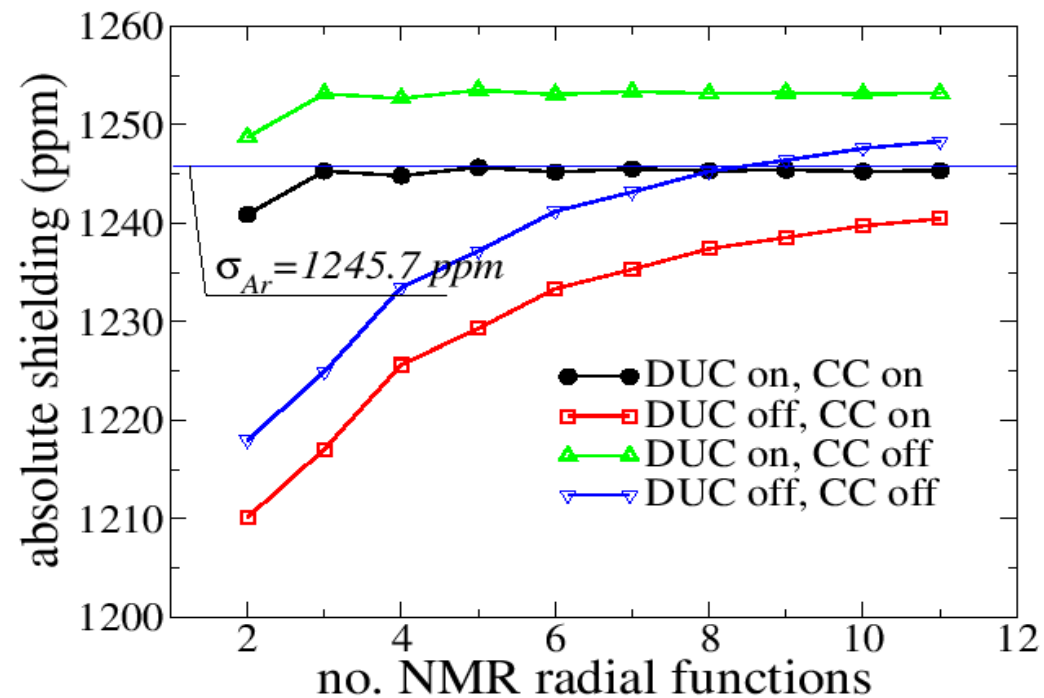
Benchmark: spherical Ar atom

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



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 +/- \mathbf{q}

results in:

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

x_nmr -mode lapw1

integrates the Biot-Savart law and computes the shielding

x_nmr -mode integ

computes induced current

x_nmr -mode current

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

x_nmr -mode lapw2

executes *x lcore* (core wave-functions)

x_nmr -mode lcore

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 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_e atom l

x_nmr -filt_cxyz_o atom l

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