NMR: chemical and Knight shifts

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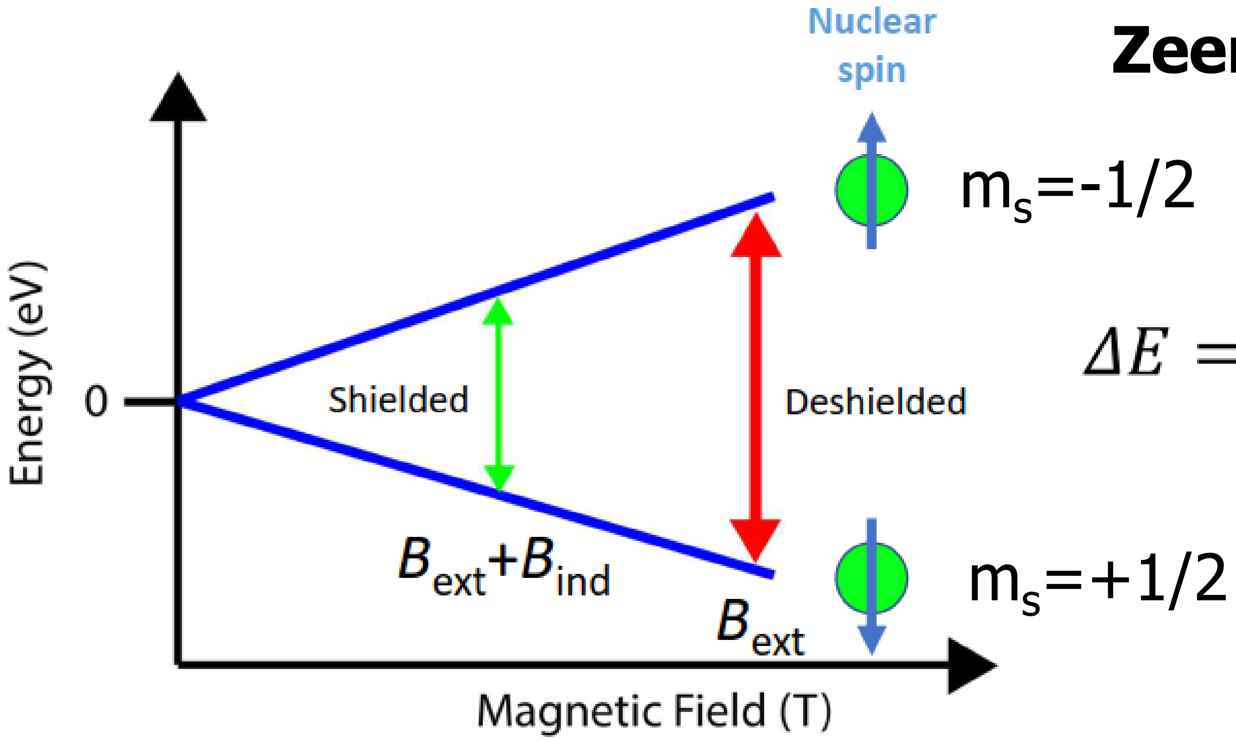
NMR shielding



Zeeman-effect

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

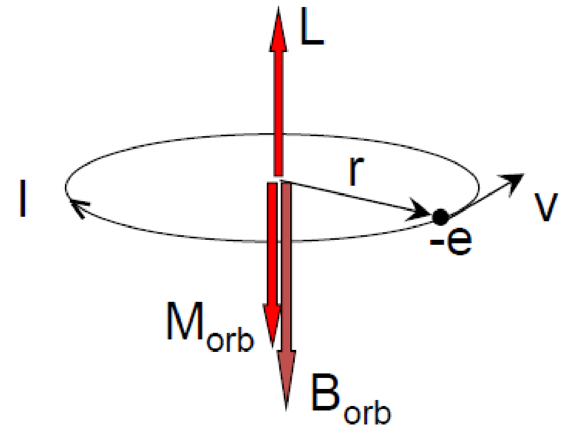
Magnetic Shielding

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

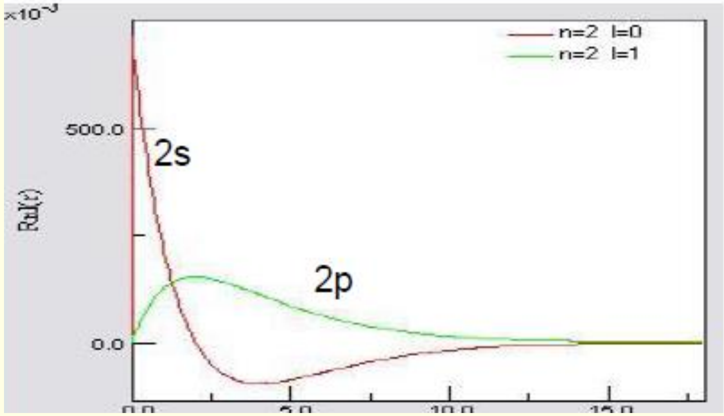
Sources of magnetic fields at the nuclear site

$$B_{tot} = B_{orb} + B_{fermi} + B_{dip} + B_{lat}$$

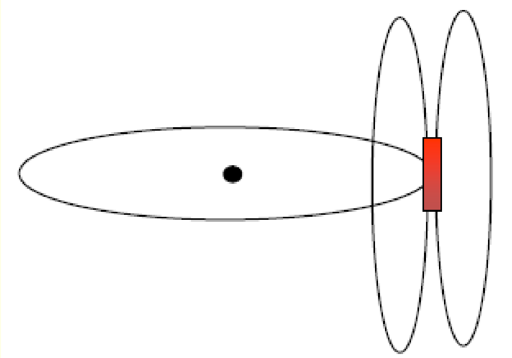
B_{orb} = electron as current loop



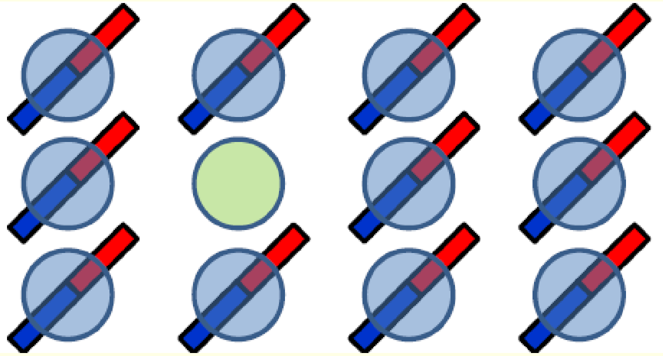
B_{fermi} = electron inside the nucleus ~ $(\rho_\uparrow - \rho_\downarrow)$



B_{dip} = electron as bar magnet



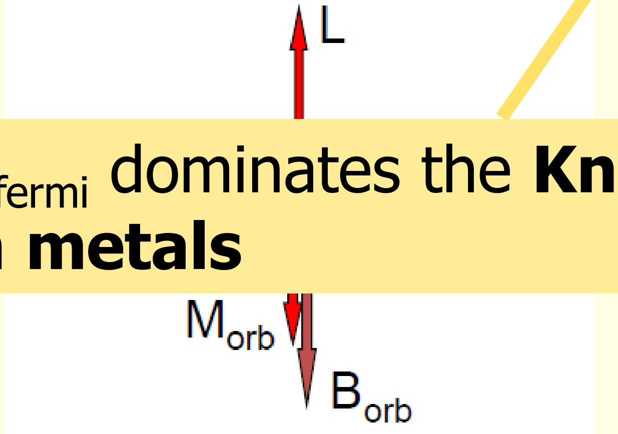
B_{lat} = neighbors as bar magnets



Sources of magnetic fields at the nuclear site

$$B_{tot} = B_{orb} + B_{fermi} + B_{dip} + B_{lat}$$

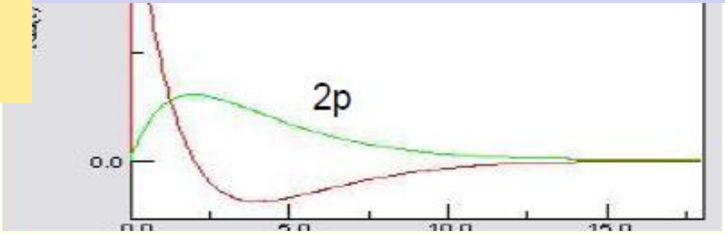
B_{orb} = electron as current loop



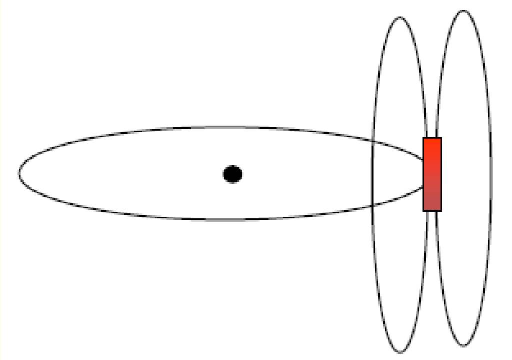
B_{fermi} dominates the **Knight** shift in **metals**

$_{\uparrow} - \rho_{\downarrow})$

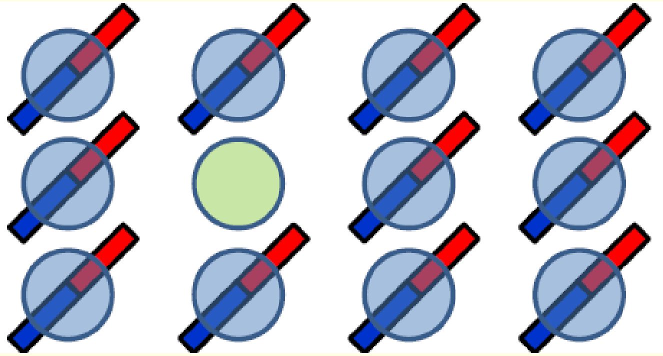
B_{orb} is the only major component for **molecules** and **insulators** **al shift)**



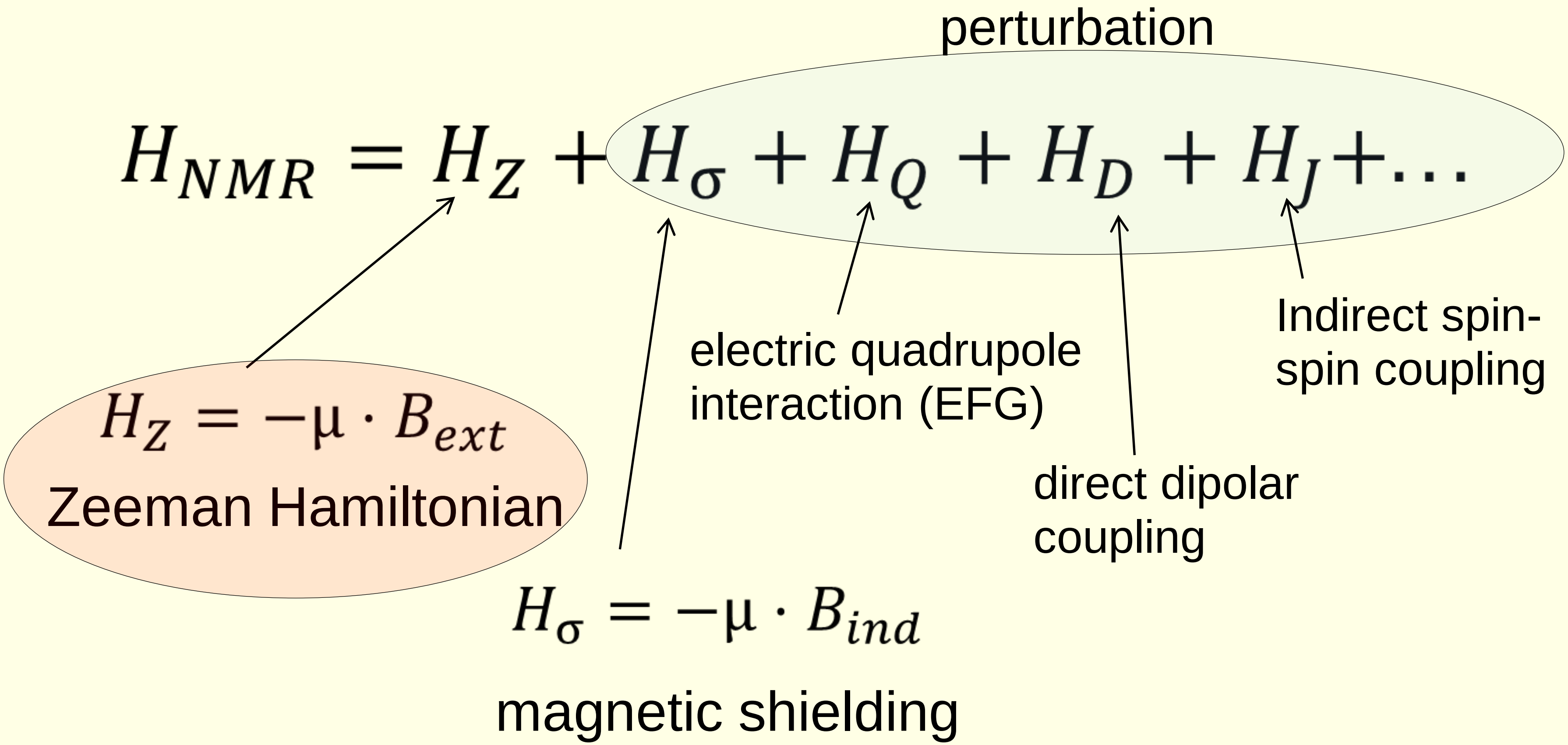
B_{dip} = electron as bar magnet



B_{lat} = neighbors as bar magnets



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 interaction (EFG)

Indirect spin-spin coupling

direct dipolar coupling

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

magnetic shielding

NMR Hamiltonian

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

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

Zeeman Hamiltonian

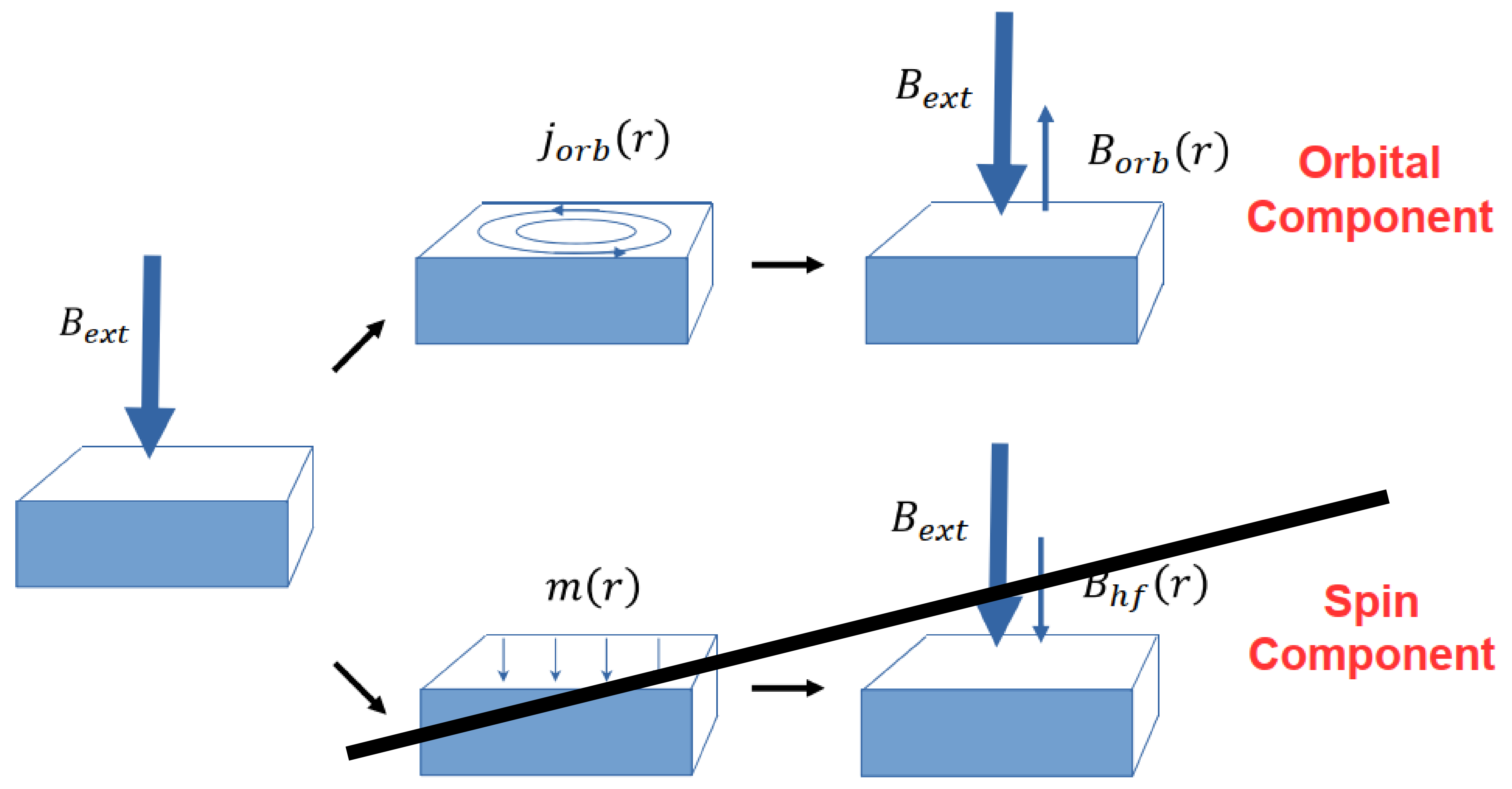
$$H_\sigma = -\mu \cdot B_{ind}$$

magnetic shielding

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

quadrupole interaction

sources of magnetic shielding

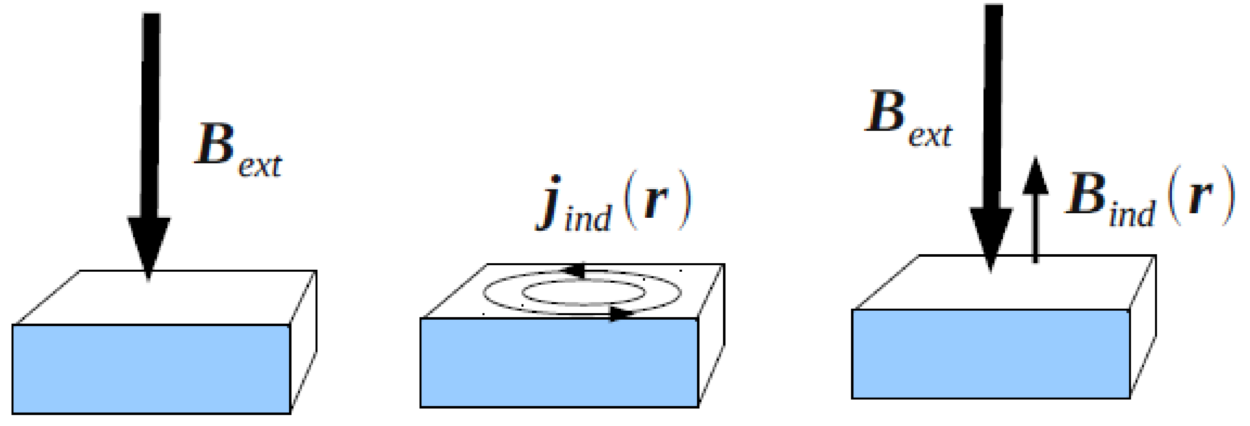


Orbital Component

Spin Component

- for insulator:

NMR shielding, chemical shift:



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

$$\mathbf{B}_{ind}(\mathbf{R}) = -\overline{\sigma}(\mathbf{R})\,\mathbf{B}_{ext}$$

$\sigma(\mathbf{R})$ is the **shielding tensor** at the nucleus $\mathbf{R}$

chemical shift: δ (ppm) = $(\sigma_{ref} - \sigma) \times 10^6$

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:

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

wave function in presence of B

current operator

NMR theory

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

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

first order perturbation of the occupied states

All empty states !

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

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

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

ill defined for extended systems

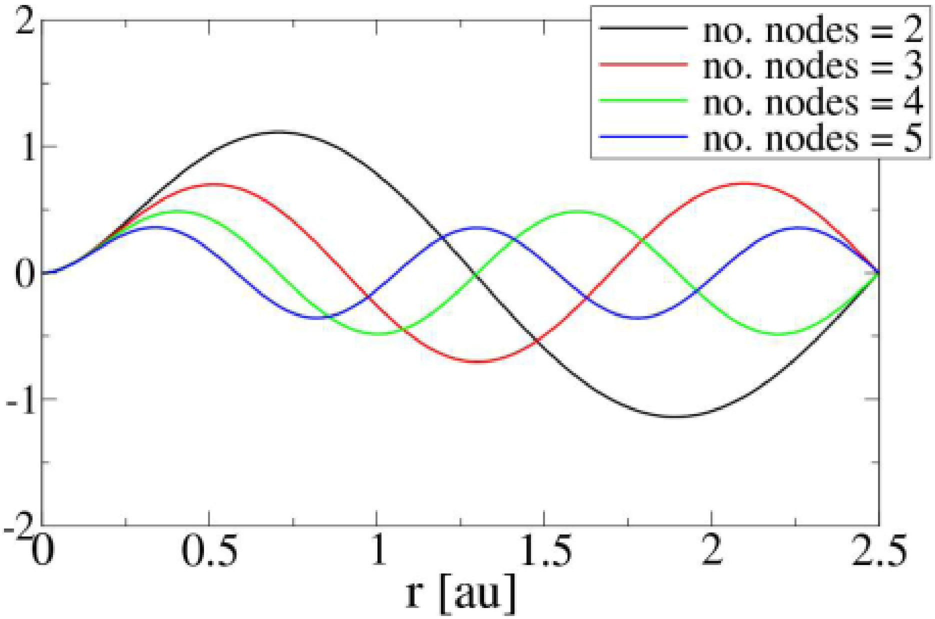
r operator in periodic system:

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

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

APW description of unoccupied states:

- 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

Sternheimer correction (DUC)

- 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

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

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

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

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

Core corrections

- 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:

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

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

Correction

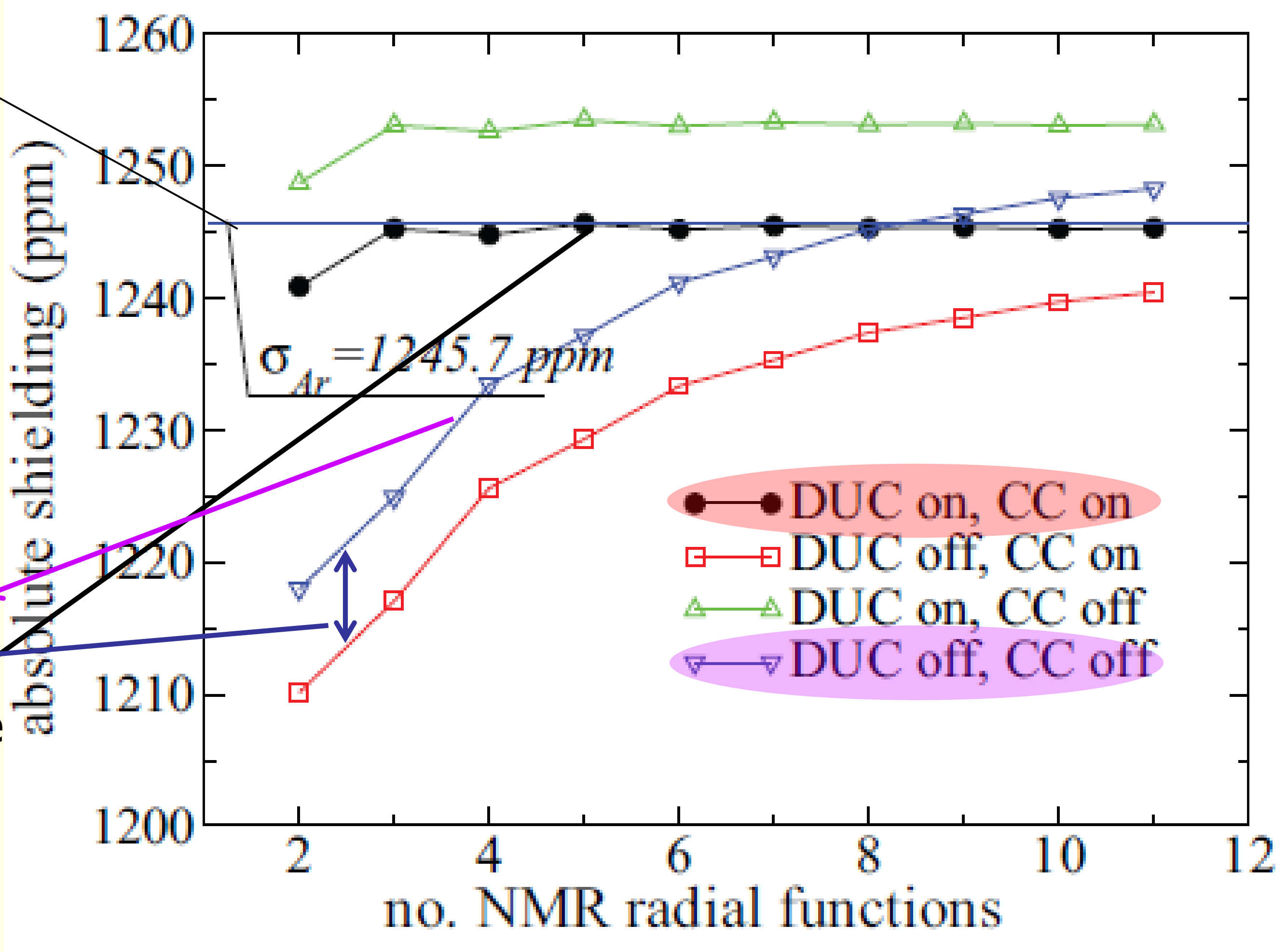
PRB **89**, 014402 (2014)

“absolutely” converged results:

- NMR shielding σ of the Ar atom:

diamagnetic current
for closed shell spherical
atom from **density** ρ :

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



high-E LOs: converge
very slowly

CC: constant shift

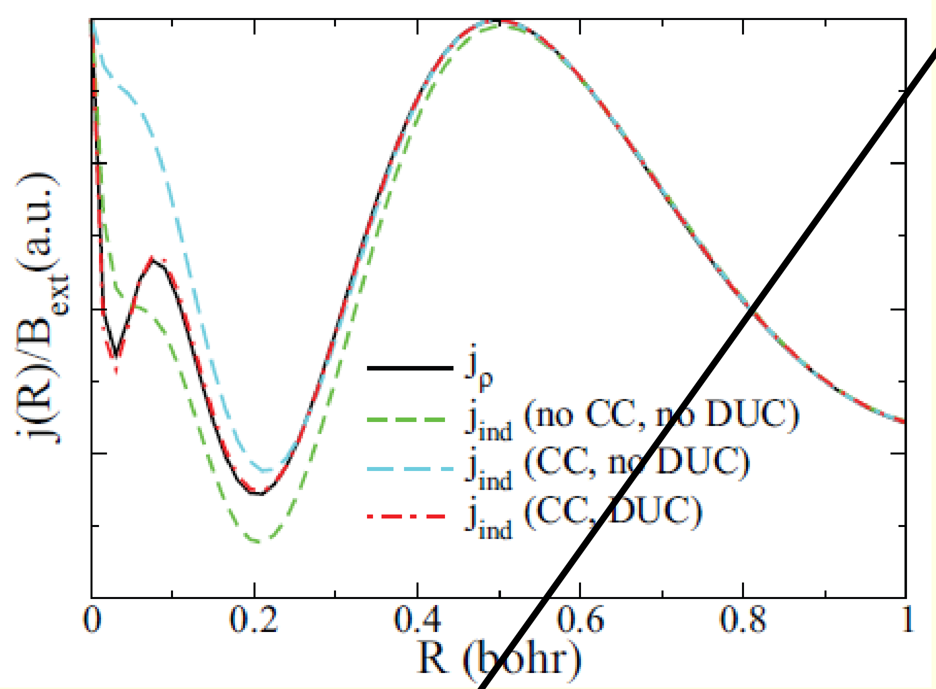
DUC: rapid convergence

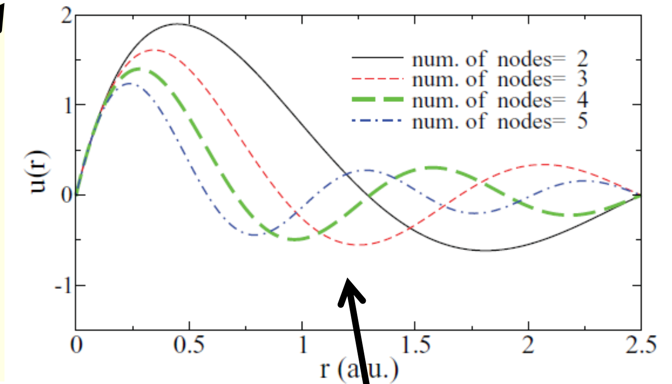
R.Laskowski, P.B., PRB, **89** (2014), 014402

Test of method

- **Induced current** in free **Ar atom** (*where j(r)* can be calculated directly ("exactly'

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





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

- ***j(r)*** from perturbation theory does not agree with exact current (small *r*)
- we need basis set improvements for unoccupied states (**high E-LOs** + "**Sternheimer**" (DUC) basis functions) and **core-corrections**

Theory – Orbital fields in solids:

In insulators the induced **magnetic field** (***B**$_{ind}$*) is obtained from the **induced orbital current** (***j**$_{ind}$*) using **Biot-Savart's** law:

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

in DFT the **current density *j(r)*** can be obtained from :

$$\begin{aligned}\mathbf{j}_{\mathrm{ind}}(\mathbf{r}') = \sum_o \Big[& \langle\Psi_o^{(1)}|\mathbf{J}^{(0)}(\mathbf{r}')|\Psi_o^{(0)}\rangle + \langle\Psi_o^{(0)}|\mathbf{J}^{(0)}(\mathbf{r}')|\Psi_o^{(1)}\rangle \\ & + \langle\Psi_o^{(0)}|\mathbf{J}^{(1)}(\mathbf{r}')|\Psi_o^{(0)}\rangle\Big],\end{aligned}$$

paramagnetic

diamagnetic contributions

perturbed w.f. *$\Psi^{(1)}$* is obtained from perturbation theory

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

Greens function approach

$H^{(1)}$ is the **external magnetic field** in symmetric gauge

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

the magnetic field breaks periodic boundary conditions

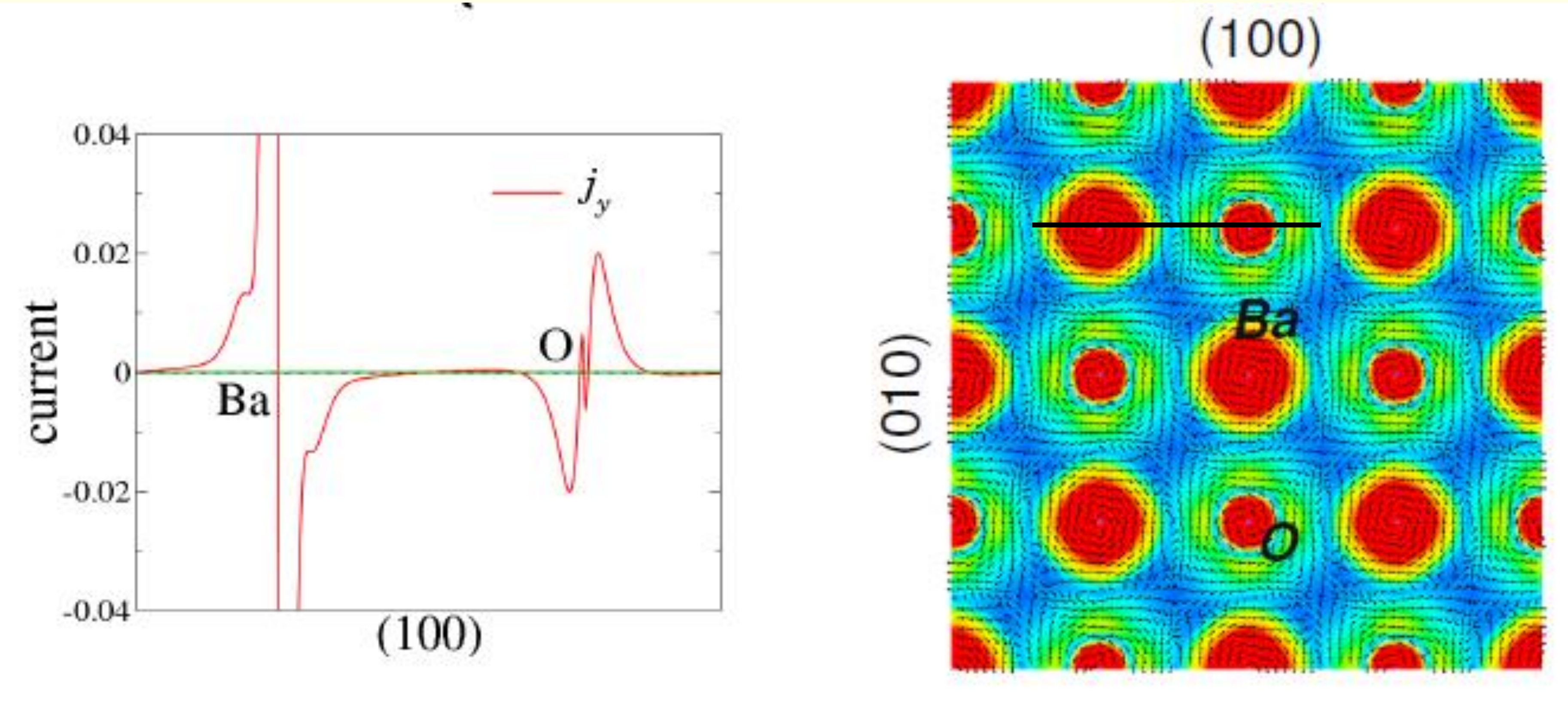
→ the ***r*** operator is ill defined

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

pioneered by F.Mauri et al.
„GIPAW" method

Induced current in LAPW

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

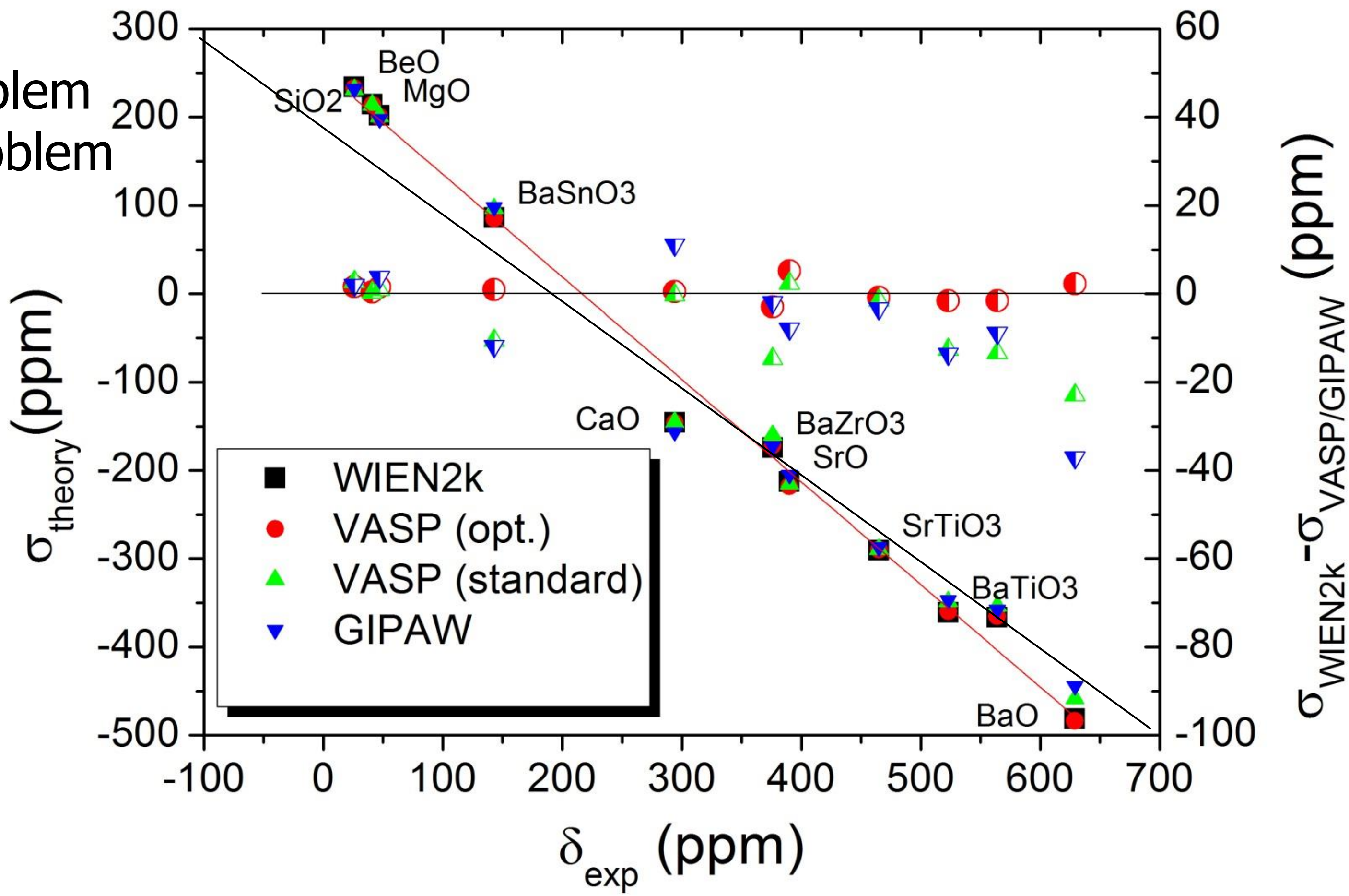


$$\mathbf{j}_{ind}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} \mathbf{j}_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, & \mathbf{r} \in I \\ \sum_{l,m} \mathbf{j}^{\alpha}_{l,m}(r) Y_{l,m}(\hat{r}). & \mathbf{r} \in S_{\alpha} \end{cases}$$

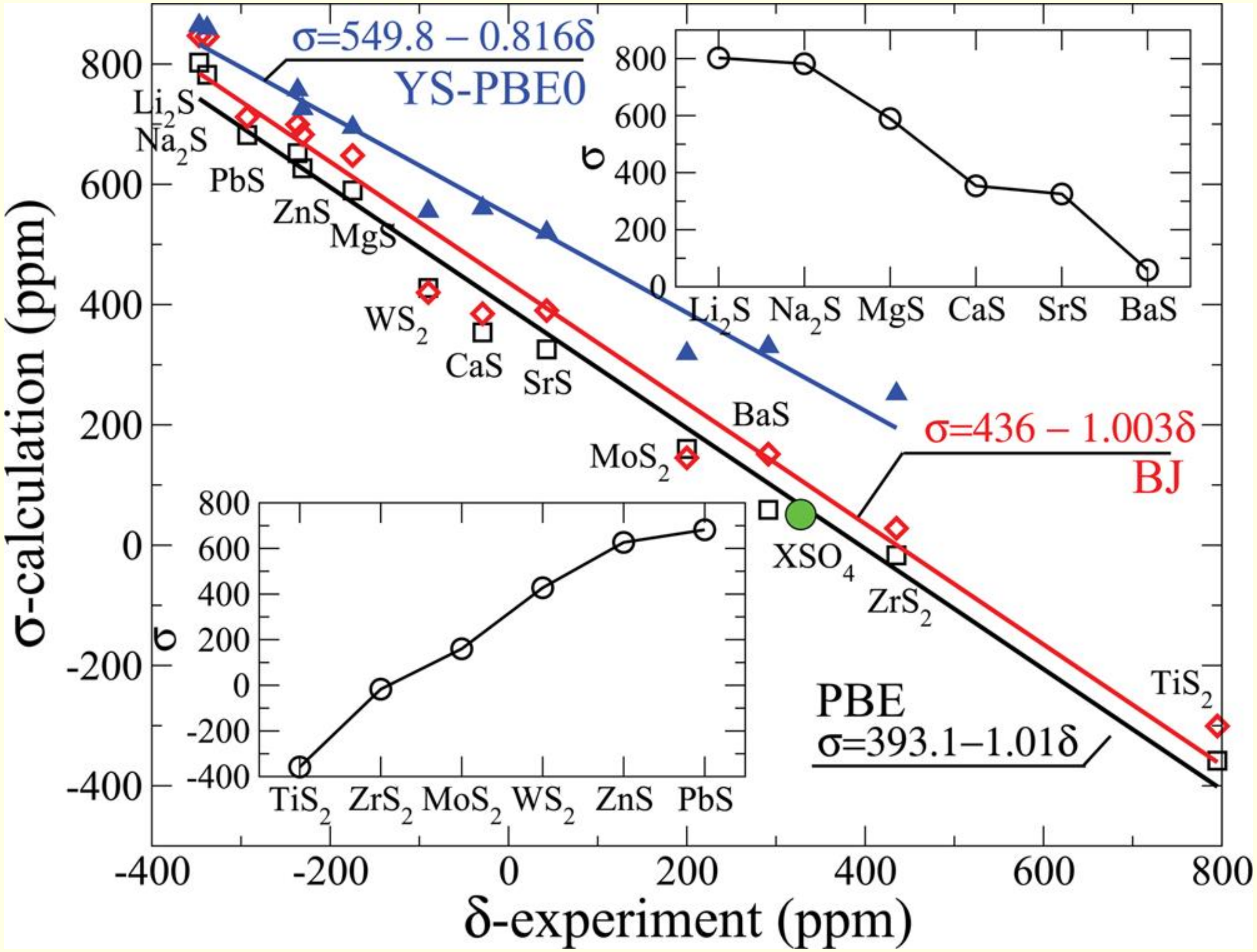
Comparison WIEN2k-VASP-CASTEP

- bulk oxides or fluorides (O and F-NMR)
  - *VASP agrees very well with WIEN2k when optimized potentials are used*

slope-problem
= DFT-problem



Chemical shift of ^{33}S

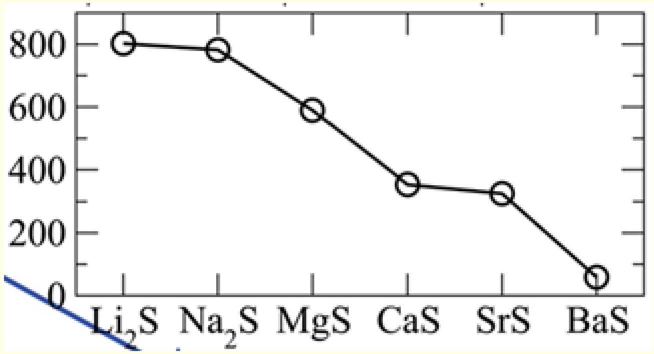


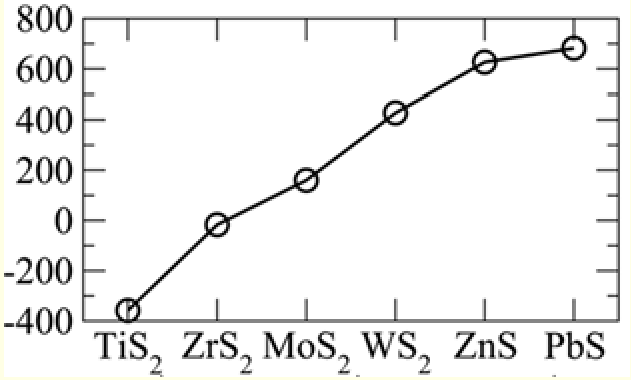
- **Ionic** sulfides: σ **decreases** with Z
- **TM** sulfides: σ **increases** with Z
- why has **Na_2S** and **PbS** almost the **same** shielding

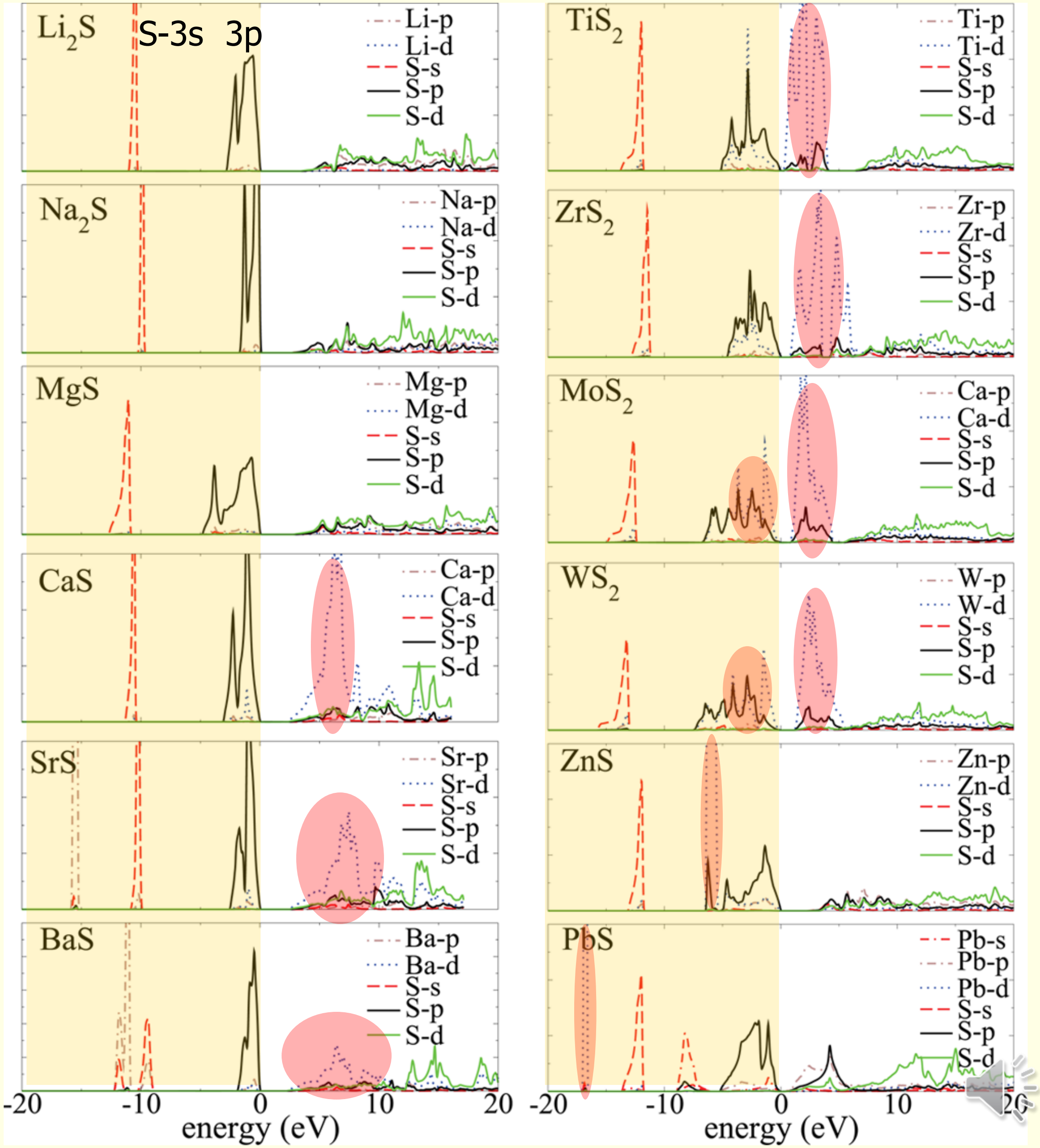
?

position/occupation of Me-d states determines CS

- **empty d-states near the CBM give large negative (paramagnetic) shift**







How to run the code

- Master script: x_nmr [options]

- 1) run SCF calculation

- 2) prepare case.in1_nmr (add NMR LO): x_nmr -mode in1
- case.in1_nmr: (no HDLOs in case.in1 !!)

```
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

how to run the code:

- 3) run x_nmr: does the following steps for you:
  - *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 (x_nmr -mode lapw1)*
  - *2) computes weights for each k-mesh, (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)*
  - ***produces: 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*
  - ...

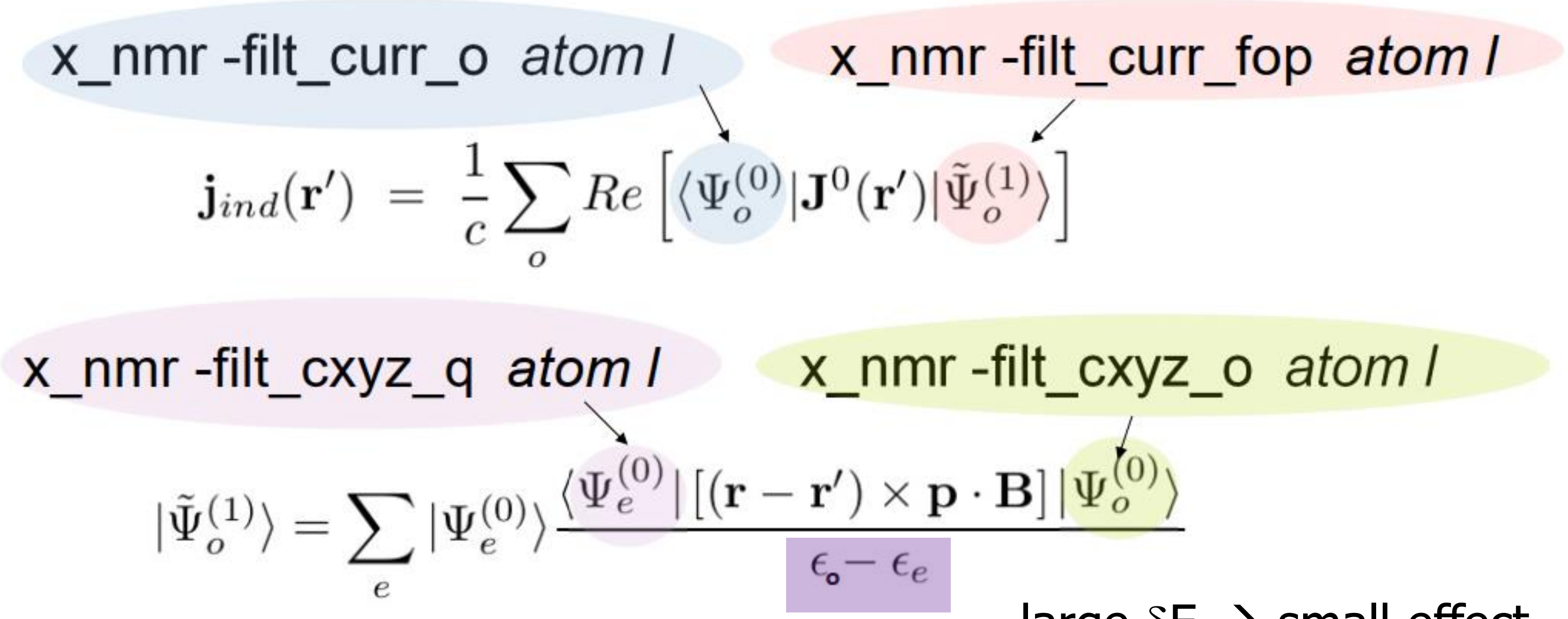
- x_nmr -h   prints help
- x_nmr –p   runs in parallel

where does it come from ?

- 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*

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

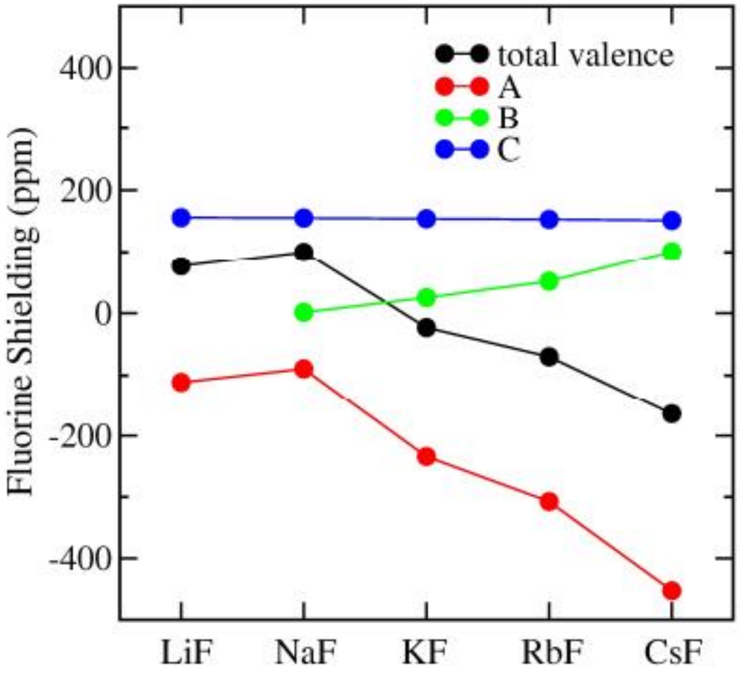
x_nmr -filt_cxyz_q *atom l*

x_nmr -filt_cxyz_o *atom l*

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

large δE → small effect

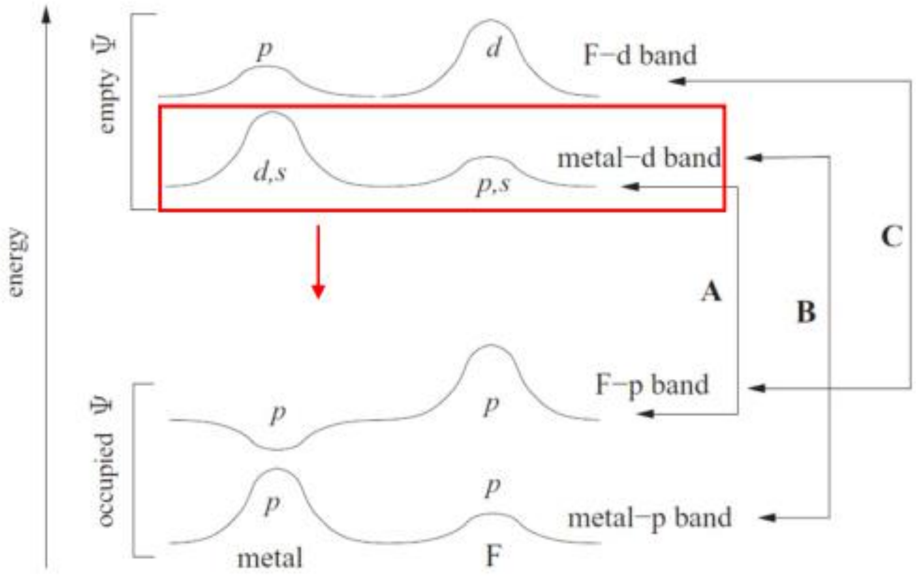
Origin of shielding in fluorides



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

+320 ppm from F-1s,2s (constant)

PRB **85**, 245117 (2012)



Schematic diagram representing major couplings contributing to NMR shielding

A real application: LLZO, a fast Li-ion conductor

- room T: tetragonal phase
- high-T cubic phase:
  - *10^{-4} S/cm, 2 orders better cond. than tetragonal phase*

- cubic LLZO by Al^{3+}-doping
  - *Al^{3+} replaces Li^+, but crystallographic site is unknown*
  - *^{27}Al NMR: 2 signals, 14 ppm apart 4-fold coordinations ??*
  - *neutron diffraction: Al in 6-fold coord.*

$Li_7La_3Zr_2O_{12}$

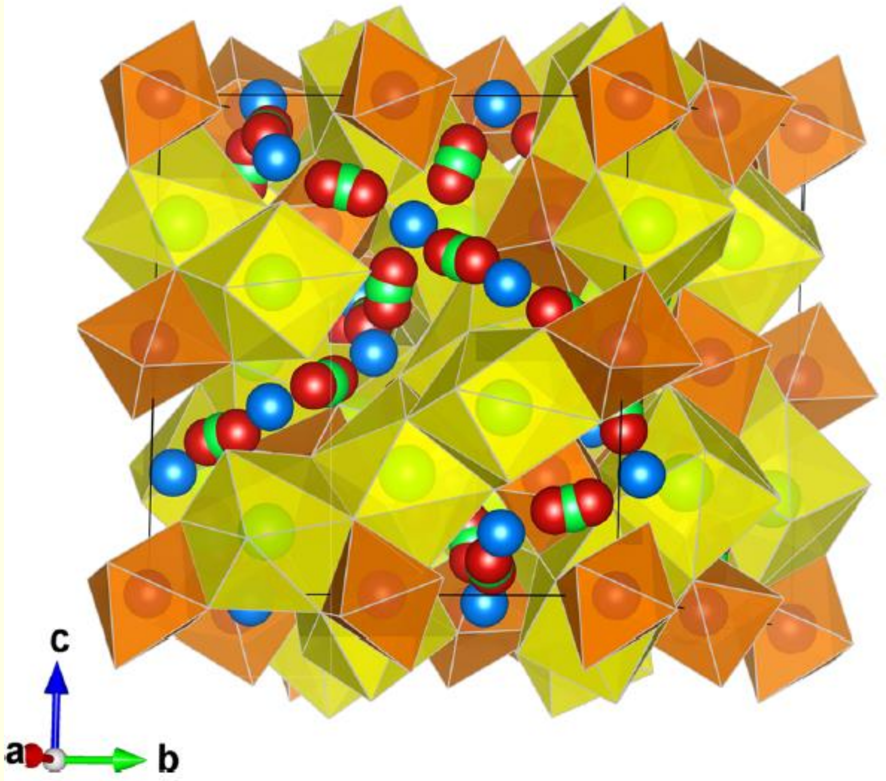
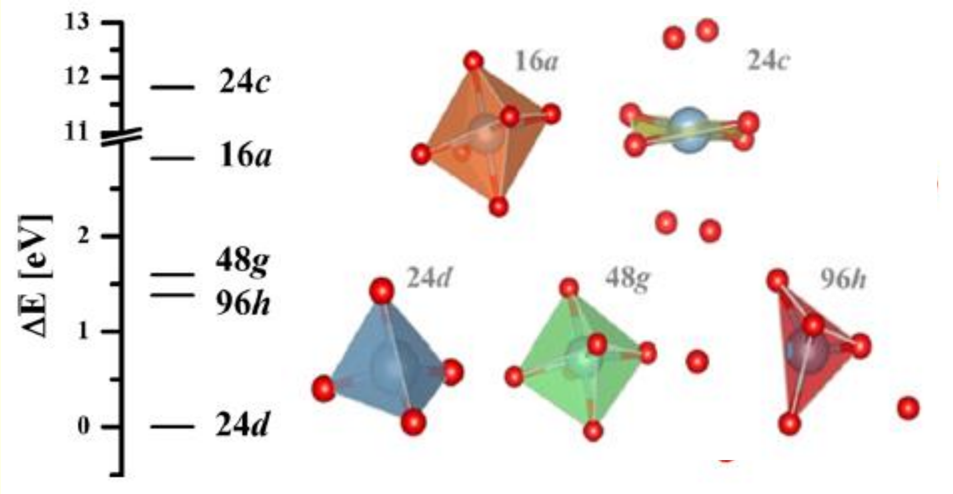
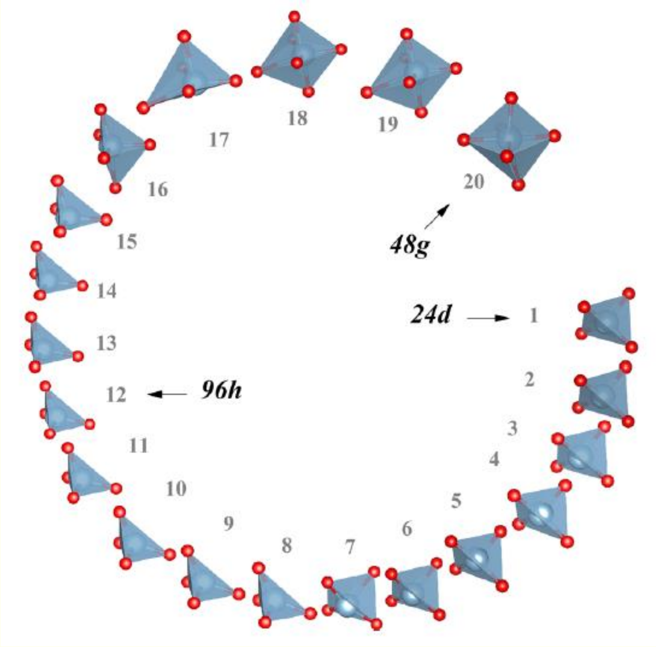


Figure 1. Crystal structure of cubic LLZO. The yellow dodecahedrally coordinate La^{3+} (at the Wyckoff position 24*c*) and orange octahedrally coordinate Zr^{4+} (16*a*). The blue spheres correspond to tetrahedrally coordinated (24*d*) Li^+, green spheres to octahedrally coordinated (48*g*) Li^+, and red ones to distorted 4-fold coordinated (96*h*) Li^+.

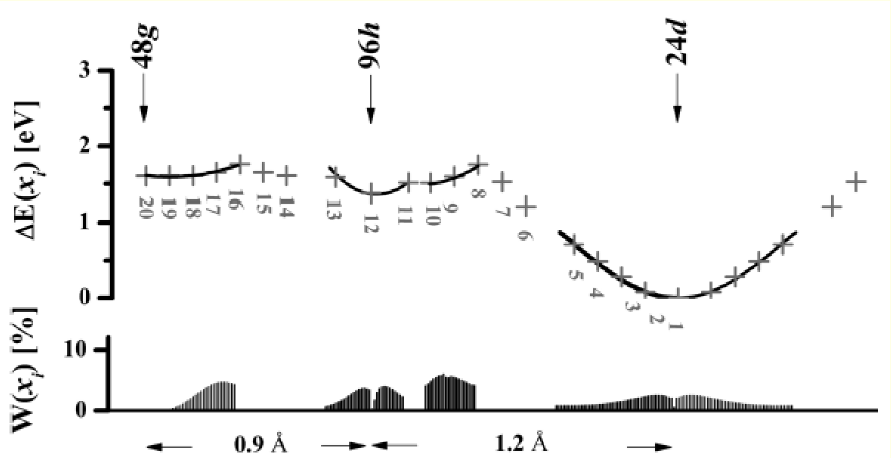
D. Rettenwander et al., Chem.Mat. 26, 2617 (2014)

total energies as function of Al^{3+} position





- 4-fold **24d** lowest energy
- followed closely by
  - *dist. 4-fold* ***96h***
  - *6-fold* ***48g***



NMR chemical shifts

48h ←

~200 ppm

- only 2 NMR signals found so far.
- agrees well with 4-fold 24d and 96h pos.
- 6-fold 48h pos. has a very different shift (200 ppm)

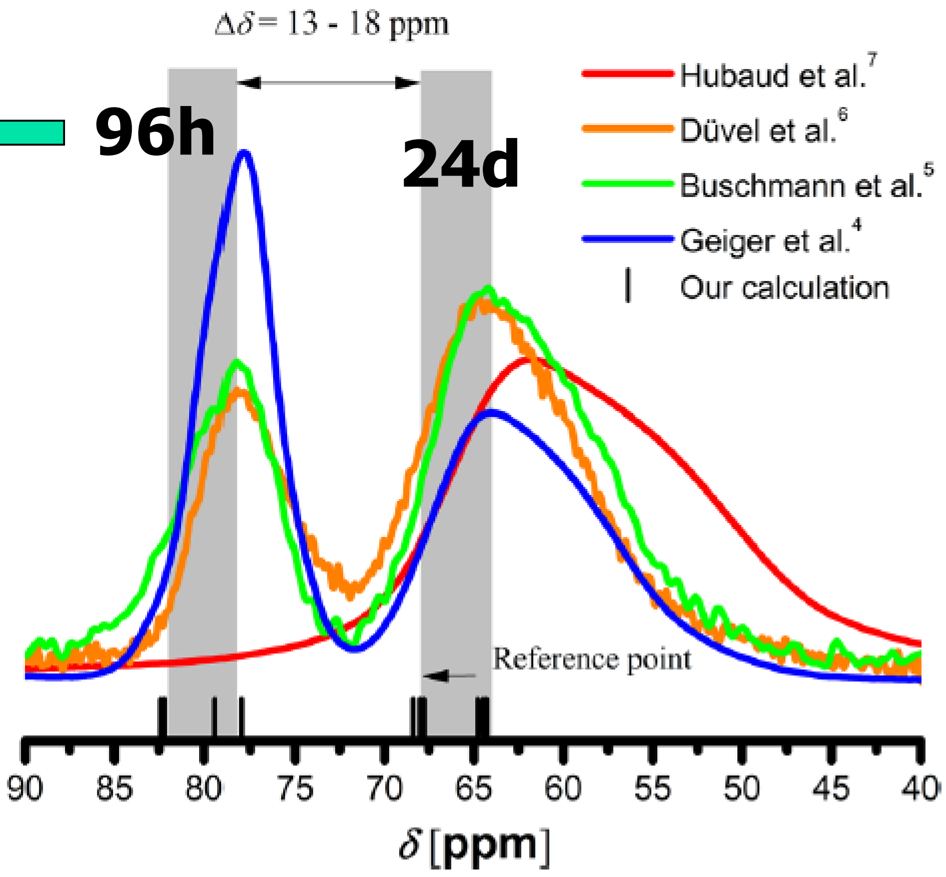


Figure 5. Experimental ^{27}Al NMR MAS spectra[4−7] compared to calculated δ values. The gray areas represent the variation in chemical shift values, Δδ, (13 to 18 ppm) in literature. The reference point refers to Δδ = 0 given by the calculations.

NMR in metals: Knight shifts

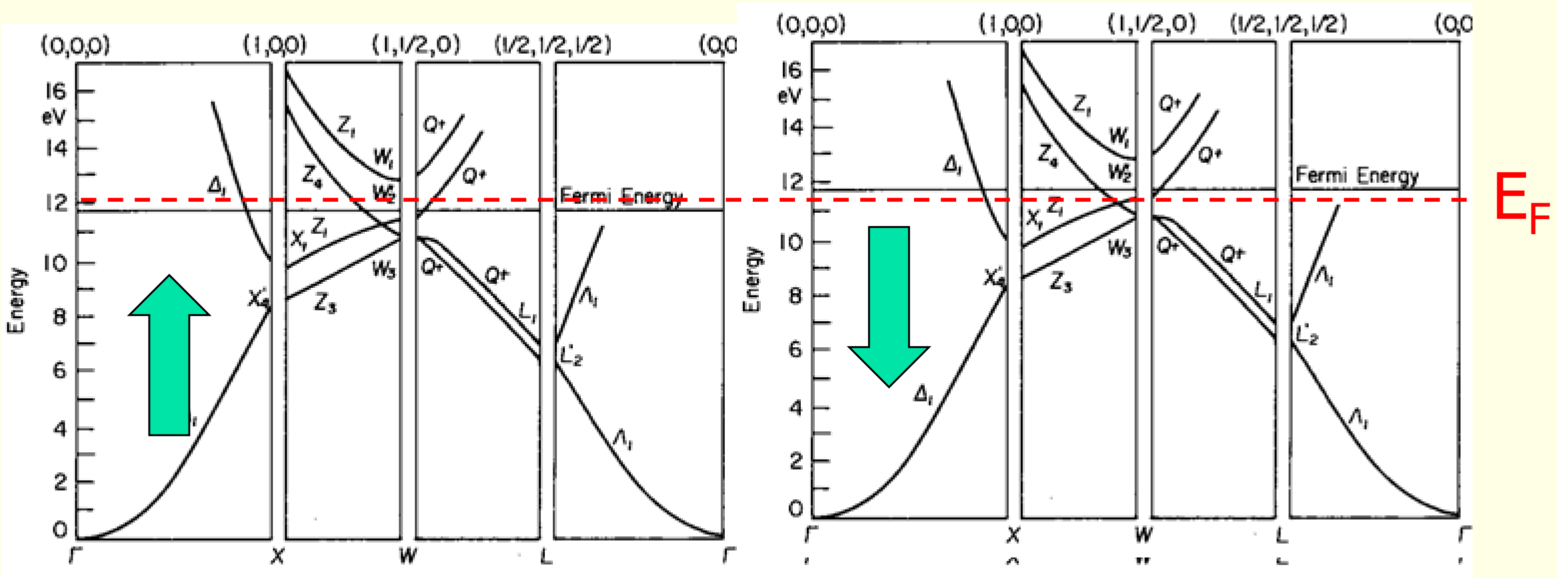
- In **insulators** the **orbital** current determines the shielding
  - *σ it is usually small (ppm) and often diamagnetic* ($B_{ind} = -\sigma B_{ext}$)

- In **metals** there is in addition a **spin** current
  - *the shift can be much larger (%) and often the spin current dominates (paramagnet)*
  - *the external magnetic field leads to an exchange splitting of the spin-up and dn bands and an effective spin magnetization density. This results in a hyperfine field at the nucleus (Fermi contact term) and a dipolar contribution (usually small):*

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

***m*$_{av}$**: *spin density at the nucleus (averaged over $r_{Thomson}$)*

exchange splitting

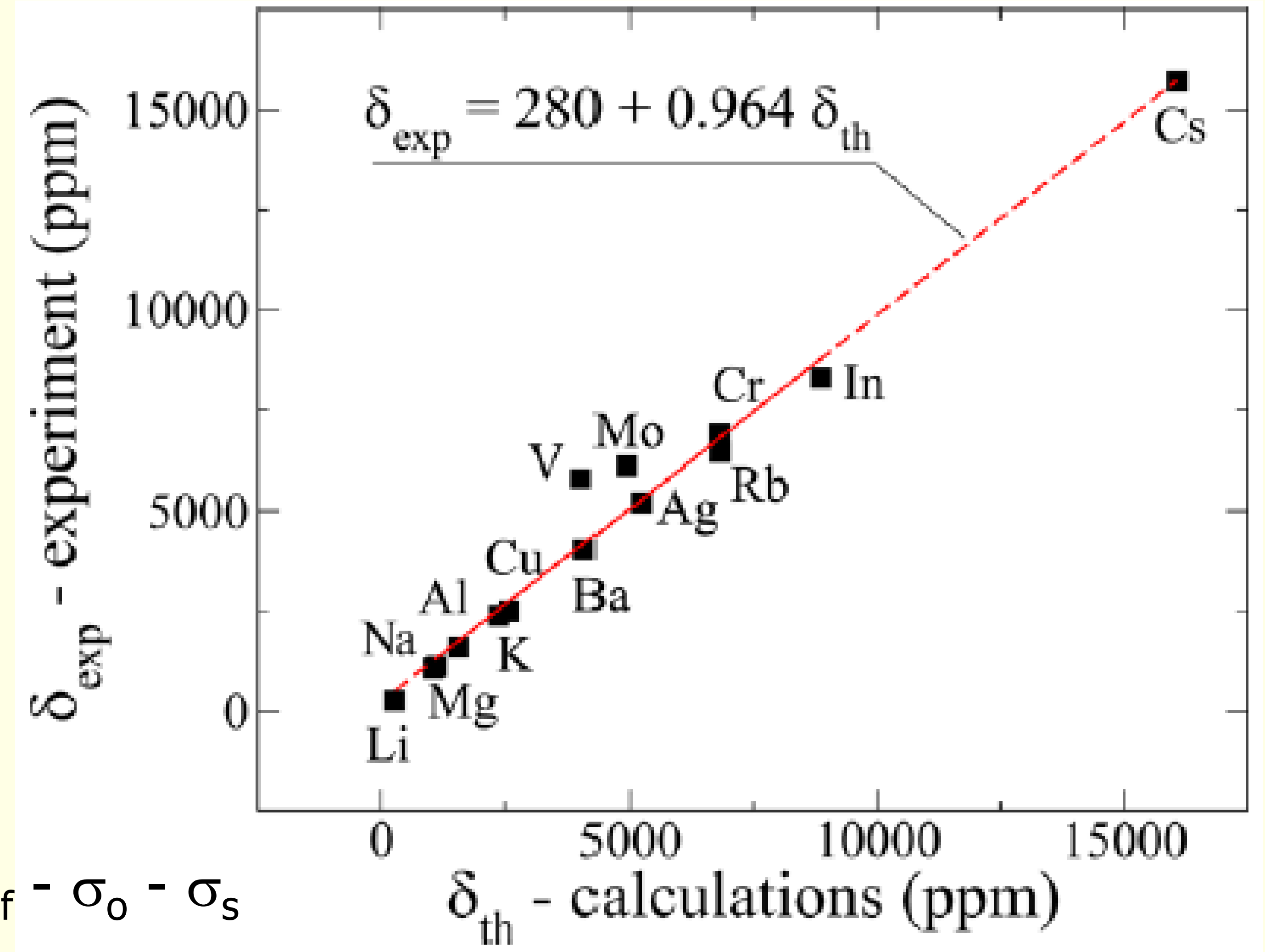


→ ***valence*** *(4s) hyperfine field due to direct polarization*

→ ***core*** *(1s,..) field due to response to induced 3d moments*

- even "big" magnetic fields correspond to tiny energies
  - *100 T ~ 1 mRy*
- numerical difficulty:
  - *enormous k-meshes (1.000.000 k-points in Al)*
  - *temperature smearing (2 mRy = 300 K)*

comparison with experiment



$$\delta_{th} = \sigma_{ref} - \sigma_{o} - \sigma_{s}$$

- very good agreement given the rather old experimental data and problems with the “reference”.

NMR shifts and shielding for metals

experiment measures vs. a reference compound (sometimes liquids)

$$\delta_{th} = \sigma_{ref} - (\sigma_o + \sigma_s)$$

	σ_o	$\sigma_{o(ref)}$	σ_s	δ_{th}	δ_{exp}	δ_{th}-δ_{exp}
Li / Li_2O	81	96	-264	279	260	19
Na / NaBr	518	551	-1021	1054	1070	-16
K / KBr	1126	1153	-2560	2589		
Rb / RbCl	3031	3028	-6826	6822		
Cs / CsCl	5473	5380	-16177	16083		
Mg / $MgCl_2$	505	552	-1078	1124		
Ba / $BaCl_2$	5730	5661	-4160	4092		
Al / $AlPO_4$	519	512	-1591	1584		
In / $In_2(SO_4)_3$	2807	3676	-8012	8881		
V / $NaVO_3$	-5988	-1453	488	4046		
Cr / Na_2CrO_4	-9847	-2567	461	6818		
Mo / K_2MoO_4	-5795	-825	-27	4997	6100	-1103
Cu / CuBr	-330	492	-1568	2390	2380	10
Ag / $AgNO_3$	2219	3772	-3670	5223	5210	13

Often it is argued that the **orbital** shifts of **metal** and **reference cancel** and only the Knight (spin) shift remains.

This is true only for **sp-elements**.

NMR shifts and shielding for metals

experiment measures vs. a reference compound (sometimes liquids)

$$\delta_{th} = \sigma_{ref} - \sigma_o - \sigma_s$$

	σ_o	$\sigma_{o(ref)}$	σ_s	δ_{th}	δ_{exp}	$\delta_{th}-\delta_{exp}$
Li / Li_2O	81	96	-264	279	260	19
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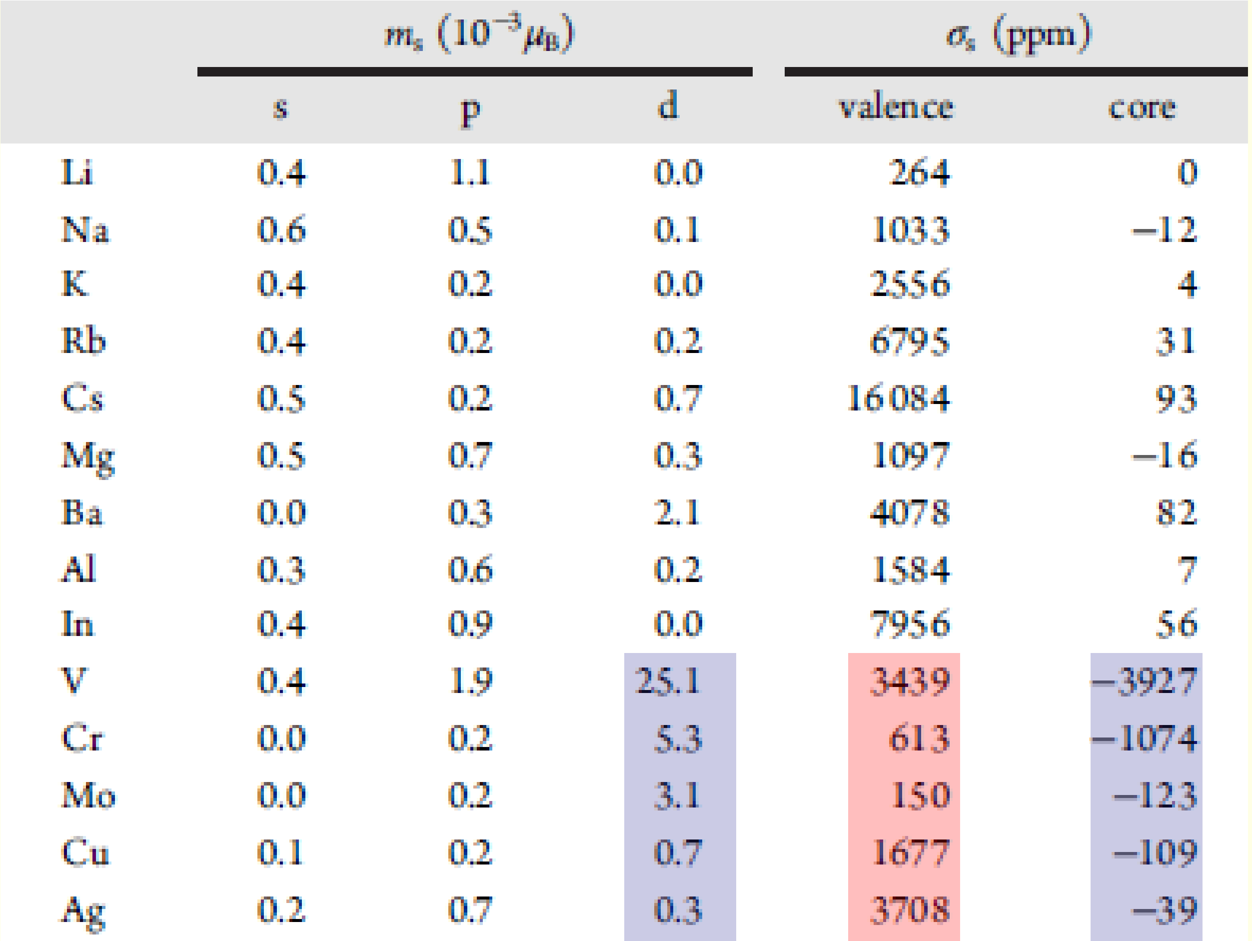
Why is the Knight (**spin**) shift not always strongly **paramagnetic** (negative) ???

It should be directly **proportional** to the **valence-s DOS** at E_F .

Contributions to spin HFF:

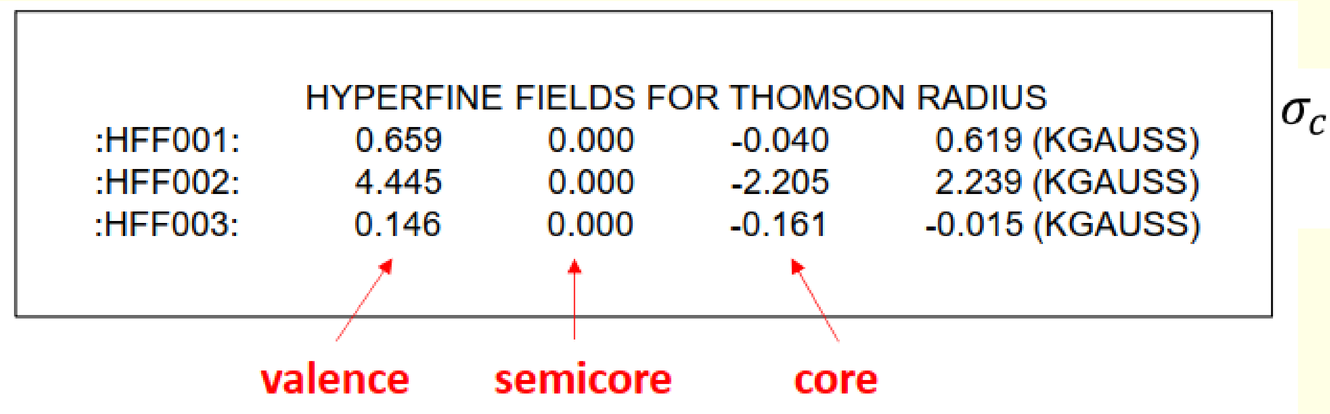
- The induced magnetic moment of “d”-character polarizes the core states (usually in opposite way).
- This core shift can be even larger than the valence shift and fully compensate it.



	m_s ($10^{-3}\mu_B$)			σ_s (ppm)	
	s	p	d	valence	core
Li	0.4	1.1	0.0	264	0
Na	0.6	0.5	0.1	1033	−12
K	0.4	0.2	0.0	2556	4
Rb	0.4	0.2	0.2	6795	31
Cs	0.5	0.2	0.7	16084	93
Mg	0.5	0.7	0.3	1097	−16
Ba	0.0	0.3	2.1	4078	82
Al	0.3	0.6	0.2	1584	7
In	0.4	0.9	0.0	7956	56
V	0.4	1.9	25.1	3439	−3927
Cr	0.0	0.2	5.3	613	−1074
Mo	0.0	0.2	3.1	150	−123
Cu	0.1	0.2	0.7	1677	−109
Ag	0.2	0.7	0.3	3708	−39

How is it done ?

- 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 in kGauss*



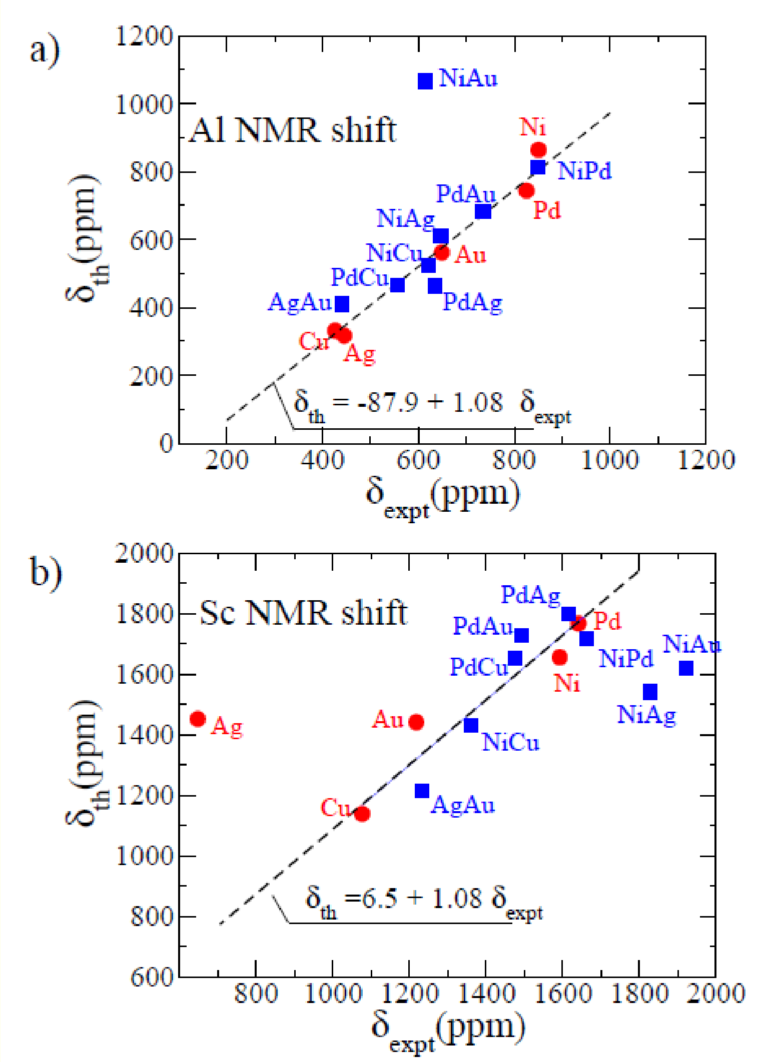
```
                 HYPERFINE FIELDS FOR THOMSON RADIUS
:HFF001:      0.659       0.000       -0.040        0.619 (KGAUSS)
:HFF002:      4.445       0.000       -2.205        2.239 (KGAUSS)
:HFF003:      0.146       0.000       -0.161       -0.015 (KGAUSS)
```

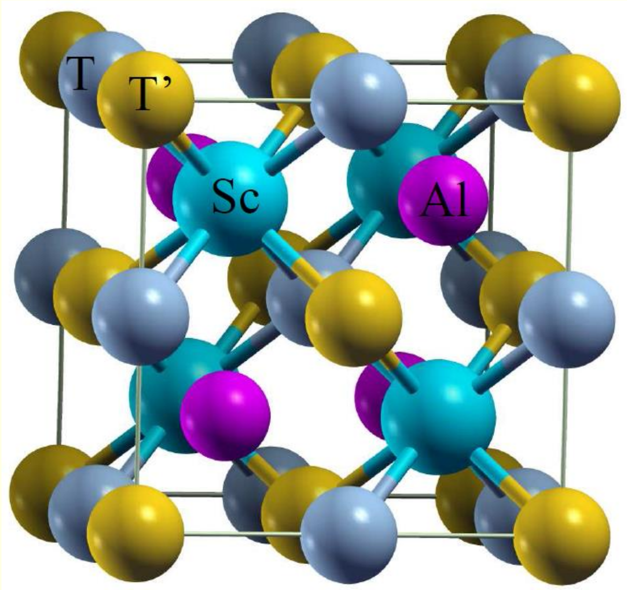
$$\sigma_c[ppm] = -HFF * 1000$$

for B_{ext} = 100T

Al and Sc NMR in ScTT‘Al Heusler phases

- Ternary and quaternary compounds with TT‘=Ni,Cu,Ag,Au,Pd





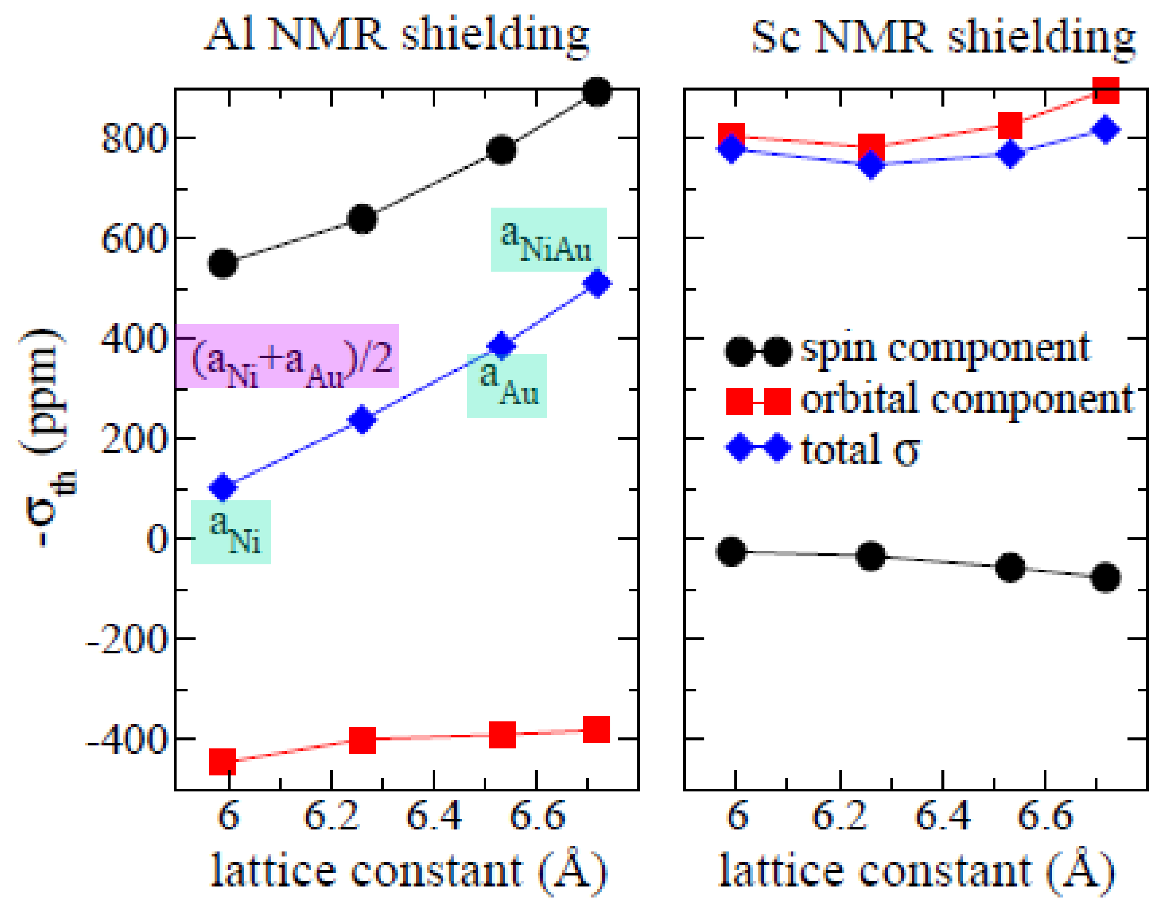
Overall good correlation with experiment but a few exceptions:

- Al and Sc-NMR in ScNiAuAl
- Sc-NMR in $ScAg_2Al$

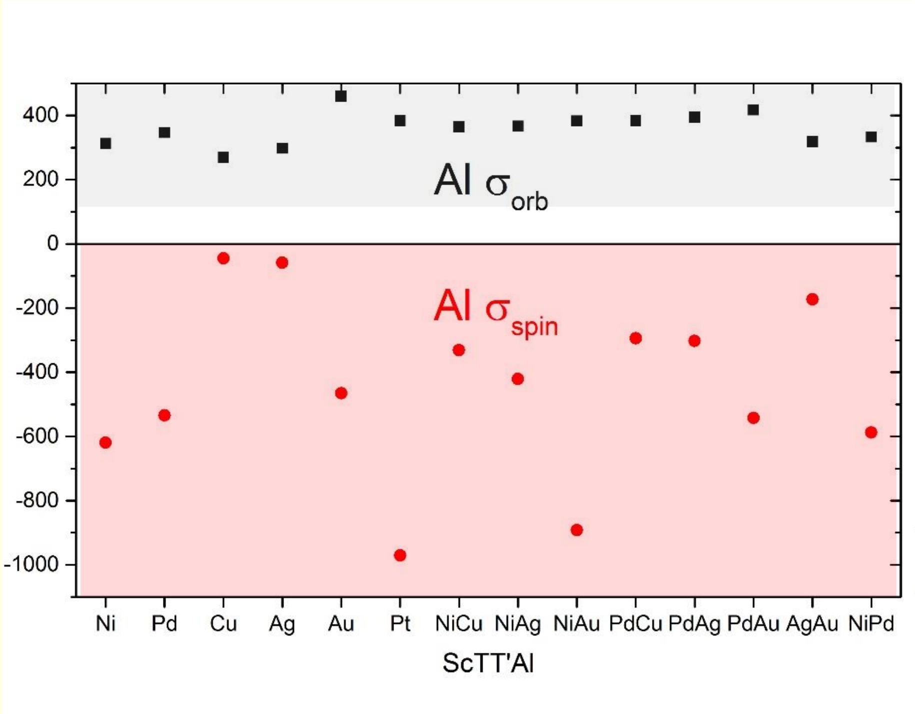
Benndorf et al., Z.anorg.allgem.Chemie 641, 168 (2015)

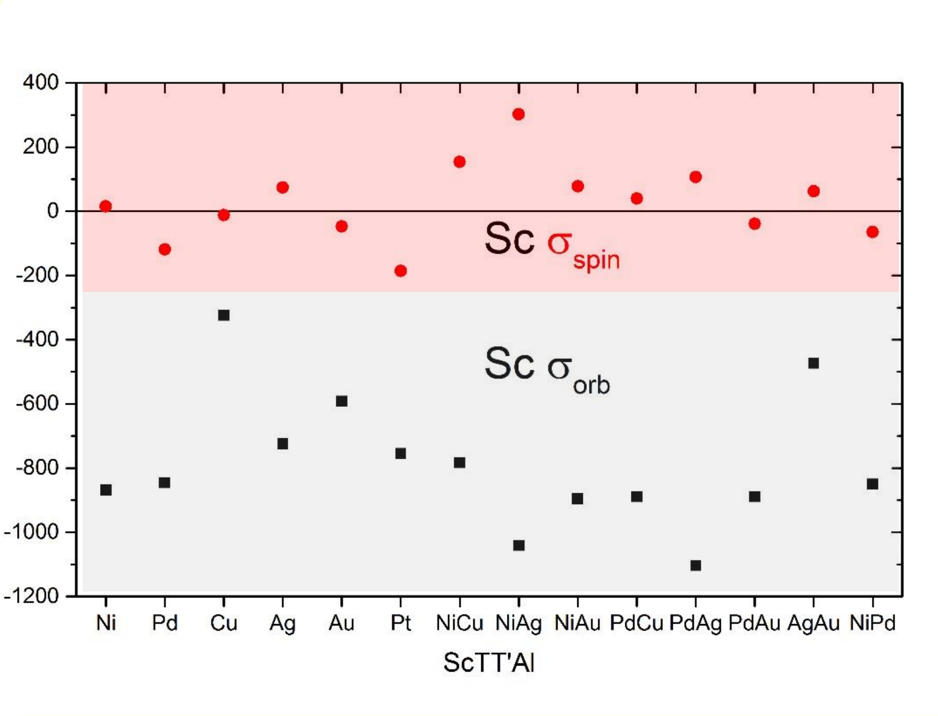
Analysis of Al-shift in ScNiAuAl

- exp. lattice parameter disagrees with Vegards law and theoretical a_0
- → 300 ppm shift for Al !!! correcting most of the differences



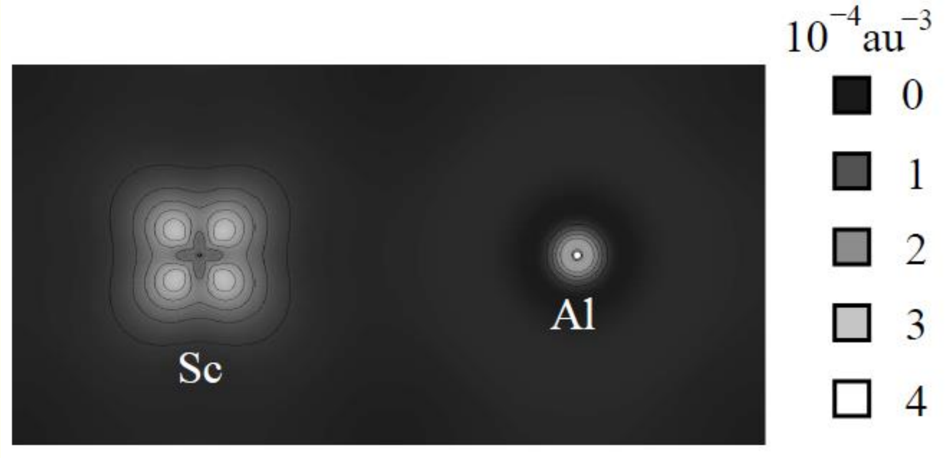
σ_{orb} and σ_{spin} in ScTT‘Al





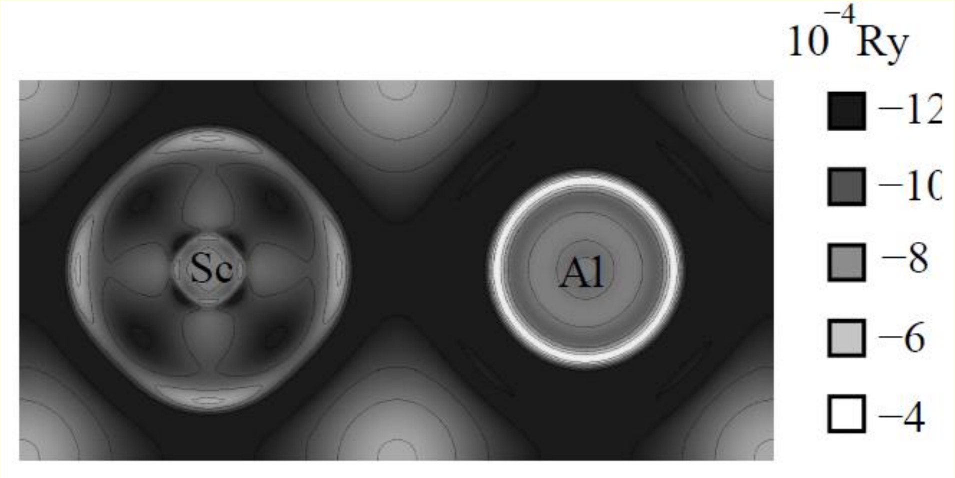
	Al	Sc
σ_{orb}:	small **diamagnetic** variation	huge **paramagnetic** variation
σ_{spin}:	large **paramagnetic** variation	small **dia/paramagn**. variation
σ_{tot}:	determined by σ_{spin}	determined by σ_{orb}
	only 3sp valence e^-	3d valence e^-

Induced density and potential in ScNiAuAl



induced spin-density (100T):

Al: small and spherical symmetric
Sc: large 3d-"t2g" like spin-density
➡ large induced Sc magn.moment

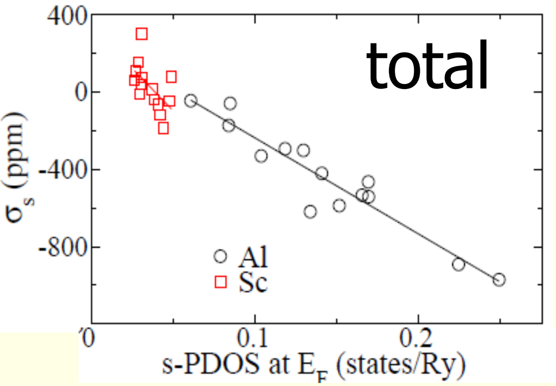


induced scf difference potential $V_{up} - V_{dn}$:

- 100T = constant 8.5 10^{-4} Ry
- ΔV not constant at all
- radial differences due to contraction/ expansion of spin-up/dn wf.
- non-spherical around Sc

Decomposition of Knight shift in ScTT'Al

$$\sigma_{spin}^{total} = \sigma_{spin}^{para} + \sigma_{spin}^{core\text{-}SCF} + \sigma_{spin}^{val\text{-}SCF}$$



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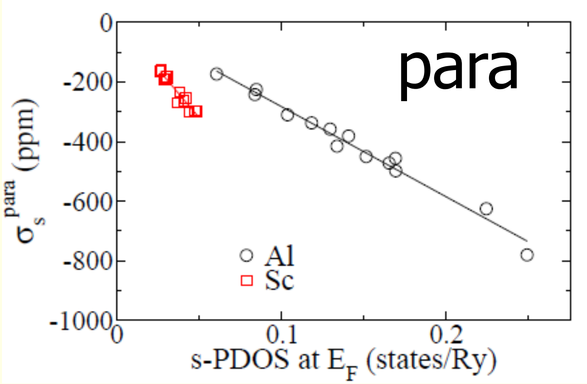
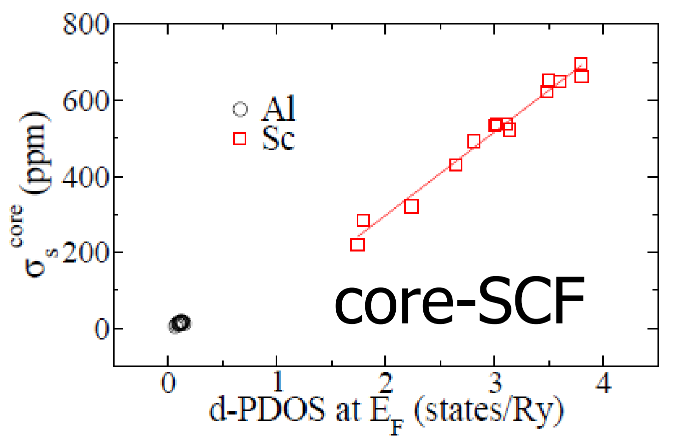
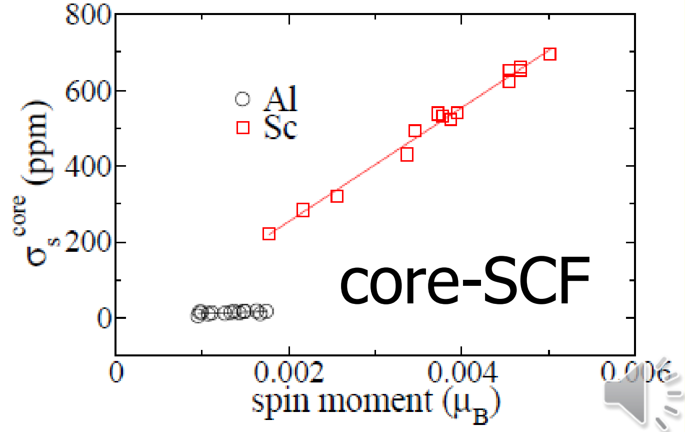
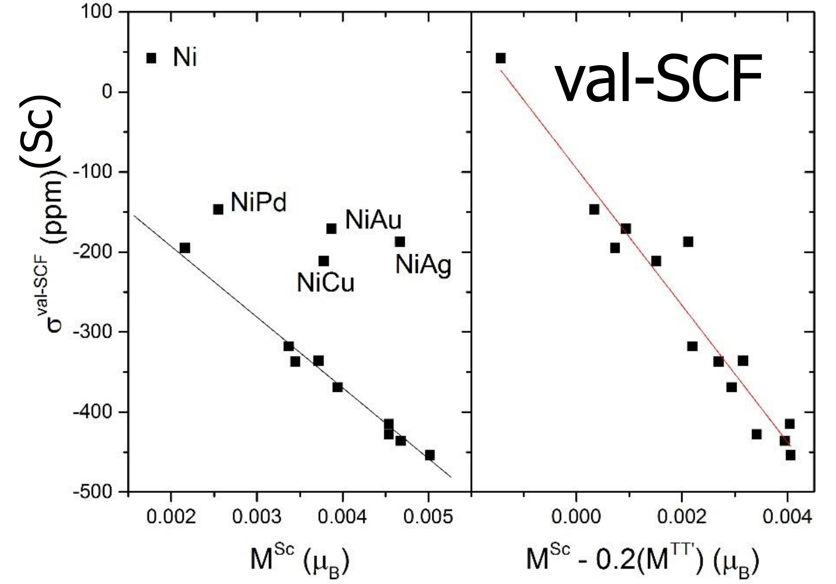


\+ core-polarization

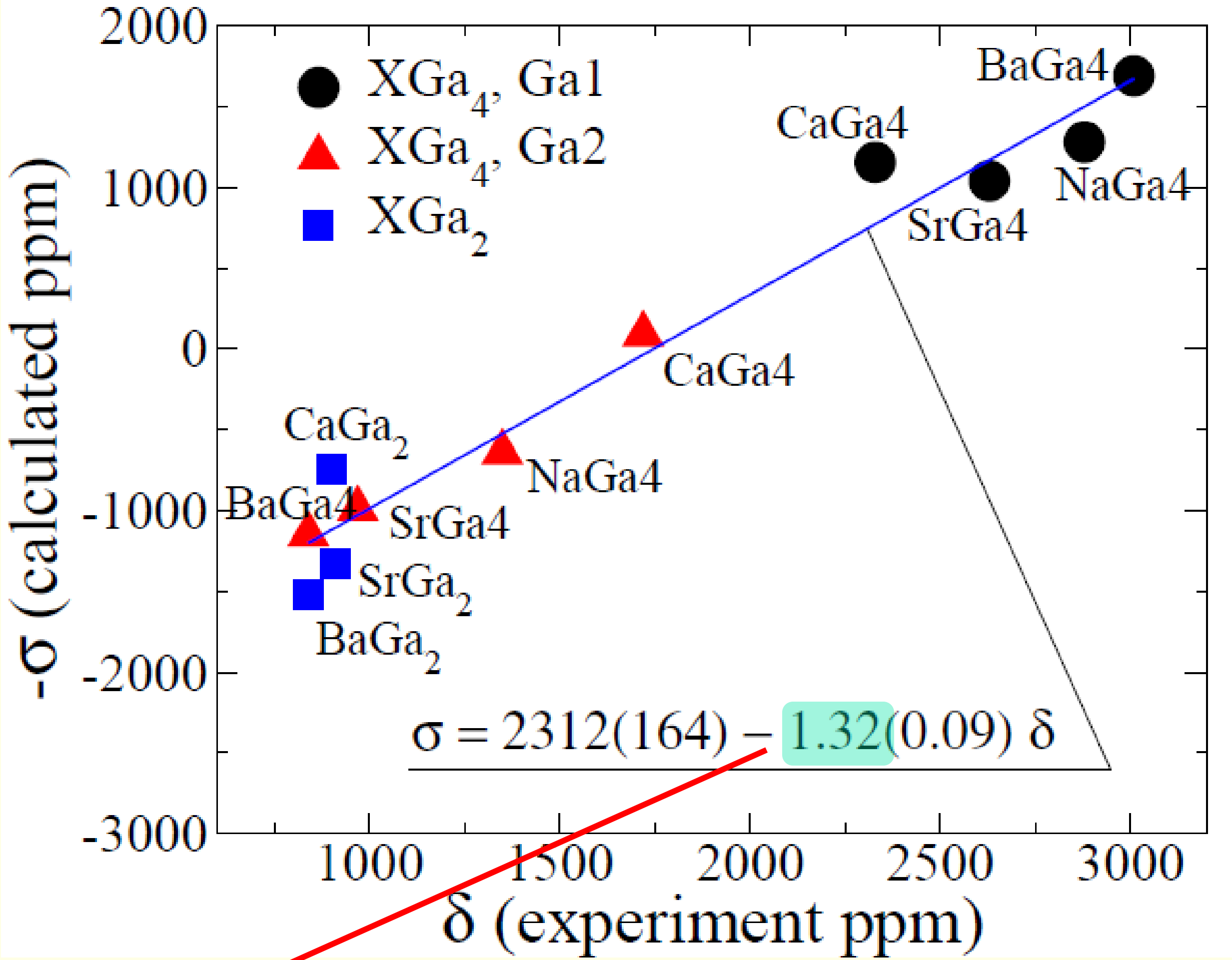




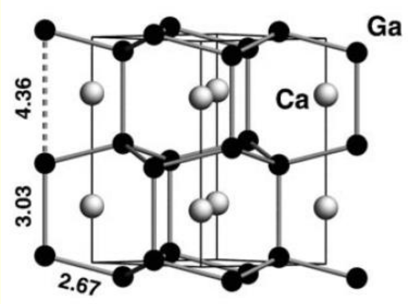
\+ onsite + transfered HFF



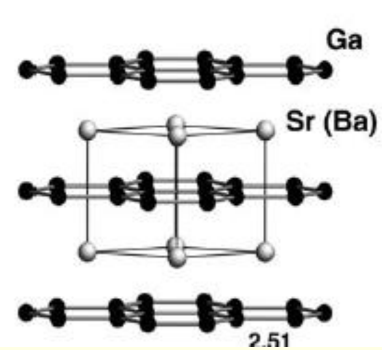
Ga-NMR in intermetallic gallides



slope ???



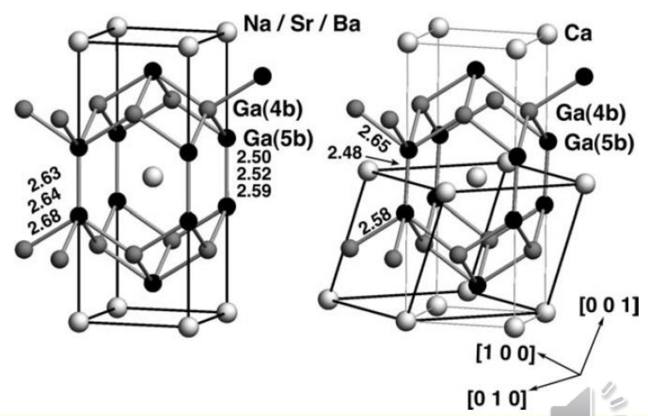
$CaGa_2$



$SrGa_2$

$BaGa_2$

Na/Sr/$BaGa_4$ $CaGa_4$



R.Laskowski et al., J.Phys.Chem. C **121**, 753 (2017)

Summary:

routine NMR calculations for Knight and Chemical shifts in solids are now possible

- *huge k-meshes and Fermi broadening necessary, but manageable*
- ***orbital** shift: **paramagnetic** part when **d-e$^-$** are **present/available above E$_F$,** either on the **NMR-atom** or its **neighbor***
- *spin-contact term dominates in metals, but orbital part not negligible and for d elements sometimes more important than spin-part*
- *core-polarization due to induced 3d (4d) moments can dominate (cancel) the direct 4s (5s) valence contribution*
- *important spin-dipolar term when charge asymmetry at E$_F$ exists*
- ***"Slope"-**problem **=** DFT-problem **?***