Nuclear hyperfine interactions

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Introduction

- What is it about? Why is it interesting in solid-state physics?
  - It is about the energy levels of the spin states of a nucleus.
  - An electric or magnetic field at the position of the nucleus may lead to a splitting of the nuclear spin states
  - The energy splitting depends on the intensity of the field, which in turns depends on the environment around the nucleus $\Longrightarrow$
    The measured spin nuclear transition energy provides information on the charge distribution around the nucleus

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- Outline of the talk
  - Hyperfine interactions
    - Electric (isomer shift, electric-field gradient)
    - Magnetic (Zeeman effect, hyperfine field)
  - Nuclear magnetic resonance
    - Calculation of chemical shielding (orbital and spin contributions)

Hyperfine interactions → Shift and splitting of energy levels of a nucleus

- Interactions between a nucleus and the electromagnetic field produced by the other charges (electrons and other nuclei) in the system.
- Beyond the point charge model for the nucleus.
- Produces hyperfine structure (shift and splitting of the nucleus energy levels).

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Different types of hyperfine interactions:

- Electric:
  - Electric monopole interaction (isomer shift, shift of the spectrum)
  - Electric quadrupole interaction (quadrupole splitting of the spectral lines)
- Magnetic:
  - Magnetic dipole interaction (Zeeman splitting of the spectral lines)

Experimental study of hyperfine structure

Nuclear hyperfine structure can be experimentally studied using:

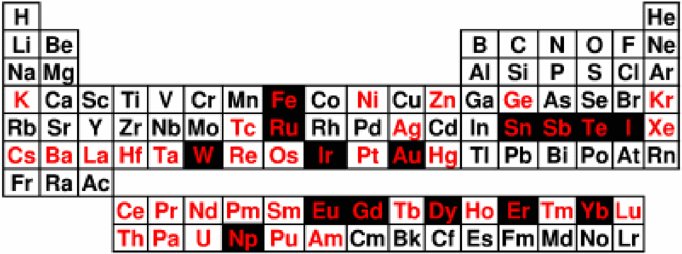
- Nuclear magnetic resonance (NMR)
- Nuclear quadrupole resonance (NQR)
- Time differential perturbed angular correlation (TDPAC)
- Time differential perturbed angular distribution (TDPAD)
- Muon spin resonance (μSR)
- Mössbauer spectroscopy

~~Electron hyperfine structure can be experimentally studied using:~~

- ~~Electron paramagnetic resonance (EPR)~~

Mössbauer spectroscopy [1]

- Mössbauer effect (1958): In solids, emission and absorption of γ-ray can occur at the same energy (resonance)
- Reason: recoil-free transition in the nucleus (no exchange of vibration energy with the lattice)
- Allows for precise measurement of
  - Energy changes due to electrical, magnetic or gravitational fields
  - Isomer shift, quadrupole splitting, Zeeman splitting
- The fraction of recoil-free events and lifetime of the excited state limit the number of isotopes that can be used successfully for Mössbauer spectroscopy:



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

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[1] R. Mössbauer, 1961 Nobel Prize in physics

Electric interactions

ρ_n: charge density of a nucleus
V_el: electrostatic potential due to all charges outside the nucleus

$$\begin{aligned} E &= \int \rho_\mathrm{n} V_\mathrm{el} d^3 r \\ &= \underbrace{V_\mathrm{el}(0) \int \rho_\mathrm{n} d^3 r}_{\text{Point charge model}} + \underbrace{\sum_{i=1}^{3} \left.\frac{\partial V}{\partial x_i}\right|_0 \int \rho_\mathrm{n} x_i d^3 r}_{\text{=0 since no electric dipole moment}} + \underbrace{\frac{1}{2} \sum_{i,j=1}^{3} \left.\frac{\partial^2 V}{\partial x_i \partial x_j}\right|_0 \int \rho_\mathrm{n} x_i x_j d^3 r}_{E_3} + \ldots \end{aligned}$$

$$E_3 = \underbrace{\frac{2\pi}{3} z \left|\psi(0)\right|^2 \langle r^2 \rangle}_{\substack{\text{Electric monopole interaction } \delta E \\ \text{Due to finite volume of nucleus}}} + \underbrace{\frac{1}{6} \sum_{i,j=1}^{3} V_{ij} Q_{ij}}_{\substack{\text{Electric quadrupole interaction} \\ \text{For nculei with spin } I > \frac{1}{2}}}$$

Electric monopole interaction: isomer shift

Energy of emitted γ-ray by a source:

$$E_{\rm s} = E_0 + \delta E_{\rm s}^{\rm e} - \delta E_{\rm s}^{\rm g}$$

Energy of absorbed γ-ray by an absorber:

$$E_{\rm a} = E_0 + \delta E_{\rm a}^{\rm e} - \delta E_{\rm a}^{\rm g}$$

Isomer shift (a measure of the difference in the *s* electron density at the nuclei in the source and in the absorber):

$$\delta = E_{\rm a} - E_{\rm s} \approx \alpha(\rho_{\rm a}(0) - \rho_{\rm s}(0))$$

α is the calibration constant that can be negative or positive ($\alpha = -0.24$ mm/s for ^{57}Fe).

$\rho(0)$ is :RTO in case.scf

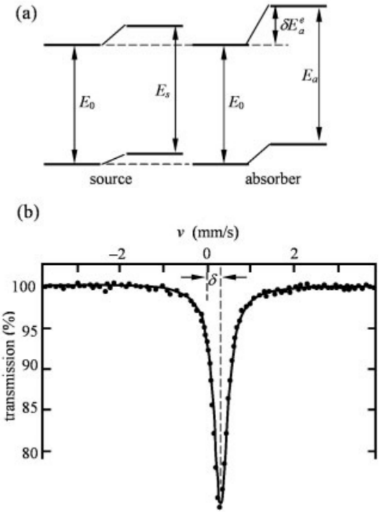

Fig. 2.1 (a) Shift of nuclear energy levels due to electric monopole interaction. (b) A typical Mössbauer spectrum in the presence of an isomer shift.

Isomer shift: YBaFe$_2$O$_5$ (charge-ordered and valence-mixed phases) [1]

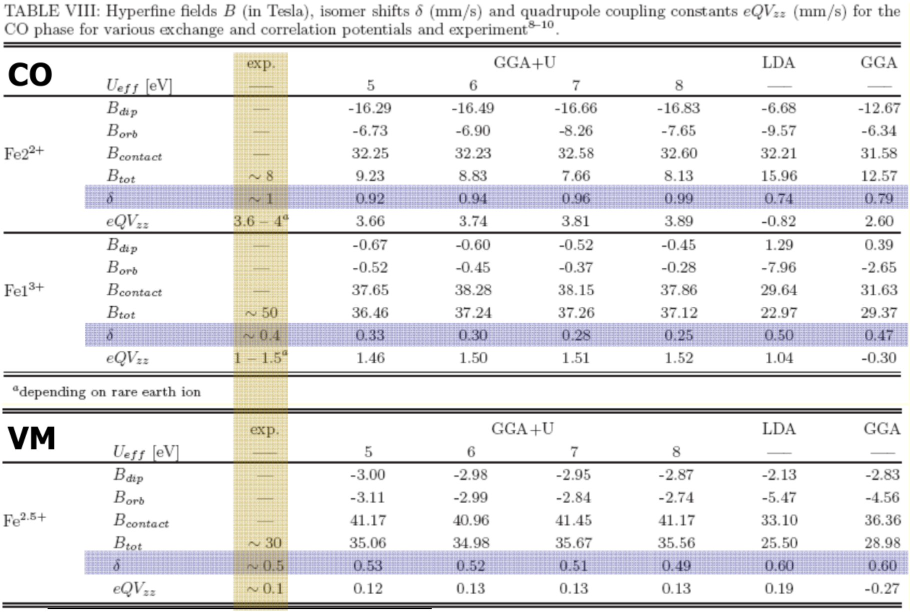

TABLE VIII: Hyperfine fields B (in Tesla), isomer shifts δ (mm/s) and quadrupole coupling constants eQV_{zz} (mm/s) for the CO phase for various exchange and correlation potentials and experiment[8–10].

CO		exp.	GGA+U				LDA	GGA
	U_{eff} [eV]	—	5	6	7	8	—	—
Fe2^{2+}	B_{dip}	—	-16.29	-16.49	-16.66	-16.83	-6.68	-12.67
	B_{orb}	—	-6.73	-6.90	-8.26	-7.65	-9.57	-6.34
	$B_{contact}$	—	32.25	32.23	32.58	32.60	32.21	31.58
	B_{tot}	~ 8	9.23	8.83	7.66	8.13	15.96	12.57
	δ	~ 1	0.92	0.94	0.96	0.99	0.74	0.79
	eQV_{zz}	3.6 – 4[a]	3.66	3.74	3.81	3.89	-0.82	2.60
Fe1^{3+}	B_{dip}	—	-0.67	-0.60	-0.52	-0.45	1.29	0.39
	B_{orb}	—	-0.52	-0.45	-0.37	-0.28	-7.96	-2.65
	$B_{contact}$	—	37.65	38.28	38.15	37.86	29.64	31.63
	B_{tot}	~ 50	36.46	37.24	37.26	37.12	22.97	29.37
	δ	~ 0.4	0.33	0.30	0.28	0.25	0.50	0.47
	eQV_{zz}	1 – 1.5[a]	1.46	1.50	1.51	1.52	1.04	-0.30

[a]depending on rare earth ion

VM		exp.	GGA+U				LDA	GGA
	U_{eff} [eV]	—	5	6	7	8	—	—
Fe$^{2.5+}$	B_{dip}	—	-3.00	-2.98	-2.95	-2.87	-2.13	-2.83
	B_{orb}	—	-3.11	-2.99	-2.84	-2.74	-5.47	-4.56
	$B_{contact}$	—	41.17	40.96	41.45	41.17	33.10	36.36
	B_{tot}	~ 30	35.06	34.98	35.67	35.56	25.50	28.98
	δ	~ 0.5	0.53	0.52	0.51	0.49	0.60	0.60
	eQV_{zz}	~ 0.1	0.12	0.13	0.13	0.13	0.19	-0.27

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[1] C. Spiel, P. Blaha, and K. Schwarz, Phys. Rev. B **79**, 115123 (2009)

Electric quadrupole interaction: Electric quadrupole splitting

Quadrupole Hamiltonian:

$$H_\mathrm{Q} = \frac{1}{2} \sum_{i,j=1}^{3} V_{ij} Q_{ij}$$

V_{ij}: electric field gradient (EFG)
Q_{ij}: nuclear quadrupole
Eigenvalues (nuclear spin $I > \frac{1}{2}$):

$$E_\mathrm{Q} = \frac{QV_{zz}}{4I(2I-1)} \left(3m^2 - I(I+1)\right) \left(1 + \frac{\eta^2}{3}\right)^{1/2}$$

m: nuclear spin magnetic quantum number
$\Longrightarrow$ quadrupole splitting of the nucleus spin levels

The EFG can be calculated by WIEN2k

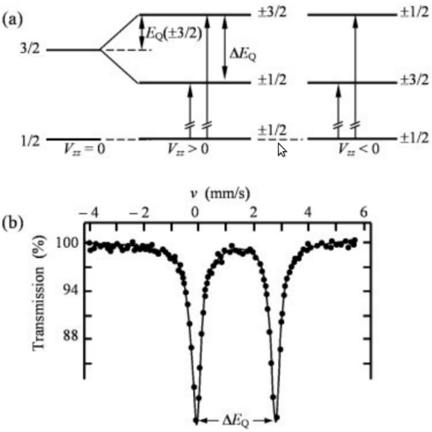


Fig. 2.6 (a) Quadrupole interaction splits the ^{57}Fe energy levels. (b) A quadrupole splitting Mössbauer spectrum.

Electric field gradient (EFG)

- $V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$: 2nd derivative of the electrostatic potential V at the position of a nucleus.
- 3×3 tensor V_{ij} made diagonal by similarity transformation:

$$\begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{21} & V_{22} & V_{23} \\ V_{31} & V_{32} & V_{33} \end{pmatrix} \Rightarrow \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix}$$

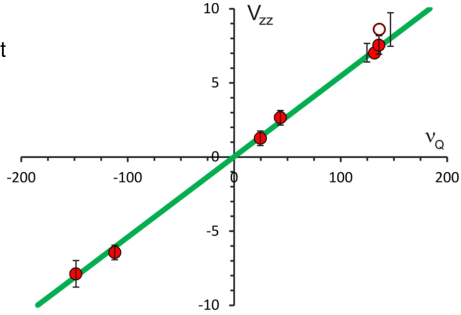
  with $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$
- Since $V_{xx} + V_{yy} + V_{zz} = 0$, only two quantities are necessary to fully characterize the EFG:
  - The largest component V_{zz} (:EFG in case.scf)
  - Assymetry parameter $\eta = |V_{xx} - V_{yy}| / |V_{zz}|$ (:ETA in case.scf)
- By symmetry, the EFG is zero for atoms with cubic point group

EFG: Nuclear quadrupole moment Q of ^{111}Cd [1]

$$\nu_Q \propto Q V_{zz}$$

- Experimental quadrupole interaction frequency ν_Q
- Calculatd EFG V_{zz}
- Q obtained from the slope of V_{zz} versus $\nu_Q \Longrightarrow$ 0.76(2) barn
- Importance of geometry and temperature effect

host lattice	ν_Q (MHz)	V_{zz} (10^{21} V/m^2)
Ga	-148.6(1)	-7.89(90)
Hg	-112(2)	-6.45(50)
bct-In	24.82(20)	1.25(50)
β-Sn	43.56(30)	2.65(50)
Sb	132(3)	7.0(6)
Cd	136.02(40)	7.53(60)
Zn	136.5(1.0)	8.6(1.1)



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[1] L. Errico *et al.*, J. Phys. Chem. C **120**, 23111 (2016)

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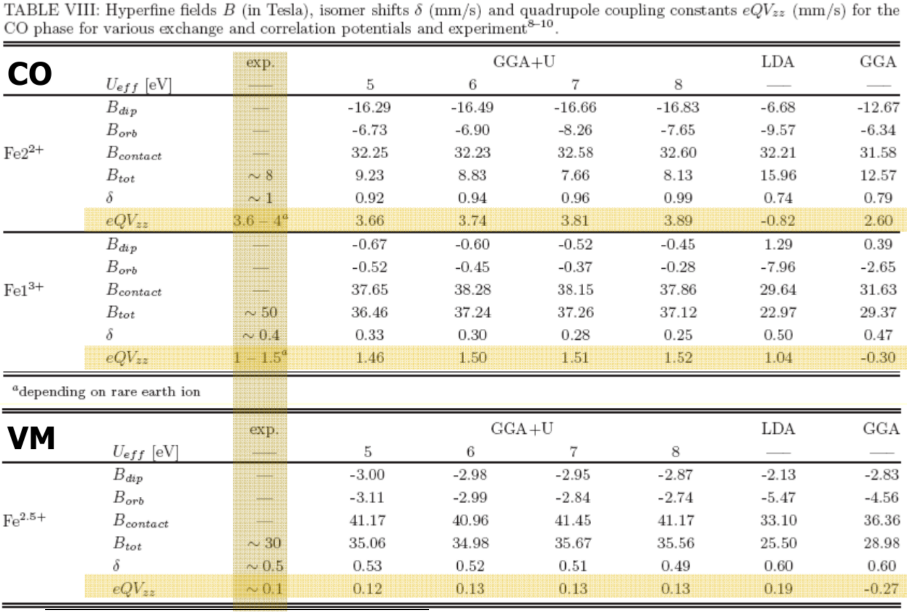

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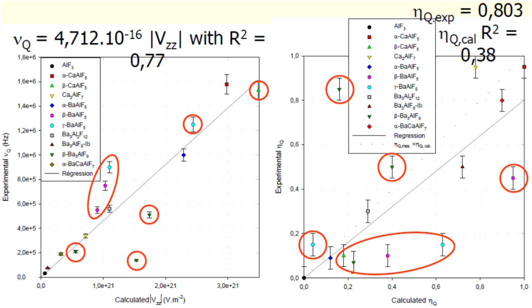
[1] C. Spiel, P. Blaha, and K. Schwarz, Phys. Rev. B **79**, 115123 (2009)

EFG: Importance of the geometry (^{27}Al) [1]

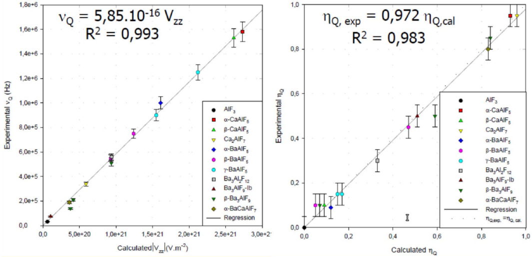
Using (inaccurate) geometry from X-ray powder diffraction data:



$\nu_Q = 4{,}712.10^{-16}\,|V_{zz}|$ with $R^2 = 0{,}77$

$\eta_{Q,exp} = 0{,}803\,\eta_{Q,cal}$ $R^2 = 0{,}38$

Much better agreement after geometry optimization:



$\nu_Q = 5{,}85.10^{-16}\,V_{zz}$ $R^2 = 0{,}993$

$\eta_{Q,\,exp} = 0{,}972\,\eta_{Q,cal}$ $R^2 = 0{,}983$

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[1] M. Body *et al*. J. Phys. Chem. A, **111**, 11873 (2007)

EFG: Effect of exchange-correlation [1]

- GLLB-SC is the most accurate method
- mBJLDA is not recommended
- Standard PBE is inaccurate for CuO and Cu_2O

EFG in 10^{21} V/m^2. Very inaccurate values are in red.

Method	Ti	Zn	Zr	Tc	Ru	Cd	CuO	Cu_2O	Cu_2Mg
LDA	1.80	3.50	4.21	-1.65	-1.56	7.47	-1.86	-5.27	-5.70
PBE	1.73	3.49	4.19	-1.61	-1.46	7.54	-2.83	-5.54	-5.70
EV93PW91	1.61	3.43	4.13	-1.57	-1.33	7.63	-3.17	-6.53	-5.82
AK13	1.65	3.86	4.17	-1.28	-1.13	8.53	-3.56	-7.92	-5.44
Sloc	1.44	3.93	2.75	-0.52	-0.35	8.01	-3.97	-11.97	-4.10
HLE16	1.70	3.29	3.78	-0.95	-0.73	7.66	-4.18	-10.10	-4.59
BJLDA	1.97	3.51	4.25	-1.27	-1.16	7.61	-5.42	-7.74	-5.20
mBJLDA	1.99	3.35	4.33	-1.20	-0.90	7.56	-13.93	-7.40	-4.89
LB94	0.94	3.78	1.83	-0.72	-1.05	7.47	-1.23	-11.16	-4.97
GLLB-SC	1.62	3.72	4.42	-1.66	-1.26	8.05	-4.65	-9.99	-5.58
HSE06	1.5	4.4	4.5	-2.0	-1.3	9.4	-8.9	-8.3	-6.3
Expt.	1.57(12)	3.40(35)	4.39(15)	1.83(9)	0.97(11)	7.60(75)	7.55(52)	10.08(69)	5.76(39)

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[1] F. Tran *et al.* Phys. Rev. Materials, **2**, 023802 (2018)

Magnetic dipole interaction

Hamiltonian of the interaction between the magnetic dipole moment $\boldsymbol{\mu}$ of a nucleus and the magnetic field **B** at the nucleus:

$$H_\mathrm{M} = -\boldsymbol{\mu} \cdot \mathbf{B} = -g\mu_\mathrm{N}\mathbf{I} \cdot \mathbf{B}$$

Eigenvalues (nuclear spin $I > \frac{1}{2}$):

$$E_\mathrm{M} = -gmB\mu_\mathrm{N}$$

where m is the nuclear spin magnetic quantum number $\Longrightarrow$ Nuclear Zeeman effect (splitting of the nucleus spin energy levels)

B can be calculated by WIEN2k

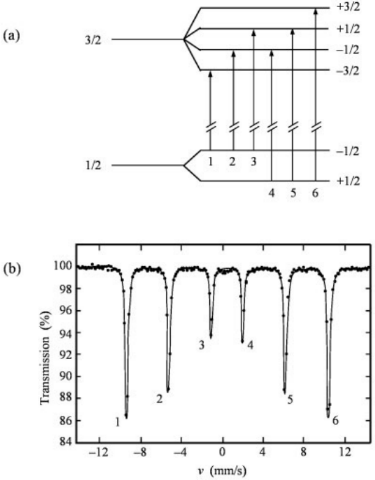
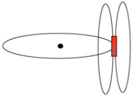


Fig. 2.14 (a) Magnetic splittings of the ^{57}Fe nuclear energy levels. (b) A Mössbauer spectrum of FeF_3 at 4.2 K showing a sextet due to magnetic splittings [44].

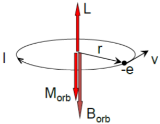
Components of the magnetic field $\mathbf{B}$ at a nucleus position

- Total:
  $\mathbf{B} = \mathbf{B}_{\text{lat}} + \mathbf{B}_{\text{ext}} + \mathbf{B}_{\text{hf}}$
- Hyperfine (from atom's own electrons):
  $\mathbf{B}_{\text{hf}} = \mathbf{B}_{\text{dip}} + \mathbf{B}_{\text{orb}} + \mathbf{B}_{\text{Fermi}}$
- Spin dipole field (from electrons spin moment):
  $\mathbf{B}_{\text{dip}} = 2\mu_{\text{B}} \langle \Phi | \frac{S(r)}{r3} \left(3(\mathbf{s}\hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{s}\right) | \Phi \rangle$
- Orbital field (from electron orbital moment):
  $\mathbf{B}_{\text{orb}} = 2\mu_{\text{B}} \langle \Phi | \frac{S(r)}{r3} \mathbf{l} | \Phi \rangle$
- Fermi contact field (electron spin density at nucleus):
  $\mathbf{B}_{\text{Fermi}} = \frac{8\pi}{3} \mu_{\text{B}} \left(\rho_{\uparrow}(0) - \rho_{\downarrow}(0)\right)$

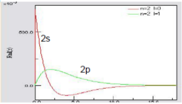
➢ B_{dip} = electron as bar magnet



➢ B_{orb} = electron as current loop

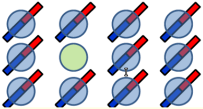


➢ B_{Fermi} = electron in nucleus



$$-\frac{2\mu_B\mu_0}{3}\left(|\psi_{e,\uparrow}(\mathbf{0})|^2 - |\psi_{e,\downarrow}(\mathbf{0})|^2\right)$$

➢ B_{lat} = neighbours as bar magnets



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- Spin-polarized calculcation (runsp_lapw)

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- Spin-polarized calculcation (runsp_lapw)
- $\mathbf{B}_{\text{Fermi}}$ (in kGauss) is :HFF in case.scf
- $\mathbf{B}_{\text{dip}}$ and $\mathbf{B}_{\text{orb}}$ are calculated by the lapwdm program:

  case.indm:

`-12.`	Emin cutoff energy
`1`	number of atoms for which density matrix is calculated
`1 1 2`	index of 1st atom, number of L's, L1
`0 0`	rindex, lsindex

  (rindex,lsindex)= `(3,5)` for $\mathbf{B}_{\text{dip}}$
  (rindex,lsindex)= `(3,3)` for $\mathbf{B}_{\text{orb}}$
  Execute "x lapwdm (-up/dn)" and search for :XOP in case.scfdm(up/dn)
  $\mathbf{B}_{\text{dip/orb}}$ (in Tesla) is the difference :XOP(up)$-$:XOP(dn)
  More details in `$WIENROOT/SRC/Bhf_3.ps`

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- Spin-polarized calculcation (runsp_lapw)
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- $\mathbf{B}_{\text{lat}}$ is calculated by the dipan program:
  Prepare case.indipan and execute "x dipan"
  More details in `$WIENROOT/SRC_dipan/dipfield.pdf`

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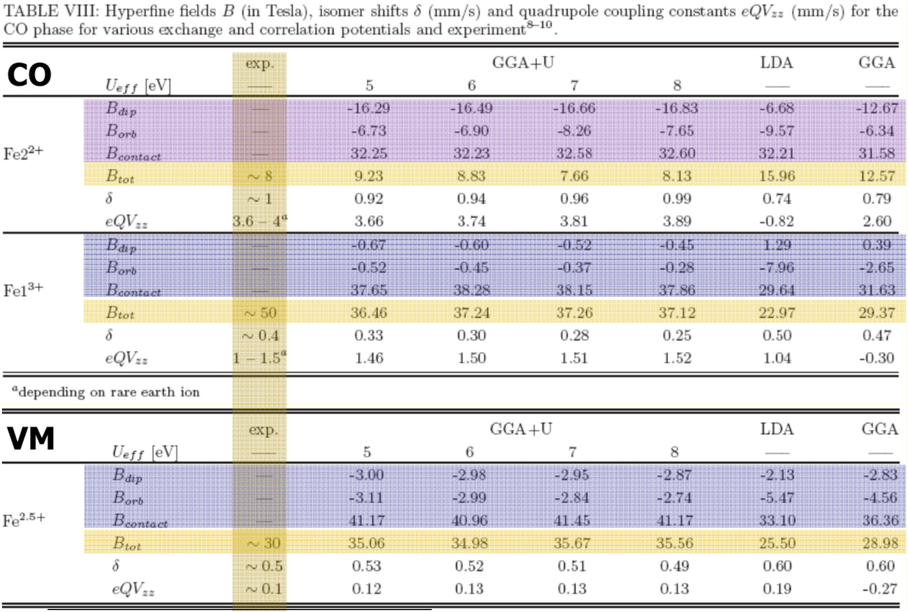


TABLE VIII: Hyperfine fields B (in Tesla), isomer shifts δ (mm/s) and quadrupole coupling constants eQV_{zz} (mm/s) for the CO phase for various exchange and correlation potentials and experiment[8–10].

CO

		exp.	GGA+U				LDA	GGA
	U_{eff} [eV]	—	5	6	7	8	—	—
Fe2^{2+}	B_{dip}	—	-16.29	-16.49	-16.66	-16.83	-6.68	-12.67
	B_{orb}	—	-6.73	-6.90	-8.26	-7.65	-9.57	-6.34
	$B_{contact}$	—	32.25	32.23	32.58	32.60	32.21	31.58
	B_{tot}	~ 8	9.23	8.83	7.66	8.13	15.96	12.57
	δ	~ 1	0.92	0.94	0.96	0.99	0.74	0.79
	eQV_{zz}	$3.6 - 4^a$	3.66	3.74	3.81	3.89	-0.82	2.60
Fe1^{3+}	B_{dip}	—	-0.67	-0.60	-0.52	-0.45	1.29	0.39
	B_{orb}	—	-0.52	-0.45	-0.37	-0.28	-7.96	-2.65
	$B_{contact}$	—	37.65	38.28	38.15	37.86	29.64	31.63
	B_{tot}	~ 50	36.46	37.24	37.26	37.12	22.97	29.37
	δ	~ 0.4	0.33	0.30	0.28	0.25	0.50	0.47
	eQV_{zz}	$1 - 1.5^a$	1.46	1.50	1.51	1.52	1.04	-0.30

[a] depending on rare earth ion

VM

		exp.	GGA+U				LDA	GGA
	U_{eff} [eV]	—	5	6	7	8	—	—
Fe$^{2.5+}$	B_{dip}	—	-3.00	-2.98	-2.95	-2.87	-2.13	-2.83
	B_{orb}	—	-3.11	-2.99	-2.84	-2.74	-5.47	-4.56
	$B_{contact}$	—	41.17	40.96	41.45	41.17	33.10	36.36
	B_{tot}	~ 30	35.06	34.98	35.67	35.56	25.50	28.98
	δ	~ 0.5	0.53	0.52	0.51	0.49	0.60	0.60
	eQV_{zz}	~ 0.1	0.12	0.13	0.13	0.13	0.19	-0.27

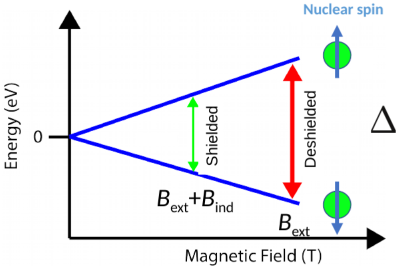
---

[1] C. Spiel, P. Blaha, and K. Schwarz, Phys. Rev. B **79**, 115123 (2009)

Non-magnetic systems: NMR spectroscopy

Non-magnetic systems:

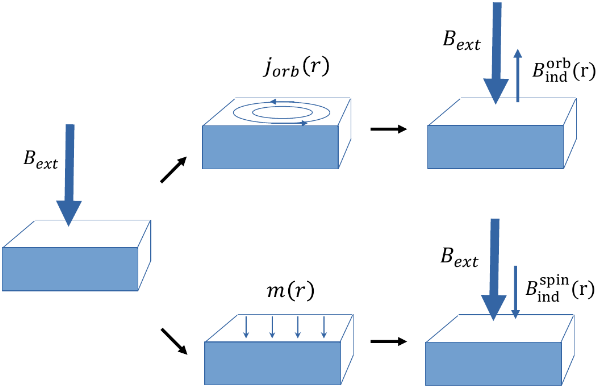
- No spontaneous magnetic field $B \Rightarrow$ no Zeeman effect
- An external magnetic field B_{ext} is applied
  $\Rightarrow$ B_{ind} is induced and depends on the environment of the nucleus
  $\Rightarrow$ Zeeman effect



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

Magnetic Shielding

NMR: Nuclear shielding and chemical shift



$$\underbrace{B^{\text{orb}}_{\text{ind}} = -\overline{\sigma}_{\text{orb}} B_{\text{ext}}}_{\substack{\text{In WIEN2k (SRC\_nmr, 2012):} \\ \text{1st-order perturbation theory}}}$$

$$\underbrace{B^{\text{spin}}_{\text{ind}} = -\overline{\sigma}_{\text{spin}} B_{\text{ext}}}_{\substack{\text{In WIEN2k (SRC\_orb, SRC\_lapwdm, } \sim \text{ 2005):} \\ \text{self-consistently, only in spheres}}}$$

- Total shielding: $\overline{\sigma} = \overline{\sigma}_{\text{orb}} + \overline{\sigma}_{\text{spin}}$
- $\overline{\sigma}_{\text{spin}}$ more important in metals
- Isotropic shielding: $\sigma = \frac{1}{3} \operatorname{Tr} \overline{\sigma}$
- Chemical shift (WRT a reference compound): $\delta = (\sigma_{\text{ref}} - \sigma) \cdot 10^6$ [ppm]

NMR: Calculation of $B_{\text{ind}}^{\text{orb}}$ and σ_{orb} (nmr module) [1]

1. Perturbed orbitals ψ_i (1st-order perturbation theory):

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

$$|\psi_i^{(1)}\rangle = \sum_{j=1}^{\infty} \frac{\langle\psi_j|H^{(1)}|\psi_i\rangle}{\epsilon_i - \epsilon_j} |\psi_j^{(0)}\rangle$$

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

Also the unoccupied orbitals need to be accurately calculated

2. Induced current:

$$\mathbf{j}_{\text{ind}}(\mathbf{r}) = \sum_{i=1}^{N} \langle\psi_i \left|\hat{\mathbf{j}}\right| \psi_i\rangle$$

3. Biot-Savart law:

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

4. $\overline{\sigma}_{\text{orb}}(\mathbf{R}) \sim \mathbf{B}_{\text{ind}}^{\text{orb}}(\mathbf{R})/\mathbf{B}_{\text{ext}}(\mathbf{R})$

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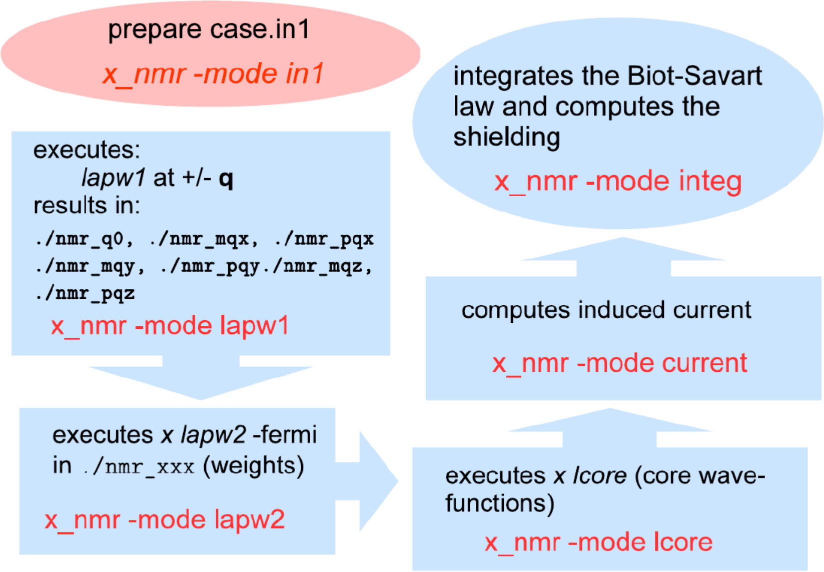
[1] R. Laskowski and P. Blaha, Phys. Rev. B **85**, 035132 (2012)

NMR: WIEN2k steps to calculate $B_{\text{ind}}^{\text{orb}}$ and σ_{orb}

1. Run usual SCF calculation:
   `run_lapw`
2. Prepare case.in1_nmr (LO basis functions added to basis set):
   `x_nmr_lapw -mode in1`
3. NMR calculation:
   `x_nmr_lapw`
4. The results are in:
   `case.outputnmr_integ`

NMR: Work flow of x_nmr_lapw



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

NMR: output (σ_{orb})

The results are in case.outputnmr_integ:

```
:NMRTOT001 ATOM: Te 1 NMR(total/ppm) Sigma-ISO= 1295.27 Sigma_xx= 1356.01 Sigma_yy= 1356.01 Sigma_zz= 1173.79
:NMRASY001 ATOM: Te 1 NMR(total/ppm) ANISO(delta-sigma)= -182.21 ASYM(eta) = 0.000 SPAN= 182.21 SKEW=-1.000
```

:NMRTOT → Isotropic value and principal components

:NMRASY →Anisotropy, asymmetry, span and skew

NMR: Calculation of $B_{\text{ind}}^{\text{spin}}$ and σ_{spin} (orb and lapwdm modules)

B_{ext} is applied $\Rightarrow$ $B_{\text{ind}}^{\text{spin}}$ is induced

$$\mathbf{B}_{\text{ind}}^{\text{spin}} = \mathbf{B}_{\text{hf}}^{\text{spin}} = \mathbf{B}_{\text{Fermi}} + \mathbf{B}_{\text{dip}}, \qquad \sigma_{\text{spin}} = \sigma_{\text{spin}}^{\text{Fermi}} + \sigma_{\text{spin}}^{\text{dip}}$$

- Fermi contact:
  1. Calculation in spin-polarized mode but with a zero moment:
     - `instgen_lapw -nm` (non-magnetic case.inst)
     - `init_lapw -b -sp -fermit 0.004 -numk XXX` (non-magnetic case.inst)
     - `runsp_c_lapw` (run SCF with a moment constraint to be zero)

     - `save_lapw` (save the calculation)

NMR: Calculation of $B_{\mathrm{ind}}^{\mathrm{spin}}$ and σ_{spin} (orb and lapwdm modules)

B_{ext} is applied $\Rightarrow$ $B_{\mathrm{ind}}^{\mathrm{spin}}$ is induced

$$\mathbf{B}_{\mathrm{ind}}^{\mathrm{spin}} = \mathbf{B}_{\mathrm{hf}}^{\mathrm{spin}} = \mathbf{B}_{\mathrm{Fermi}} + \mathbf{B}_{\mathrm{dip}}, \qquad \sigma_{\mathrm{spin}} = \sigma_{\mathrm{spin}}^{\mathrm{Fermi}} + \sigma_{\mathrm{spin}}^{\mathrm{dip}}$$

- Fermi contact:
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     - instgen_lapw -nm (non-magnetic case.inst)
     - init_lapw -b -sp -fermit 0.004 -numk XXX (non-magnetic case.inst)
     - runsp_c_lapw (run SCF with a moment constraint to be zero)
     - save_lapw (save the calculation)
  2. Copy input file specifying $B_{\mathrm{ext}} = 100$ T:
     - cp $WIENROOT/SRC_templates/case.vorbup(dn)_100T case.vorbup(dn)

NMR: Calculation of $B_{\text{ind}}^{\text{spin}}$ and σ_{spin} (orb and lapwdm modules)

B_{ext} is applied $\Rightarrow$ $B_{\text{ind}}^{\text{spin}}$ is induced

$$\mathbf{B}_{\text{ind}}^{\text{spin}} = \mathbf{B}_{\text{hf}}^{\text{spin}} = \mathbf{B}_{\text{Fermi}} + \mathbf{B}_{\text{dip}}, \qquad \sigma_{\text{spin}} = \sigma_{\text{spin}}^{\text{Fermi}} + \sigma_{\text{spin}}^{\text{dip}}$$

- Fermi contact:
  1. Calculation in spin-polarized mode but with a zero moment:
     - instgen_lapw -nm (non-magnetic case.inst)
     - init_lapw -b -sp -fermit 0.004 -numk XXX (non-magnetic case.inst)
     - runsp_c_lapw (run SCF with a moment constraint to be zero)
     - save_lapw (save the calculation)
  2. Copy input file specifying $B_{\text{ext}} = 100$ T:
     - cp $WIENROOT/SRC_templates/case.vorbup(dn)_100T case.vorbup(dn)
  3. SCF calculation with $B_{\text{ext}} = 100$ T:
     - runsp_lapw -orbc
     - $\mathbf{B}_{\text{Fermi}} =$:HFF
     - $\sigma_{\text{spin}}^{\text{Fermi}} = -1000\mathbf{B}_{\text{Fermi}}$ (in ppm and for $B_{\text{ext}} = 100$ T)

NMR: Calculation of $B_{\text{ind}}^{\text{spin}}$ and σ_{spin} (orb and lapwdm modules)

B_{ext} is applied $\Rightarrow$ $B_{\text{ind}}^{\text{spin}}$ is induced

$$\mathbf{B}_{\text{ind}}^{\text{spin}} = \mathbf{B}_{\text{hf}}^{\text{spin}} = \mathbf{B}_{\text{Fermi}} + \mathbf{B}_{\text{dip}}, \qquad \sigma_{\text{spin}} = \sigma_{\text{spin}}^{\text{Fermi}} + \sigma_{\text{spin}}^{\text{dip}}$$

- Fermi contact:
  1. Calculation in spin-polarized mode but with a zero moment:
     - `instgen_lapw -nm` (non-magnetic case.inst)
     - `init_lapw -b -sp -fermit 0.004 -numk XXX` (non-magnetic case.inst)
     - `runsp_c_lapw` (run SCF with a moment constraint to be zero)
     - `save_lapw` (save the calculation)
  2. Copy input file specifying $B_{\text{ext}} = 100$ T:
     - `cp $WIENROOT/SRC_templates/case.vorbup(dn)_100T case.vorbup(dn)`
  3. SCF calculation with $B_{\text{ext}} = 100$ T:
     - `runsp_lapw -orbc`
     - $\mathbf{B}_{\text{Fermi}} =$:HFF
     - $\sigma_{\text{spin}}^{\text{Fermi}} = -1000\mathbf{B}_{\text{Fermi}}$ (in ppm and for $B_{\text{ext}} = 100$ T)
- Spin dipole:
  1. After the steps above for $\mathbf{B}_{\text{Fermi}}$ are done, do:
     - `cp $WIENROOT/SRC_templates/case.indm case.indm`
     - Set (rindex,lsindex) to ”3 5” in case.indm
     - `x lapwdm -up/dn`
     - $\mathbf{B}_{\text{dip}} =$:XOP(up) $-$:XOP(dn)
     - $\sigma_{\text{spin}}^{\text{dip}} = -10000\mathbf{B}_{\text{dip}}$ (in ppm and for $B_{\text{ext}} = 100$ T)

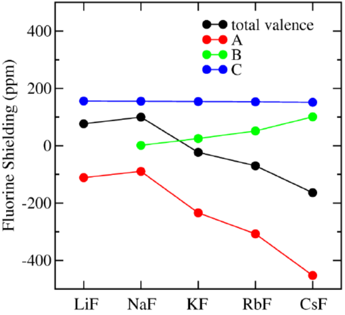
NMR: ^{19}F in alkali fluorides [1]

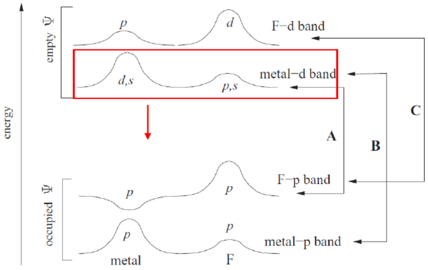
1st-order perturbation theory: $$|\psi_i^{(1)}\rangle = \sum_{j=1}^{\infty} \frac{\langle\psi_j|H^{(1)}|\psi_i\rangle}{\epsilon_i - \epsilon_j} |\psi_j^{(0)}\rangle$$

Most important contributions to the variation of σ through the series:

- Valence F-*p* – unoccupied metal–*d*: σ is negative and decreases
- Semicore metal–*p* – unoccupied metal–*d*: σ is positive and increases

Also important: covalent bonding and antibonding interaction between metal-*p* and F-*p*





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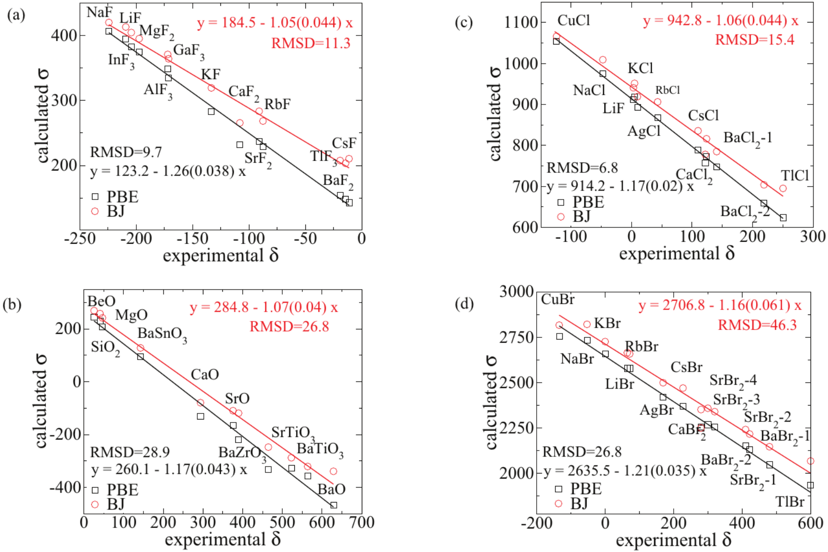
[1] R. Laskowski and P. Blaha, Phys. Rev. B **85**, 245117 (2012)

NMR: Effect of exchange-correlation [1]

Becke-Johnson leads to slope closer to 1, but larger RMSD



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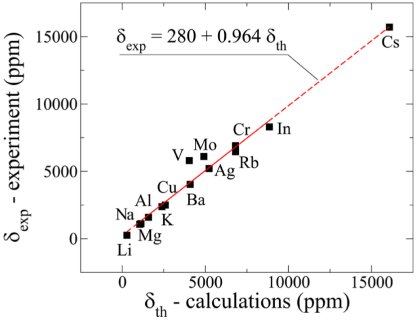
[1] R. Laskowski, P. Blaha, and F. Tran, Phys. Rev. B **87**, 195130 (2013)

NMR: Metals [1]

The orbital and spin contributions are both important

	reference	σ_o	σ_s
Li	Li_2O	81 (0)	−264 (0)
Na	NaBr	518 (0)	−1021 (−1)
K	KBr	1126 (8)	−2560 (−2)
Rb	RbCl	3031 (3)	−6826 (−1)
Cs	CsCl	5473 (4)	−16 177 (587)
Mg	$MgCl_2$	505 (−0)	−1078 (4)
Ba	$BaCl_2$	5730 (−28)	−4160 (−80)
Al	$AlPO_4$	519 (−4)	−1591 (11)
In	$In_2(SO_4)_3$	2807 (10)	−8012 (−43)
V	$NaVO_3$	−5988 (62)	488 (6)
Cr	Na_2CrO_4	−9847 (−46)	461 (0)
Mo	K_2MoO_4	−5795 (−44)	−27 (−30)
Cu	CuBr	−330 (−8)	−1568 (2)
Ag	$AgNO_3$	2219 (5)	−3670 (−1)



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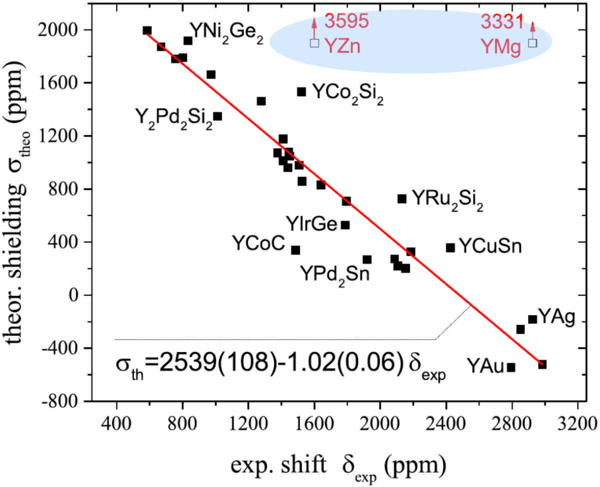
[1] R. Laskowski and P. Blaha, J. Phys. Chem. C **119**, 19390 (2015)

NMR: ^{89}Y in intermetallic compounds [1]



Possible reasons for the strong disagreement with experiment for YMg and YZn:

- Probably disorder
- Overestimation of magnetism by DFT?

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[1] L. Kalantari *et al.*, J. Phys. Chem. C **121**, 28454 (2017)

Brief summary

Nuclear hyperfine interactions

- Electric interactions:
  - Monopole interaction:
    - $\Longrightarrow$ Isomer shift
    - Related to electron density ρ at nucleus
  - Quadrupole interaction:
    - $\Longrightarrow$ Quadrupole splitting
    - Related to EFG at nucleus
    - Non-zero for nucleus with $I > \frac{1}{2}$ and non-cubic point groups
- Magnetic interactions:
  - Dipole interaction:
    - $\Longrightarrow$ Zeeman splitting
    - Related to hyperfine field
    - Magnetic systems
    - Non-magnetic systems in B_{ext} (NMR spectroscopy)