Calculations of NMR Shielding in Solids

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NMR Shielding

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

\[ \Delta E = -\gamma m \hbar (B_{ext} + B_{ind}) \]
NMR Hamiltonian

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

- **Zeeman Hamiltonian**
  \[ H_Z = -\mu \cdot B_{ext} \]

- **Magnetic Shielding**
  \[ H_\sigma = -\mu \cdot B_{ind} \]

- **Electric Quadrupole**
  \[ H_Q \approx eQ \Phi / h \]

- **Indirect Spin-Spin Coupling**

- **Direct Dipolar Coupling**

Perturbation
Sources of Magnetic Shielding

- Orbital Component: $j_{orb}(r) \rightarrow B_{orb}(r)$
- Spin Component: $m(r) \rightarrow B_{hf}(r)$
Isotropic Shift

\[ B_{\text{ind}}(R) = B_{\text{orb}} + B_{\text{spin}} \quad \text{where} \quad B_{\text{orb}} = -\bar{\sigma}_o(R)B_{\text{ext}} \]
\[ B_{\text{spin}} = -\bar{\sigma}_s(R)B_{\text{ext}} \]

\[ \bar{\sigma}(R) = \bar{\sigma}_o(R) + \bar{\sigma}_s(R) \]

\[ \sigma(R) = \frac{1}{3} Tr[\bar{\sigma}(R)] \]

\[ \delta(\text{ppm}) = (\sigma_{\text{ref}} - \sigma) \times 10^6 \]
Orbital Component of NMR Shielding
Orbital Shielding

- The induced magnetic field $B_{orb}$ 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

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

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

• Linear response theory
• Wavefunction in first-order perturbation

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

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

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

- \( H^{(1)} \) couples \( k \) and \( k \pm q \) states
- Eigenfunctions have to be computed on k-meshes shifted by \( \pm q \) for small q
APW (WIEN2k) Basis Set

LAPW plane waves

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

Local orbitals

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

Wave function

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

- NMR LO has a 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 to number of NMR LO - Adding $r^*du/dr$ radial functions to the basis helps

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

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

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

\[
G(\epsilon_i) = \sum_e \frac{|\Psi_e^{(0)}\rangle\langle\Psi_e^{(0)}|}{\epsilon_i - \epsilon_e} + \sum_k \frac{|\phi_k\rangle\langle\phi_k|}{\langle\phi_k|(\epsilon_i - H)|\phi_k\rangle}
\]
Core Contributions

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

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

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

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

\[
+ \sum_{\text{core}} |\Psi_{\text{core}}^{(0)}\rangle \frac{\langle \Psi_{\text{core}}^{(0)} | H^{(1)} | \Psi_o^{(0)} \rangle}{\epsilon_o - \epsilon_{\text{core}}}
\]

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

\[ j_\rho(r') = \frac{-B \times r'}{2c} \rho(r') \]
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
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

\texttt{x_nmr -mode in1}

integrates the Biot-Savart law and computes the shielding

\texttt{x_nmr -mode integ}

executes:
\texttt{lapw1} at +/- q
results in:
./nrm_q0, ./nrm_mqz, ./nrm_pqx
./nrm_mqv, ./nrm_pqv./nrm_mqz,
./nrm_pqz
\texttt{x_nmr -mode lapw1}

computes induced current

\texttt{x_nmr -mode current}

executes \texttt{x lapw2 -fermi in ./nrm_xxx} (weights)
\texttt{x_nmr -mode lapw2}

executes \texttt{x lcore} (core wave-functions)
\texttt{x_nmr -mode lcore}
output

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

```plaintext
:NMRTOT001 ATOM: Ba1 1 NMR(total/ppm) Sigma-ISO = 5384.00 Sigma_xx = 5474.82 Sigma_yy = 5385.93 Sigma_zz = 5291.24
:NMRTOT002 ATOM: S 1 2 NMR(total/ppm) Sigma-ISO = 111.31 Sigma_xx = 85.34 Sigma_yy = 107.93 Sigma_zz = 140.67

:NMRASY001 ATOM: Ba1 1 NMR(total/ppm) ANISO (delta-sigma) = -139.13 ASYM (eta) = 0.958 SPAN = 183.57 SKEW = -0.032
: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

\[ x_{\text{nmr}} - \text{emin e1 -emax e2} \]

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

\[ x_{\text{nmr}} - \text{filt_curr_o atom l} \]

\[ x_{\text{nmr}} - \text{filt_curr_fop atom l} \]

\[ x_{\text{nmr}} - \text{filt_cxyz_q atom l} \]

\[ x_{\text{nmr}} - \text{filt_cxyz_o atom l} \]

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

\[
|\tilde{\Psi}_{o}^{(1)}\rangle = \sum_{e} |\Psi_{e}^{(0)}\rangle \frac{\langle \Psi_{e}^{(0)} | [ (\mathbf{r} - \mathbf{r}') \times \mathbf{p} \cdot \mathbf{B} ] |\Psi_{o}^{(0)}\rangle}{\epsilon_{o} - \epsilon_{e}}
\]
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)
Correlation of calculated NMR shielding vs measured chemical shifts for inorganic sulphides (left) and sulphates (right)

JPCC 119, 731 (2015)
Spin Component of NMR Shielding
Spin Shielding (Knight Shifts)

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

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

- contact term
- dipole term

JPCC 119, 19390 (2015)
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
- `grelpline :HFF0XX case.scf` # get the hyperfine field

: \( HFF0XX \) is contact hyperfine field in kGauss

\[
\sigma_c [ppm] = -HFF \times 1000 \quad \text{for } B_{ext} = 100T
\]

<table>
<thead>
<tr>
<th>Hyperfine Fields for Thomson Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>:HFF001: 0.659 0.000 -0.040 0.619 (KGAUSS)</td>
</tr>
<tr>
<td>:HFF002: 4.445 0.000 -2.205 2.239 (KGAUSS)</td>
</tr>
<tr>
<td>:HFF003: 0.146 0.000 -0.161 -0.015 (KGAUSS)</td>
</tr>
</tbody>
</table>

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

\[
\sigma_{sd}[ppm] = -(XOP_{up} - XOP_{dn}) \times 10000 \quad \text{for } B_{ext} = 100\text{T}
\]
Results

Correlation of measured vs calculated NMR shifts for various metallic elements

JPCC 119, 19390 (2015)
Conventional Wisdom on Spin Shielding

- 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)

$$m(r = 0) = N_{l=0}(\epsilon_F)(\Delta\epsilon\downarrow(B_{ext}) - \Delta\epsilon\uparrow(B_{ext}))u_{l=0}(0)^2$$
Core Polarization Effects

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

**Paramagnetic**

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

**Diamagnetic**

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

$u_\uparrow(0)$ decreases and $u_\downarrow(0)$ increases
Contact Contribution for MGa$_n$

$\sigma_c$ vs s-partial DOS at $\varepsilon_F$ for MGa$_n$

Paramagnetic $\sigma_c^{\text{para}}$ from reoccupation of spin up and down states vs s-partial DOS at $\varepsilon_F$ for MGa$_n$

JPCC 121, 753 (2017)
Self-Consistency Effects

Valence d-states

Semicore s-states
Self-Consistency Effects

$B_{\text{ext}}$ induces $m_d(r)$

Valence d-states

Semicore s-states

Linear response

$B_{\text{ext}}$ induces $m_d(r)$
Self-Consistency Effects

$B_{\text{ext}}$ induces $m_d(r)$

Linear response

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

- Diamagnetic contribution of semicore states to $\sigma_c$ increased after self-consistency
- Core/semicore contribution to $\sigma_c$ scales with $d$-partial DOS at $\epsilon_F$

Linear response

$B_{\text{ext}}$ induces $m_d(r)$

Self-consistency

Exchange field due to $m_d(r)$ further splits semicore $s$-states
Core Spin Shielding for ScTT’Al Heusler Alloys

\[ \sigma_{c}^{\text{core}} \text{ vs Sc/Al } d\text{-PDOS at } \varepsilon_F (B_{\text{ext}} = 100 \text{ T}) \]

\[ \sigma_{c}^{\text{core}} \text{ vs induced spin moment at } \varepsilon_F (B_{\text{ext}} = 100 \text{ T}) \]

JPCC 121, 12398 (2017)
Thank you for your attention!!