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Hyperfine interactions

Mössbauer, PAC and NMR Spectroscopy:
Quadrupole splittings, Isomer shifts, Hyperfine fields (~~NMR shifts~~)

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Definition of Hyperfine Interactions

hyperfine interactions

=

all aspects of nucleus-electron interactions which go beyond an electric point charge for a nucleus

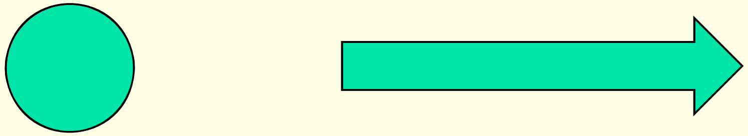
and is

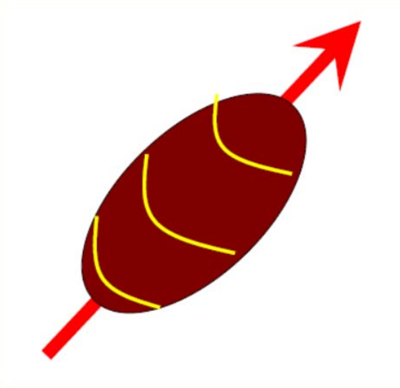
measured at the nucleus

(affects the nucleus)

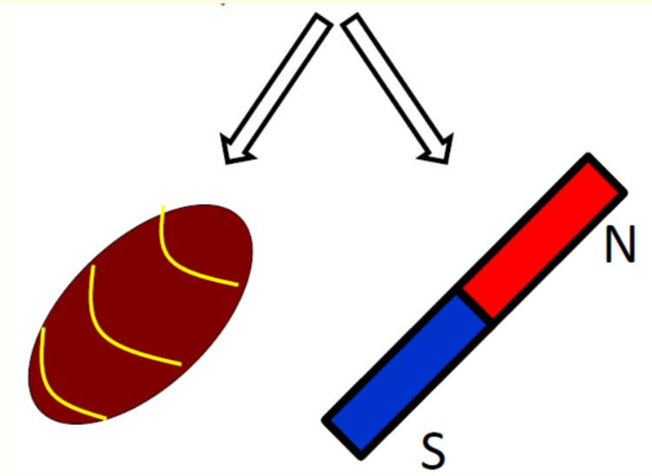
= = = > information about **nucleus** and the **electron (spin) density** around it

description of the nucleus:





electric point charge (Z/r)



nucleus with volume, shape and magnetic moment

How to measure hyperfine interactions ?

- **NMR**
- **NQR**
- **Mössbauer spectroscopy**
- **TDPAC**

Electric Hyperfine-Interaction

- between nuclear charge distribution (σ) and external potential

$$E = \int \sigma_n(x)\, V(x)\, dx$$

- Taylor-expansion at the nuclear position

$$E = V_0 Z \qquad (V_{00}(r)\ \sigma_n(x))$$

direction independent constant
(monopole interaction)

$$+ \sum_i \frac{\partial V(0)}{\partial x_i} \int \sigma(x)\, x_i\, dx$$

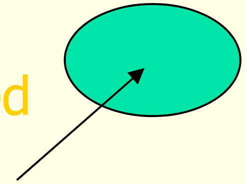
electric field x
nuclear dipol moment (=0)

$$+ \frac{1}{2} \sum_{ij} \frac{\partial^2 V(0)}{\partial x_i \partial x_j} \int\int \sigma(x)\, x_i\, x_j\, dx$$

electric fieldgradient x
nuclear quadrupol moment Q

$$+ \ldots$$

higher terms neglected



nucleus with charge Z, but not a sphere (I>1/2)

Mössbauer effect:

•***Recoil-free**, resonant **absorption** and **emission** of γ-rays by a nucleus.*
1958 by *Rudolf Mößbauer* (Nobelprice 1963)

•The **decay** of a **radioactive** nucleus produces a highly excited isotope of a neighboring element (Z-1).

•This isotope can get into its ground state by **emission** of γ-photons (recoil-free, otherwise E-loss; requires a "solid", no phonon excitation; the "**source**") !.

•The nucleus in the "**probe**" can **absorb** this photon (of eg. 14.4 keV), but the nuclear level splitting will be slightly modified by the chemical environment of the probe (only by ~ 10 neV !!!). Bring them in **resonance** with the **Doppler** effect (mm/s) !

•The most important isotopes are: ^{57}Fe, Sn, Sb, Te, I, W, Ir, Au, Eu and Gd.

Electric monopole interaction

- Mössbauer Isomer Shift δ:
  - *integral over nuclear radius of electron density x nuclear charge*
  - *nuclear radii are different for ground and excited state*

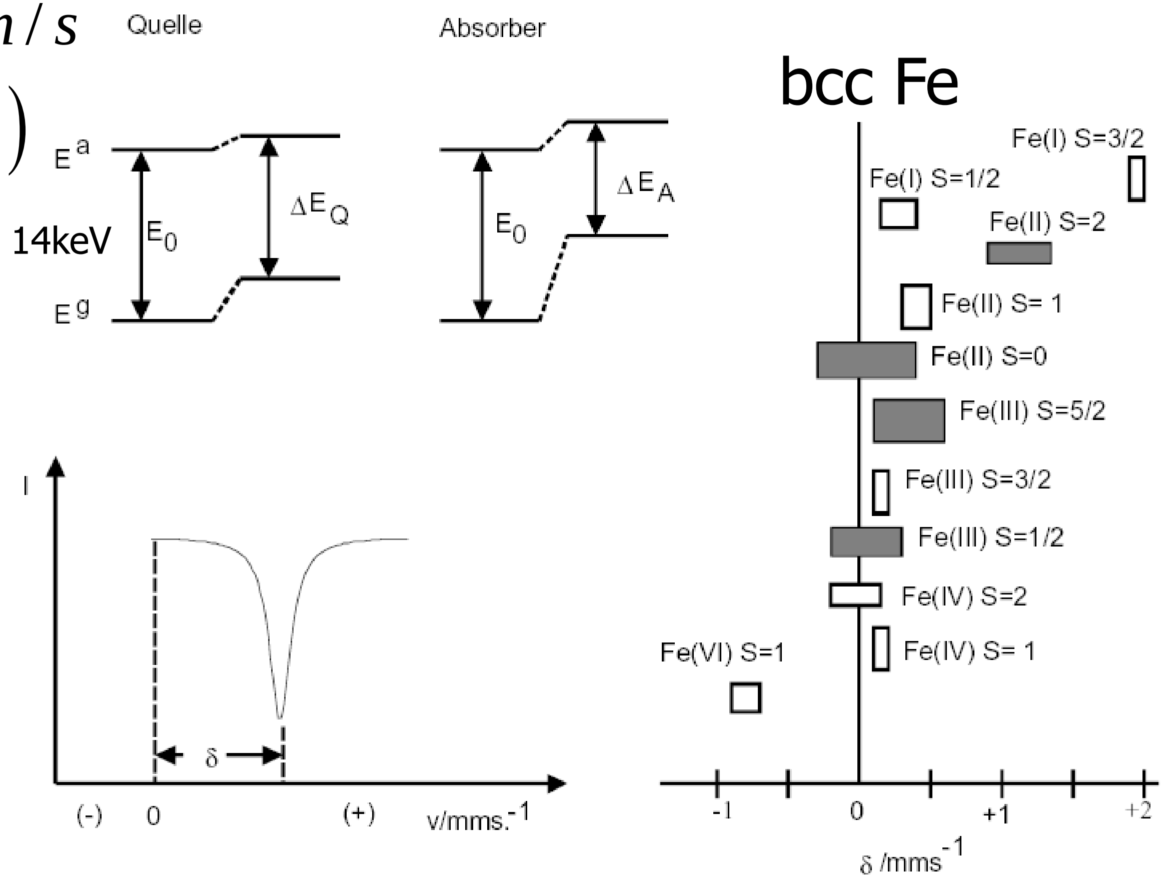
$$\delta = \Delta E_A - \Delta E_Q \sim neV \sim mm/s$$
$$= \left(\rho_A(0) - \rho_Q(0)\right)\left(R_A^2 - R_Q^2\right)$$
$$= \alpha\left(\rho_A(0) - \rho_Q(0)\right)$$

α (^{57}Fe)=-0.24 mm/s a_0^3

→ large $\rho_A(0)$→ neg. IS

Fe^{2+}, Fe^{3+},…

:RTOxxx = ρ(0)



Quadrupole interaction

$$E = \frac{1}{2} \sum_{ij} V_{ij}\, Q$$

Q(^{57}Fe)=0.16 barn

V_{ij}: traceless 3x3 tensor of **electric field gradient** EFG

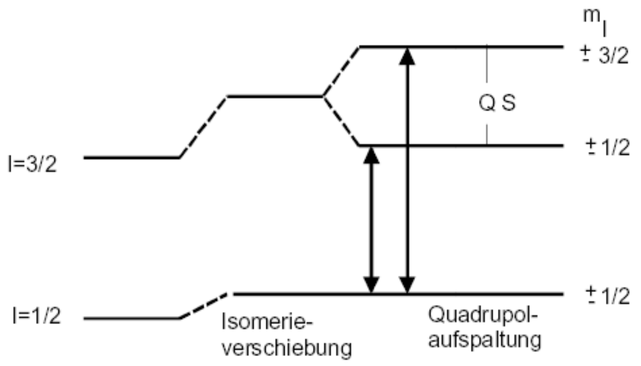
(2nd derivative of V(0)) $$V_{ij} = \frac{\partial^2 V(0)}{\partial x_i \partial x_j}$$

similarity transformation

$$\begin{vmatrix} V_{aa} & V_{ab} & V_{ac} \\ V_{ba} & V_{bb} & V_{bc} \\ V_{ca} & V_{cb} & V_{cc} \end{vmatrix} \Rightarrow \begin{vmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{vmatrix}$$

with $$V_{xx} + V_{yy} + V_{zz} = 0$$

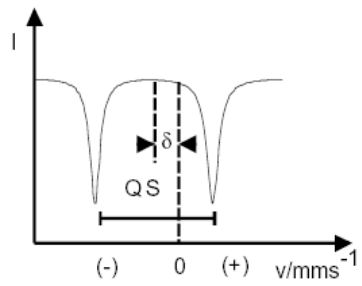
$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$$



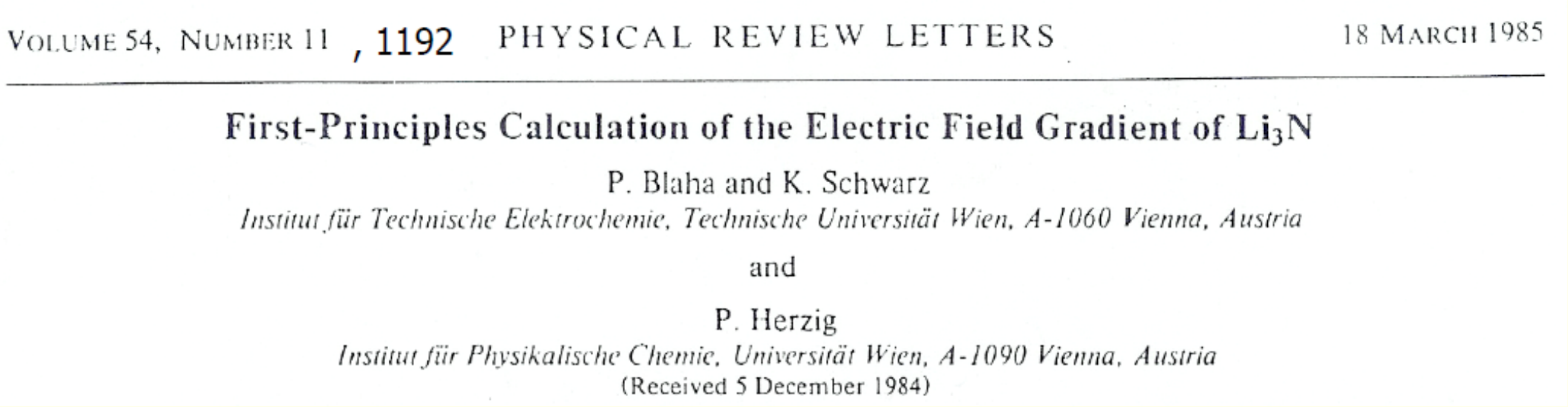
EFG characterized by principal component $\mathbf{V_{zz}}$
and asymmetry parameter η

$$\eta = \frac{/V_{yy}/-/V_{xx}/}{/V_{zz}/}$$

$$QS = \frac{1}{2} eQV_{zz} \sqrt{1 + \frac{\eta^2}{3}}$$



First-principles calculation of EFG



VOLUME 54, NUMBER 11 , 1192 PHYSICAL REVIEW LETTERS 18 MARCH 1985

First-Principles Calculation of the Electric Field Gradient of Li_3N

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(Received 5 December 1984)

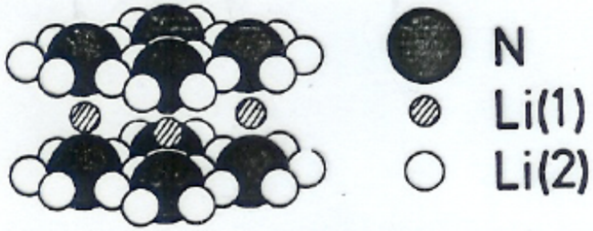


Fig. 1. Crystal structure of Li_3N with increased c dimension

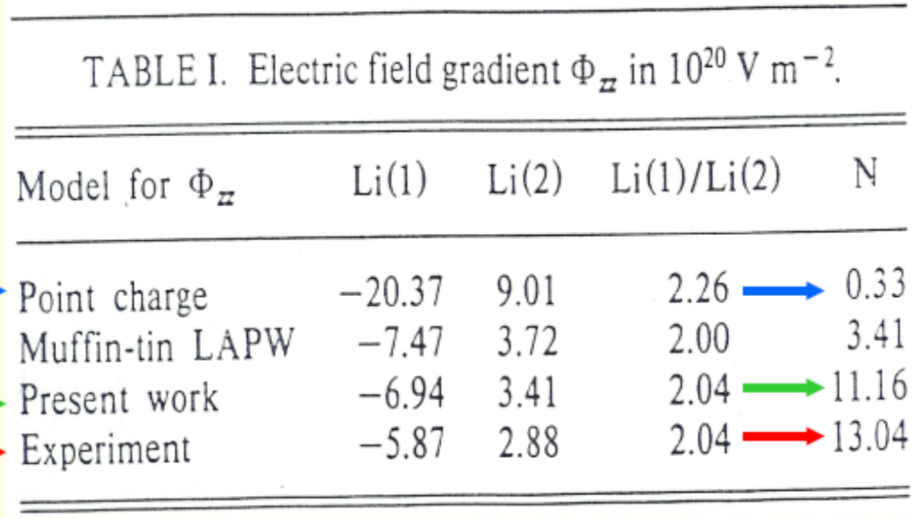
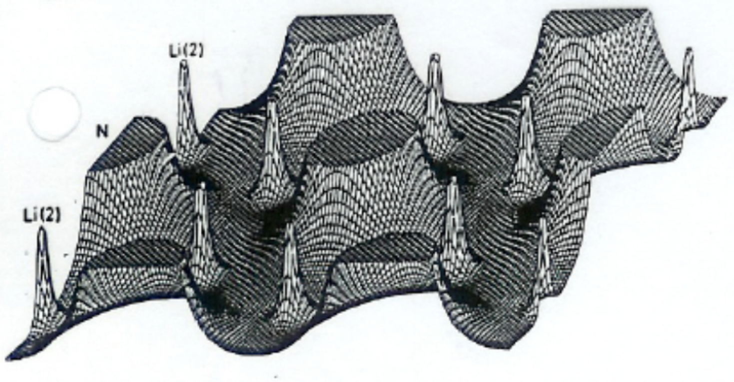


TABLE I. Electric field gradient Φ_{zz} in 10^{20} V m^{-2}.

Model for Φ_{zz}	Li(1)	Li(2)	Li(1)/Li(2)	N
Point charge	−20.37	9.01	2.26	0.33
Muffin-tin LAPW	−7.47	3.72	2.00	3.41
Present work	−6.94	3.41	2.04	11.16
Experiment	−5.87	2.88	2.04	13.04



Previous: point charge model and
Sternheimer factor to experimental value

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Determination of the Nuclear Quadrupole Moment of ^{57}Fe

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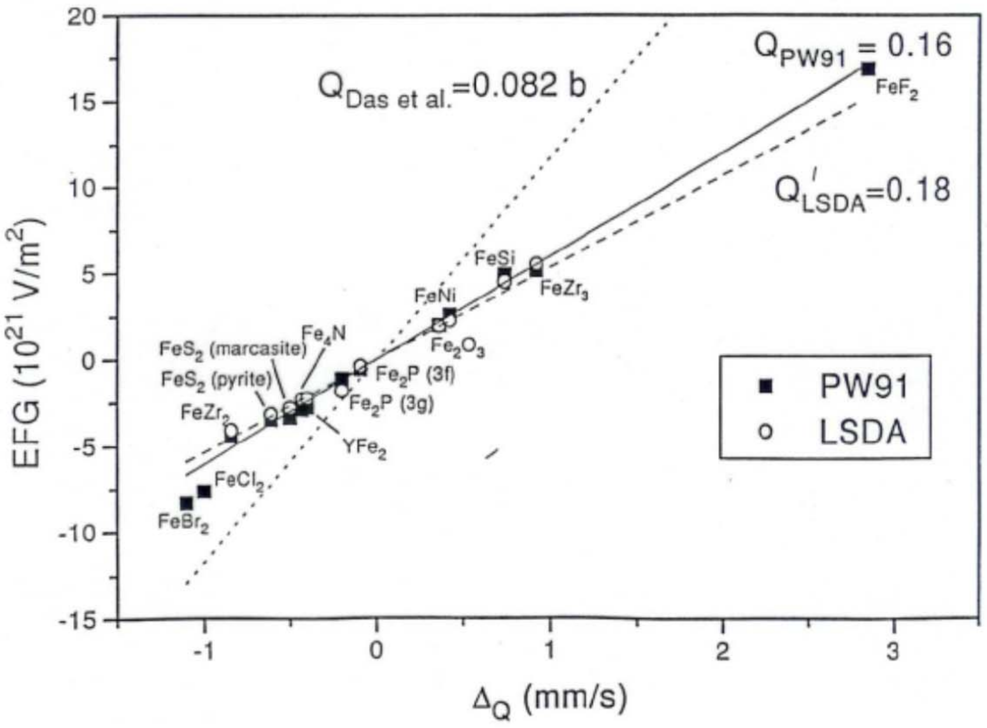
(Received 17 July 1995)

Theoretical and experimental Fe-EFG in Fe-compounds



$$E = \frac{1}{2}\sum_{ij} V_{ij}\, Q$$

- From the slope between
  - *the theoreical EFG and*
  - *experimental quadrupole splitting Δ_Q (mm/s)*
- the nuclear quadrupole moment Q of the most important Mössbauer nucleus is found to be about twice as large (Q=0.16 b) as so far in literature (Q=0.082 b)

theoretical EFG calculations

We write the charge density and the potential inside the atomic spheres in a lattice-harmonics expansion

$$\rho(r)=\sum_{LM}\rho_{LM}(\bar{r})Y_{LM}(\hat{r});\quad V_c(r)=\int\frac{\rho(r')}{r-r'}dr';\quad V_{ij}=\frac{\partial^2 V(0)}{\partial x_i\partial x_j}$$

spatial decomposition :

$$V_{zz}\propto\int\frac{\rho(r)Y_{20}}{r^3}d^3r\quad=\int_{sphere}\frac{\sum_{LM}\rho_{LM}(r)Y_{LM}Y_{20}}{r^3}d^3r+\int_{\text{interstital}}\frac{\rho(r)Y_{20}}{r^3}d^3r$$

$$V_{zz}\propto\quad=\int_{sphere}\frac{\rho_{20}(r)}{r^3}dr\quad+\quad\text{interstitial}$$

orbital decomposition :

$$\rho_{20}(r)=\int\sum_{k,n.l,l',m,m'}\phi_{lm}^{nk^*}\phi_{l'm'}^{nk}Y_{20}\;d\hat{r}\quad\Rightarrow\quad p-p;d-d;(s-d)\;contr.$$

$$V_{zz}=V_{zz}^{pp}+V_{zz}^{dd}+\ldots..+\quad\text{interstitial}$$

theoretical EFG calculations

$$V_{zz} = V_{zz}^{pp} + V_{zz}^{dd} + \ldots\ldots + \textit{interstitial}$$

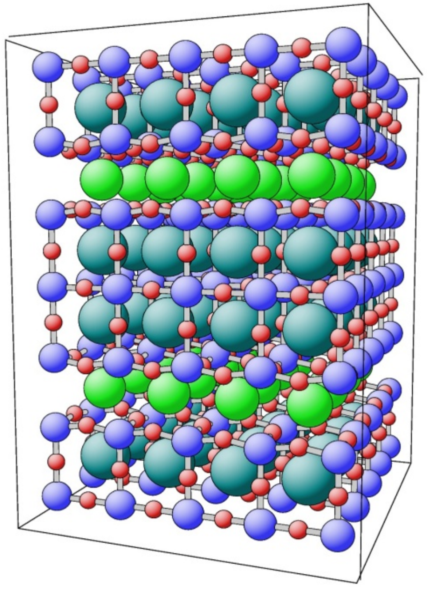
$$V_{zz}^{pp} \propto \left\langle \frac{1}{r^3} \right\rangle_p \left[\tfrac{1}{2}(p_x + p_y) - p_z \right]$$

$$V_{zz}^{dd} \propto \left\langle \frac{1}{r^3} \right\rangle_d \left[d_{xy} + d_{x^2-y^2} - \tfrac{1}{2}(d_{xz} + d_{yz}) - d_{z^2} \right]$$

- EFG is **proportial** to **differences of orbital occupations ,** e.g. between *p_x,p_y and p_z.*
- if these occupancies are the same by symmetry (cubic): $\mathbf{V_{zz}=0}$
- with “axial” (hexagonal, tetragonal) symmetry ($p_x=p_y$): η**=0**

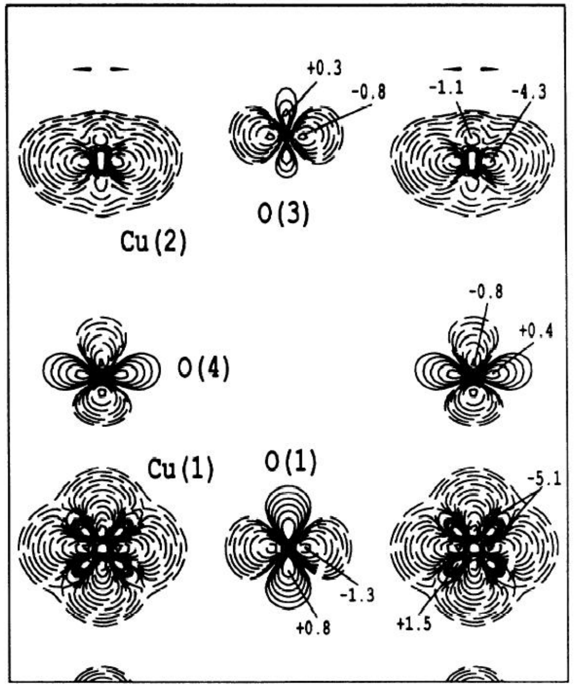
In the following various examples will be presented.

EFG (10^{21} V/m^2) in $YBa_2Cu_3O_7$



Site		Vxx	Vyy	Vzz	η
Y	theory	-0.9	2.9	-2.0	0.4
	exp.	-	-	-	-
Ba	theory	-8.7	-1.0	9.7	0.8
	exp.	8.4	0.3	8.7	0.9
Cu(1)	theory	-5.2	6.6	-1.5	0.6
	exp.	7.4	7.5	0.1	1.0
Cu(2)	theory	2.6	2.4	-5.0	0.0
	exp.	6.2	6.2	12.3	0.0
O(1)	theory	-5.7	17.9	-12.2	0.4
	exp.	6.1	17.3	12.1	0.3
O(2)	theory	12.3	-7.5	-4.8	0.2
	exp.	10.5	6.3	4.1	0.2
O(3)	theory	-7.5	12.5	-5.0	0.2
	exp.	6.3	10.2	3.9	0.2
O(4)	theory	-4.7	-7.1	11.8	0.2
	exp.	4.0	7.6	11.6	0.3

standard LDA calculations give good EFGs for all sites except Cu(2)

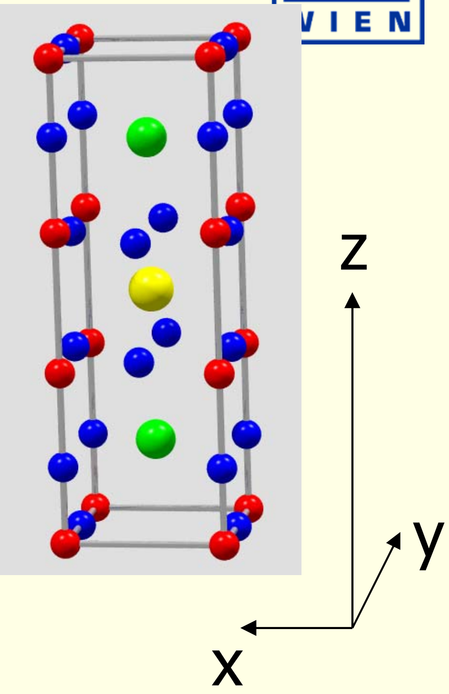


- K.Schwarz, C.Ambrosch-Draxl, P.Blaha, Phys.Rev. B42, 2051 (1990)
- D.J.Singh, K.Schwarz, K.Schwarz, Phys.Rev. B46, 5849 (1992)

EFG in $YBa_2Cu_3O_7$

- Interpretation of the EFG at the oxygen sites

	p_x	p_y	p_z	V_{aa}	V_{bb}	V_{cc}
O(1)	1.18	**0.91**	1.25	-6.1	**18.3**	-12.2
O(2)	**1.01**	1.21	1.18	**11.8**	-7.0	-4.8
O(3)	1.21	**1.00**	1.18	-7.0	**11.9**	-4.9
O(4)	1.18	1.19	**0.99**	-4.7	-7.0	**11.7**

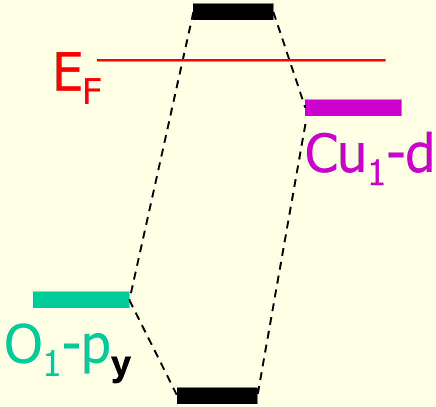


Asymmetry count

$$\Delta n_p = p_z - \frac{1}{2}(p_x + p_y)$$

EFG (p-contribution)

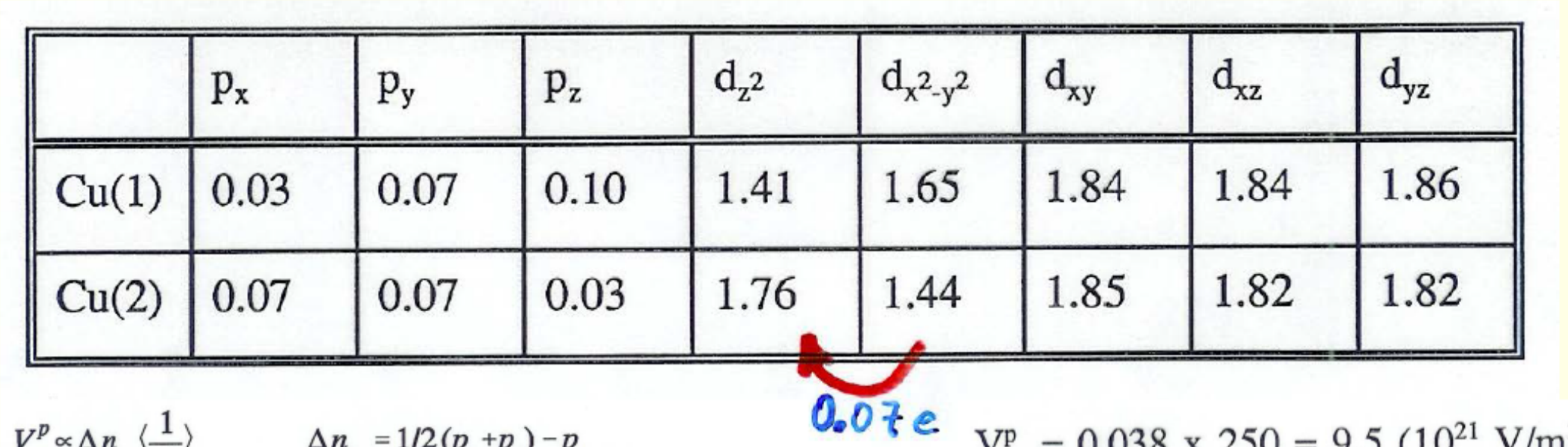
$$V_{zz}^{p} \propto \Delta n_p < \frac{1}{r^3} >_p$$



partly occupied

EFG is proportional to asymmetric charge distribution around given nucleus

Cu partial charges in $YBa_2Cu_3O_7$



	p_x	p_y	p_z	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
Cu(1)	0.03	0.07	0.10	1.41	1.65	1.84	1.84	1.86
Cu(2)	0.07	0.07	0.03	1.76	1.44	1.85	1.82	1.82

0.07 e

$$V_{zz}^p \propto \underline{\Delta n_{p_z}} \langle \frac{1}{r^3} \rangle_p \qquad \Delta n_{p_z} = 1/2\,(p_x + p_y) - p_z$$

$$V_{zz}^d \propto \underline{\Delta n_d} \langle \frac{1}{r^3} \rangle_d \qquad \Delta n_d = (d_{xy} + d_{x^2-y^2}) - 1/2\,(d_{xz} + d_{yz}) - d_{z^2}$$

$$\underline{V^p_{zz} = 0.038} \times 250 = 9.5\ (10^{21}\ V/m^2)$$

$$\underline{V^d_{zz} = -.288} \times 47 = -13.5$$

a transfer of 0.07 e into the d_{z^2} would increase the EFG from **-5.0** by

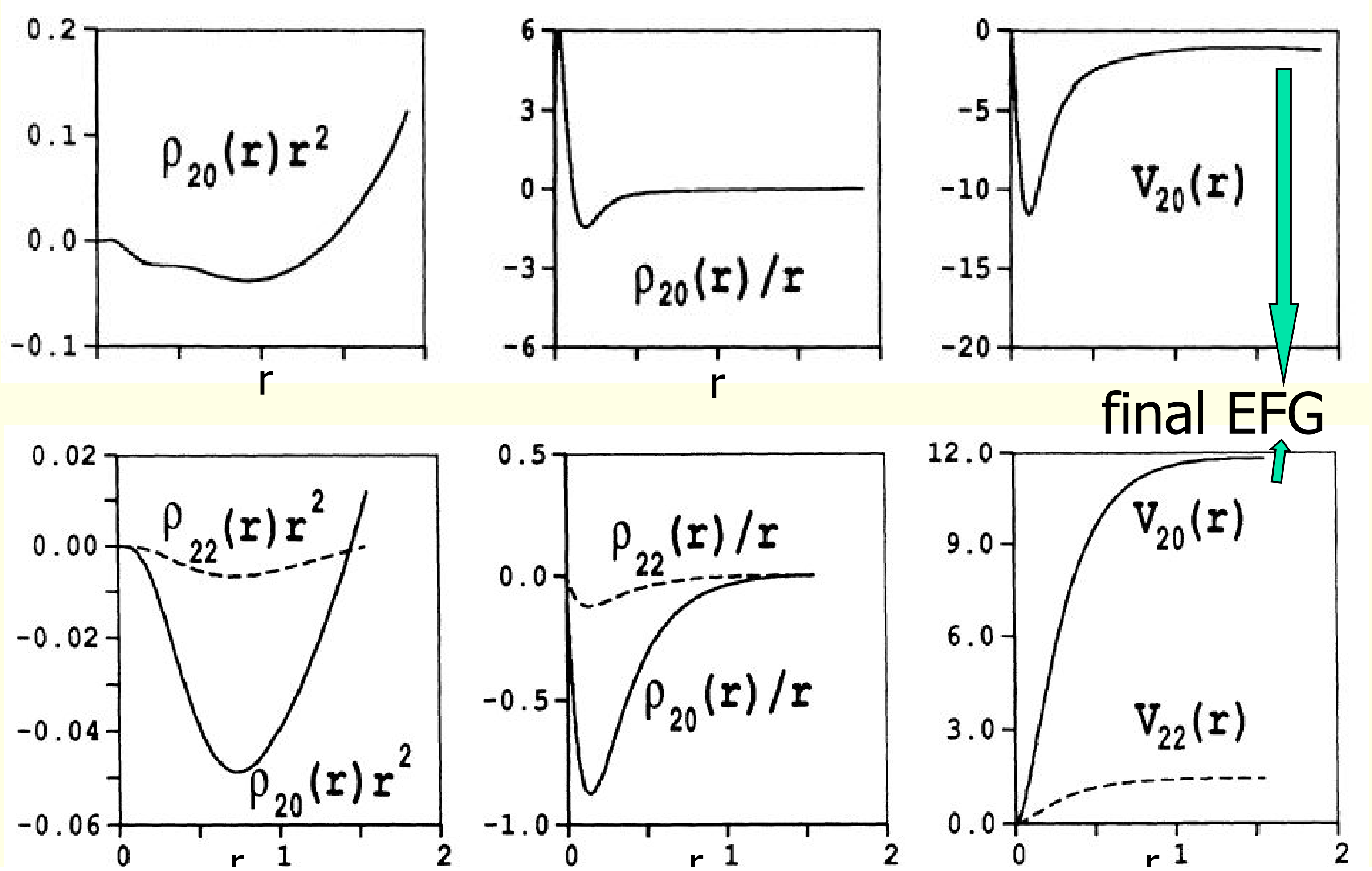
$$\underline{V^d_{zz} = -.14 \times 47} = \underline{-6.6}$$

bringing it to **-11.6** inclose to the Experimental value (**-12.3** 10^{21} V/m^2)

Cu(2) and O(4) EFG as function of r

- EFG is determined by the non-spherical charge density inside sphere

$$\rho(r)=\sum_{LM}\rho_{LM}(r)Y_{LM} \qquad V_{zz}\propto\int\frac{\rho(r)Y_{20}}{r^{3}}dr \;=\int\rho_{20}(r)\,r\,dr$$

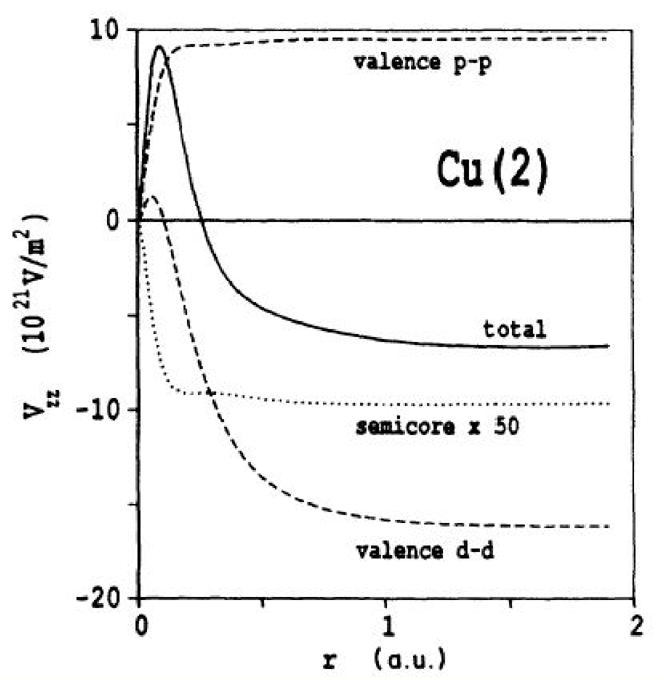


- Cu(2)
- O(4)

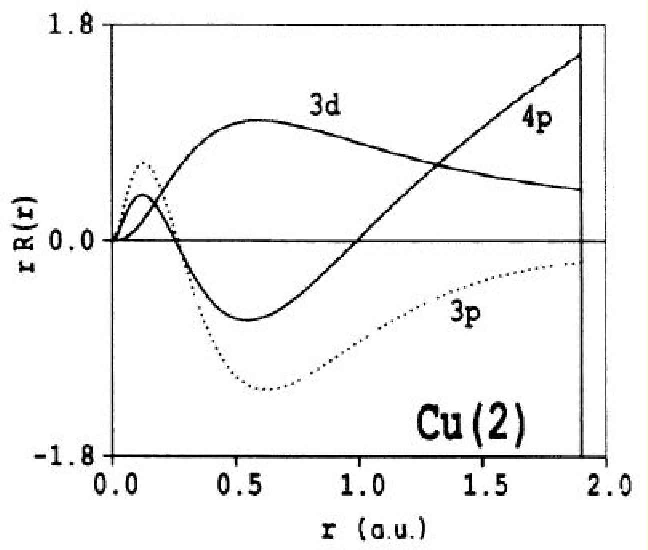
final EFG

EFG contributions:

- Depending on the atom, the main EFG-contributions come from anisotropies (in occupation or wave function)
  - *semicore p-states (eg. Ti 3p much more important than Cu 3p)*
  - *valence p-states (eg. O 2p or Cu 4p)*
  - *valence d-states (eg. TM 3d,4d,5d states; in metals "small")*
  - *valence f-states (only for "localized" 4f,5f systems)*



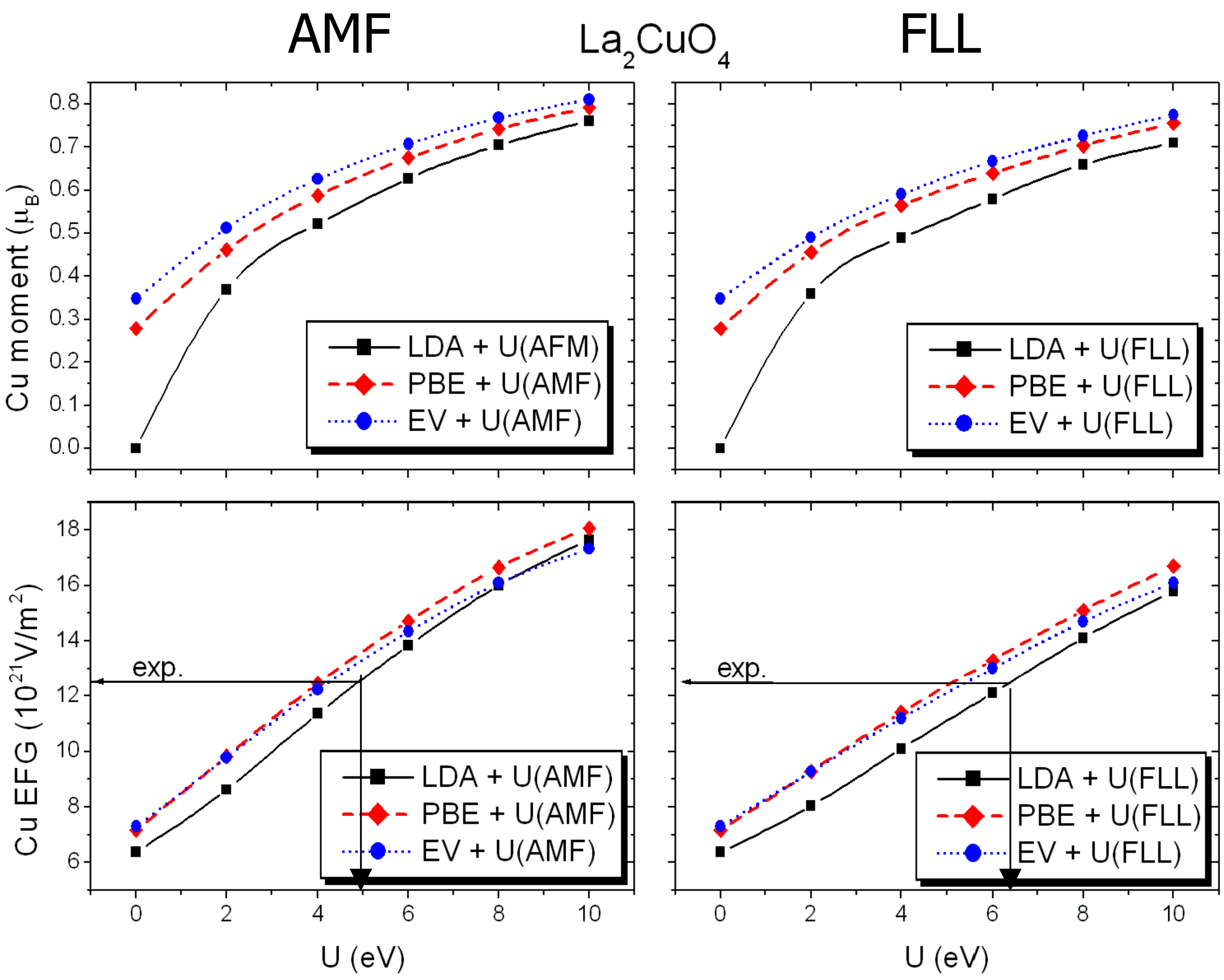
usually only contributions within the first node or within 1 bohr are important.



LDA problems in Cuprates

- Undoped Cuprates (La_2CuO_4, $YBa_2Cu_3O_6$) are nonmagnetic metals instead of antiferromagnetic insulators
- Both, doped and undoped cuprates have a “planar Cu” – EFG which is by a factor of 2-3 too small
- We need a method which giver a better description of correlated 3d electrons: can LDA+U fix these problems ??

Magn. moments and EFG in La$_2$CuO$_4$



LDA+U gives AF insulator with reasonable moment

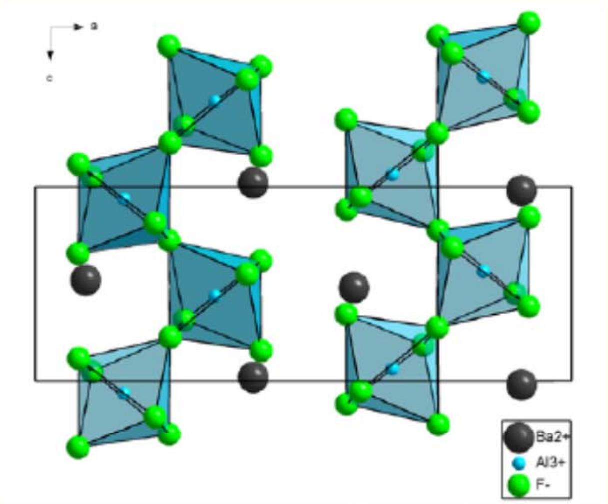
U of 5-6 eV gives exp. EFG

GGAs “mimic” a U of 1-2 eV
(EV-GGA more effective than PBE, but very bad E-tot !!)

EFGs in fluoroaluminates

10 different phases of known structures from CaF_2-AlF_3, BaF_2-AlF_3 binary systems and CaF_2-BaF_2-AlF_3 ternary system

Isolated chains of octahedra linked by corners

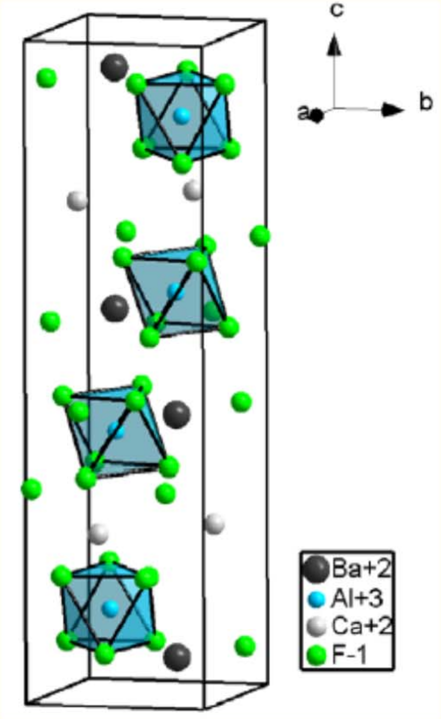


α-$BaAlF_5$

α-$CaAlF_5$, β-$CaAlF_5$,

β-BaAlF γ

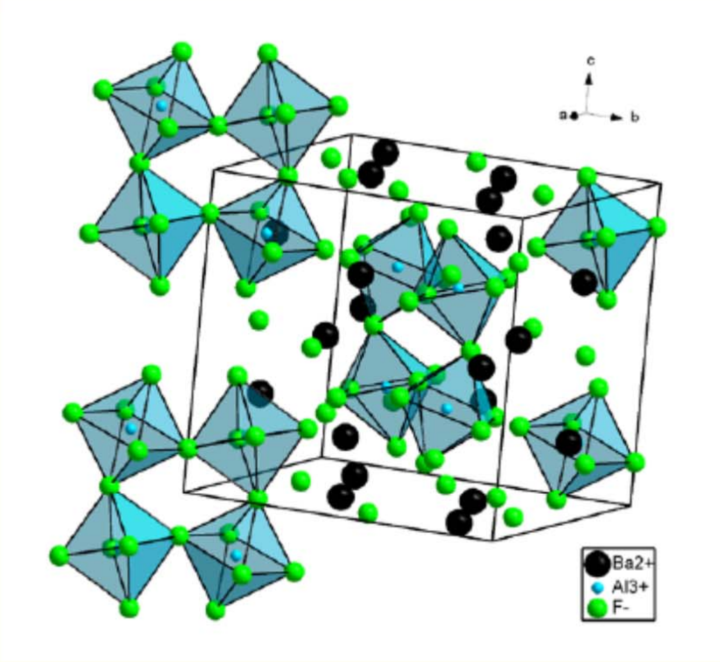
Isolated octahedra



α-$BaCaAlF_7$

Ca_2AlF_7, Ba_3AlF_9-Ib,

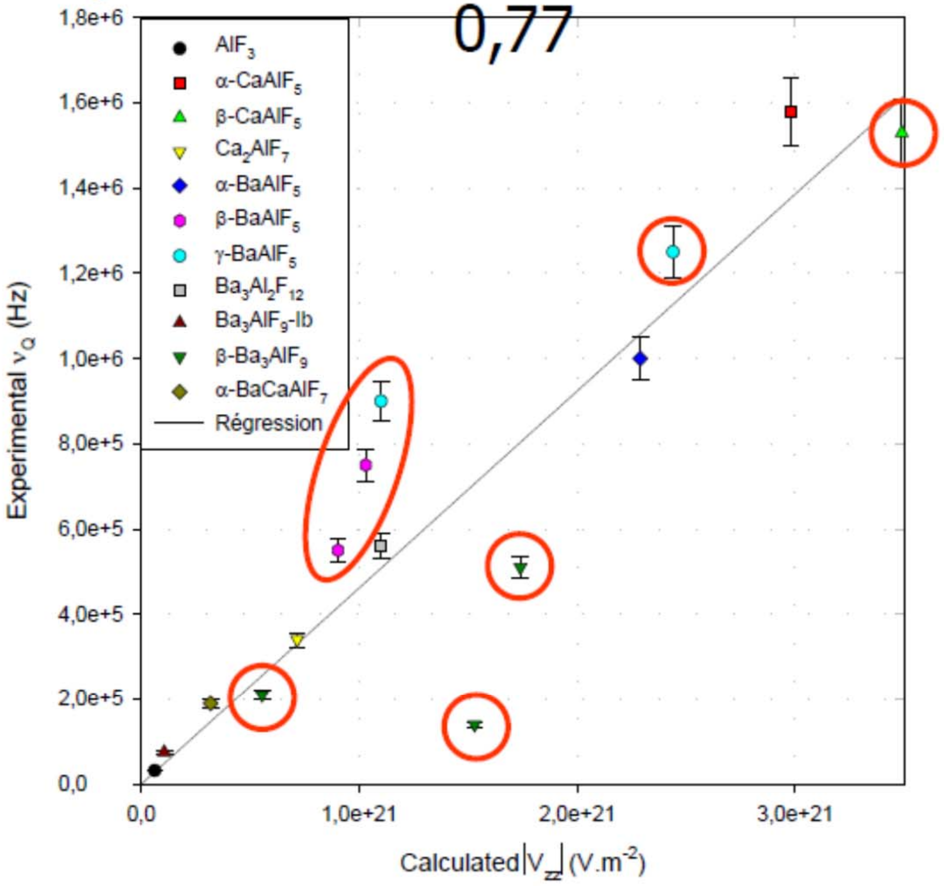
Rings formed by four octahedra sharing corners



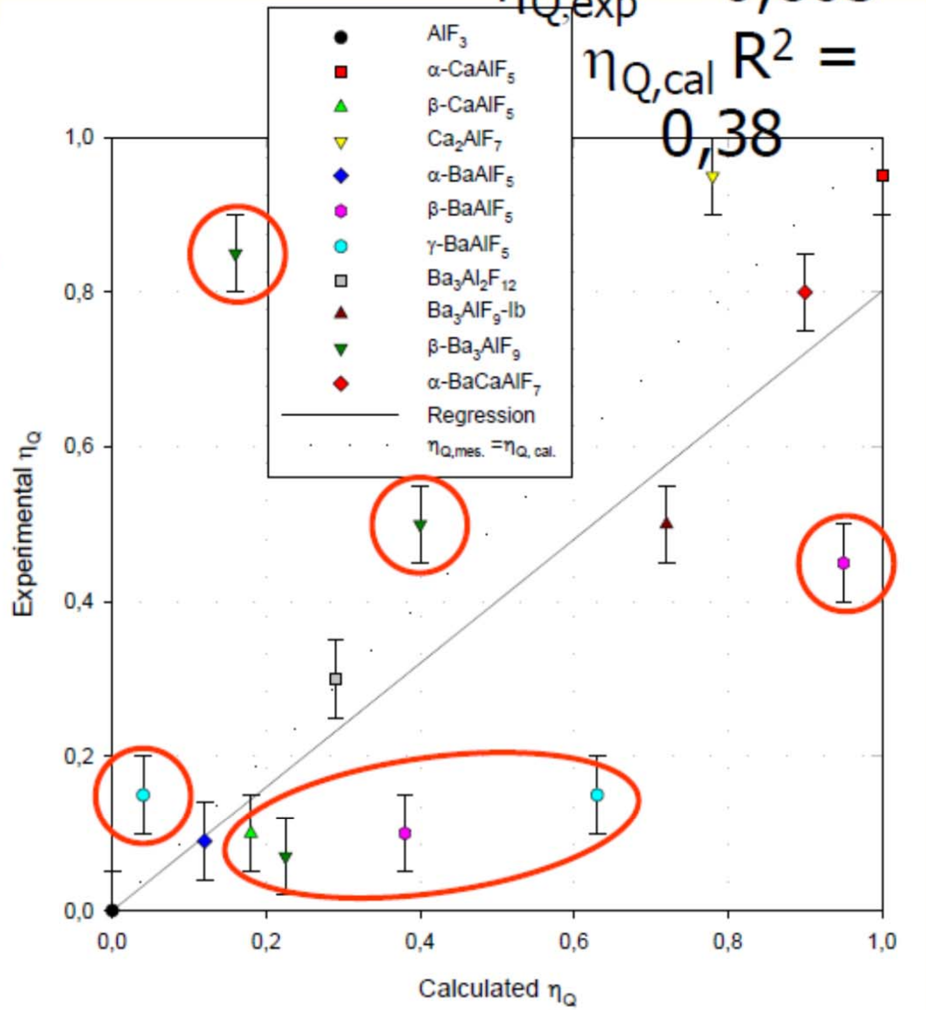
$Ba_3Al_2F_{12}$

ν_Q and η_Q calculations **using XRD data**

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

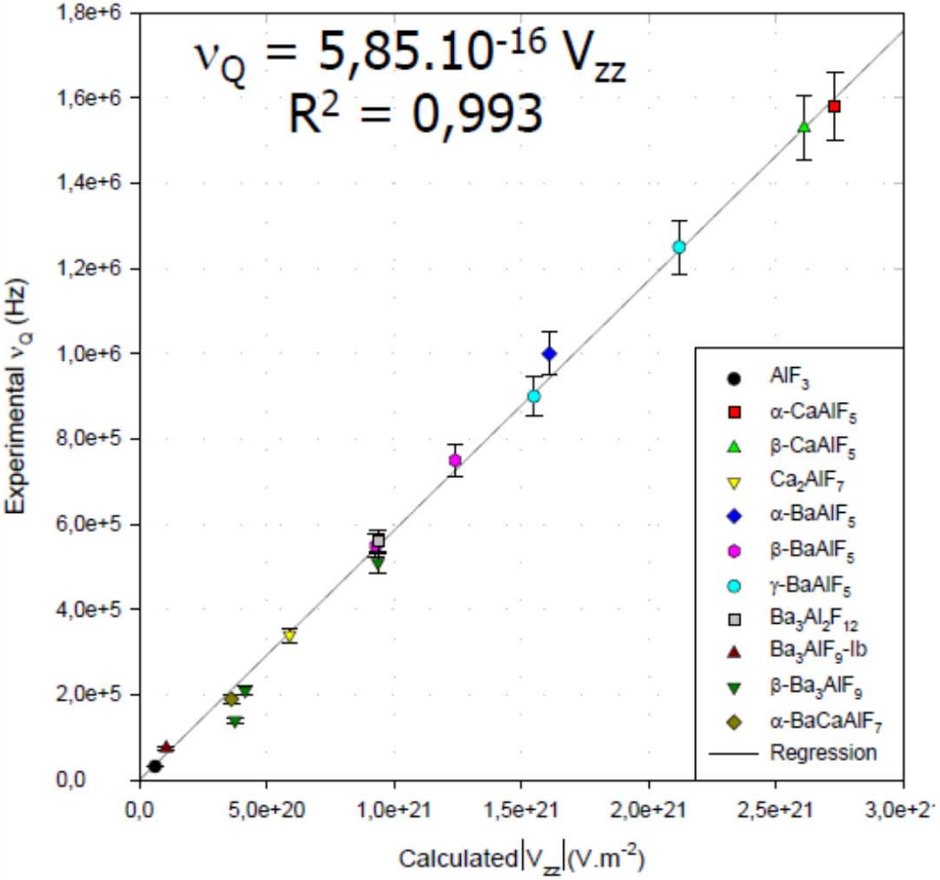


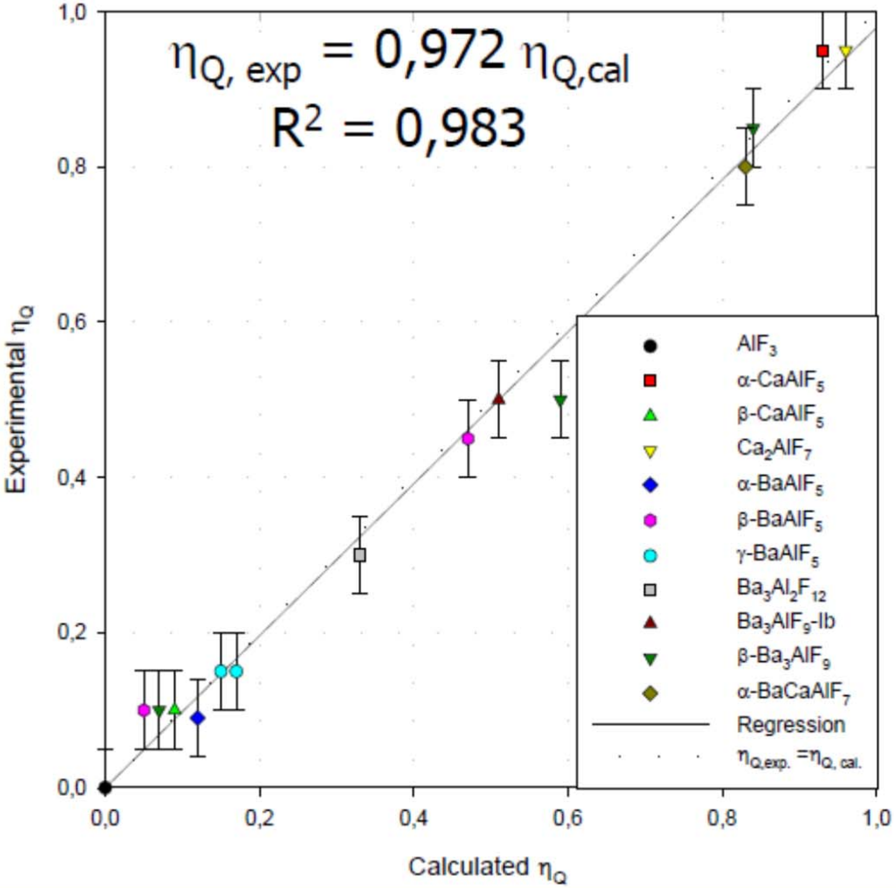
$\eta_{Q,exp} = 0{,}803\ \eta_{Q,cal}$ $R^2 = 0{,}38$



Important discrepancies when structures are used which were determined from X-ray powder diffraction data

ν_Q and η_Q after structure optimization

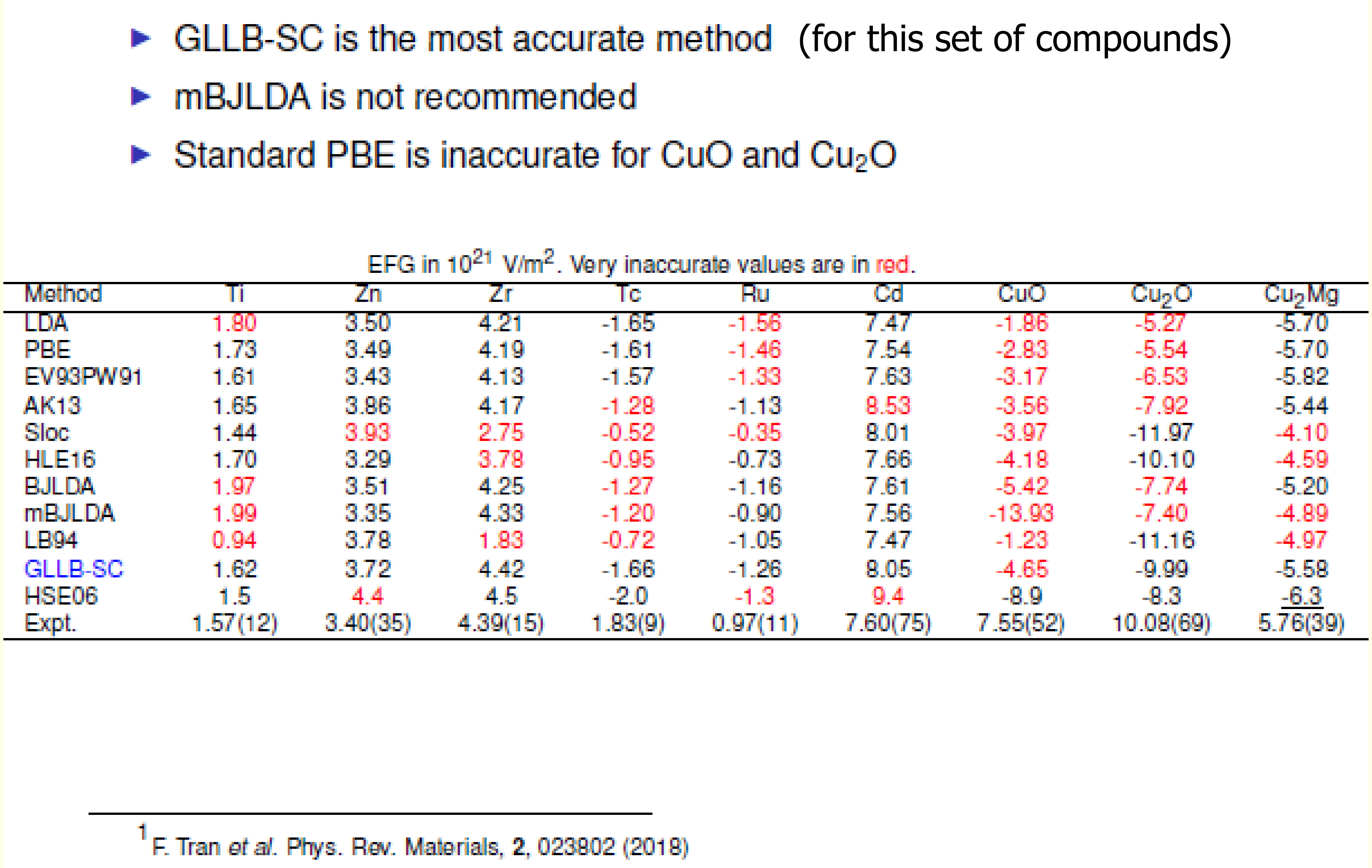




Very fine agreement between experimental and calculated values

M.Body, et al., *J.Phys.Chem. A 2007, 111, 11873*
(Univ. LeMans)

EFG: Sensitivity to the DFT-functional



- GLLB-SC is the most accurate method (for this set of compounds)
- 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)

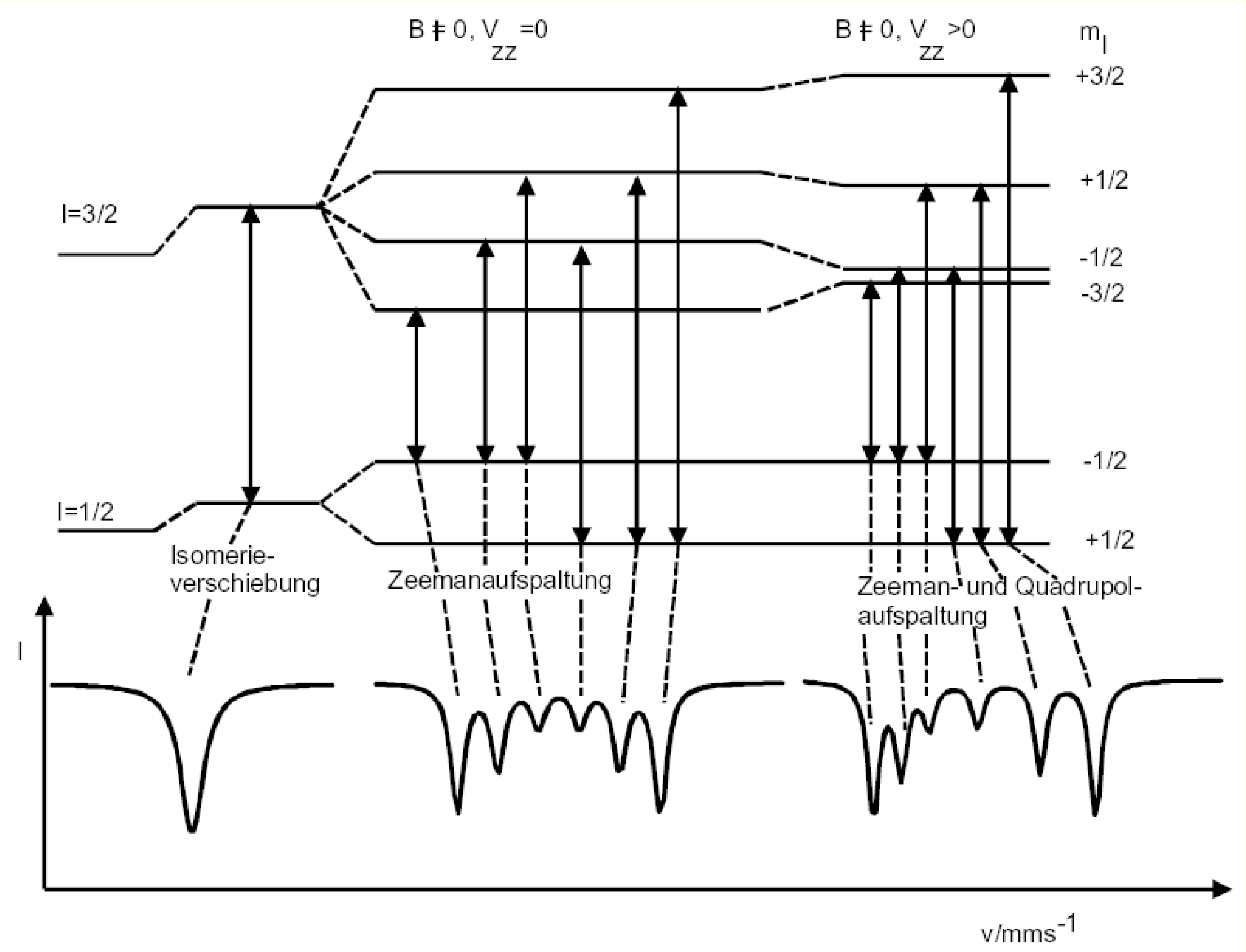
Magnetic hyperfine interaction

- Zeman - interaction between magnetic moment I of the nucleus and the external magnetic field B (at the nucleus, produced by the spin-polarized e^- in a FM)

$$B \propto \left(\rho_{\uparrow}(0) - \rho_{\downarrow}(0)\right)$$

B proportional to the **spindensity** at the nucleus

B often proportional to the magnetic moment of an atom in a solid.

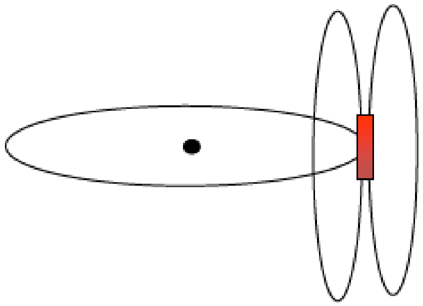


magnetic fields at nucleus:

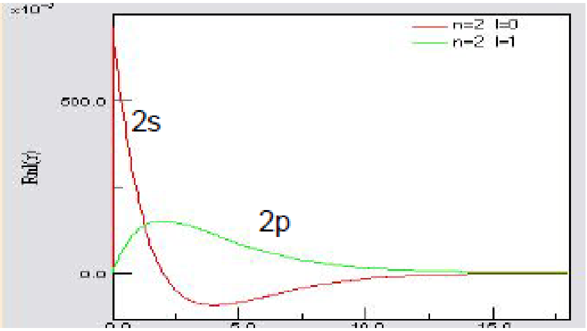
Source of magnetic fields at the nuclear site in an atom/solid

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

- B_{dip} = electron as bar magnet

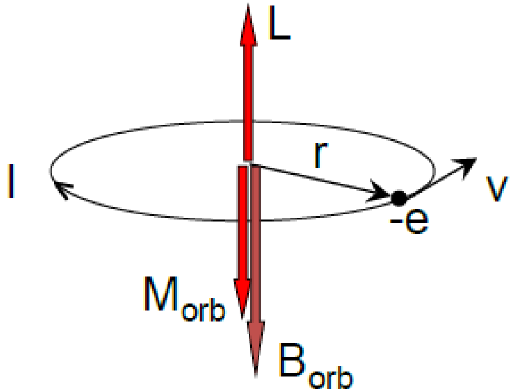


- B_{Fermi} = electron in nucleus

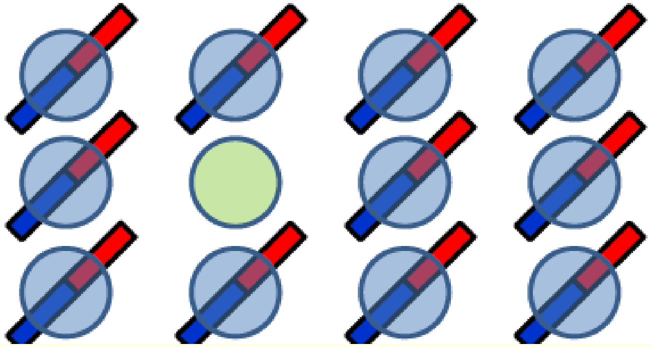


$$-\frac{2\mu_B\mu_0}{3}\left(|\psi_{e,\uparrow}(\mathbf{0})|^2 - |\psi_{e,\downarrow}(\mathbf{0})|^2\right)$$

- B_{orb} = electron as current loop



- B_{lat} = neighbours as bar magnets



Magnetic fields at the nucleus:

- Magnetic Hyperfine fields: $B_{tot}=B_{contact} + B_{orb} + B_{dip}$
  - $B_{contact} = 8\pi/3\ \mu_B [\rho_{up}(0) - \rho_{dn}(0)]$ … *spin-density at the nucleus*

$$\vec{B}_{orb} = 2\mu_B \langle\Phi|\frac{S(r)}{r^3}\vec{l}\,|\Phi\rangle$$ … *orbital-moment*

$$\vec{B}_{dip} = 2\mu_B \langle\Phi|\frac{S(r)}{r^3}\left[3(\vec{s}\,\vec{\hat{r}})\,\vec{\hat{r}} - \vec{s}\right]|\Phi\rangle$$ … *spin-moment*

S(r) is reciprocal of the relativistic mass enhancement $S(r) = \left[1 + \frac{\epsilon - V(r)}{2mc^2}\right]^{-1}$

How to do it in WIEN2k:

Magnetic hyperfine field

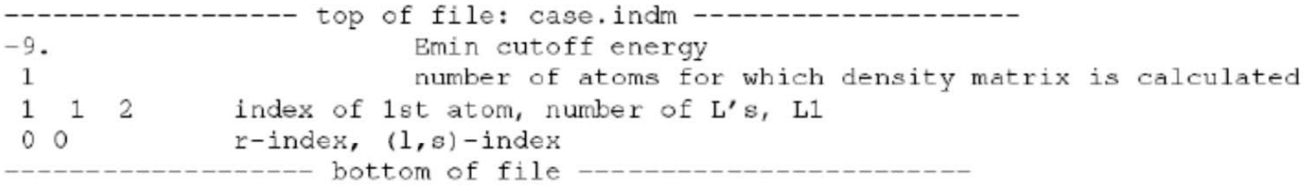
In regular scf file:

:HFFxxx (Fermi contact contribution)

After post-processing with LAPWDM :

- orbital hyperfine field (“3 3” in case.indmc)
- dipolar hyperfine field (“3 5” in case.indmc)

in case.scfdmup



```
------------------ top of file: case.indm --------------------
-9.                        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              r-index, (l,s)-index
------------------- bottom of file ------------------------
```

After post-processing with DIPAN :

- lattice contribution

in case.outputdipan

more info:
UG 7.8 (lapwdm)
UG 8.3 (dipan)

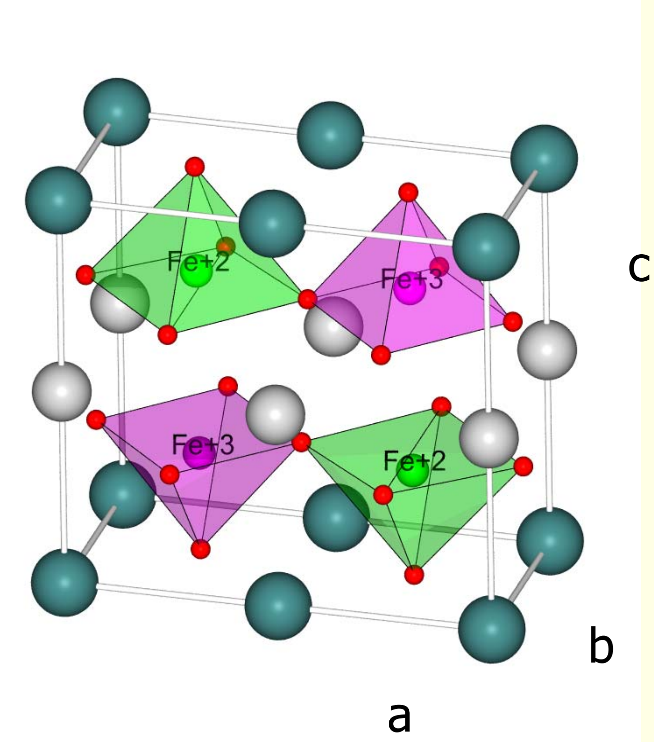
Verwey transition in $YBaFe_2O_5$

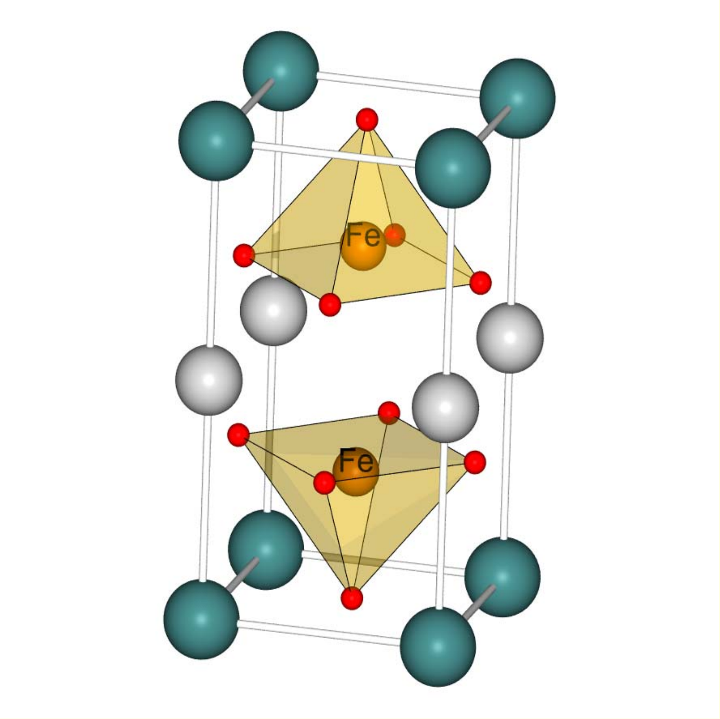
charge ordered (CO) phase:

Pmma a:b:c=2.09:1:1.96 (20K)

valence mixed (VM) phase:

Pmmm a:b:c=1.003:1:1.93 (340K)



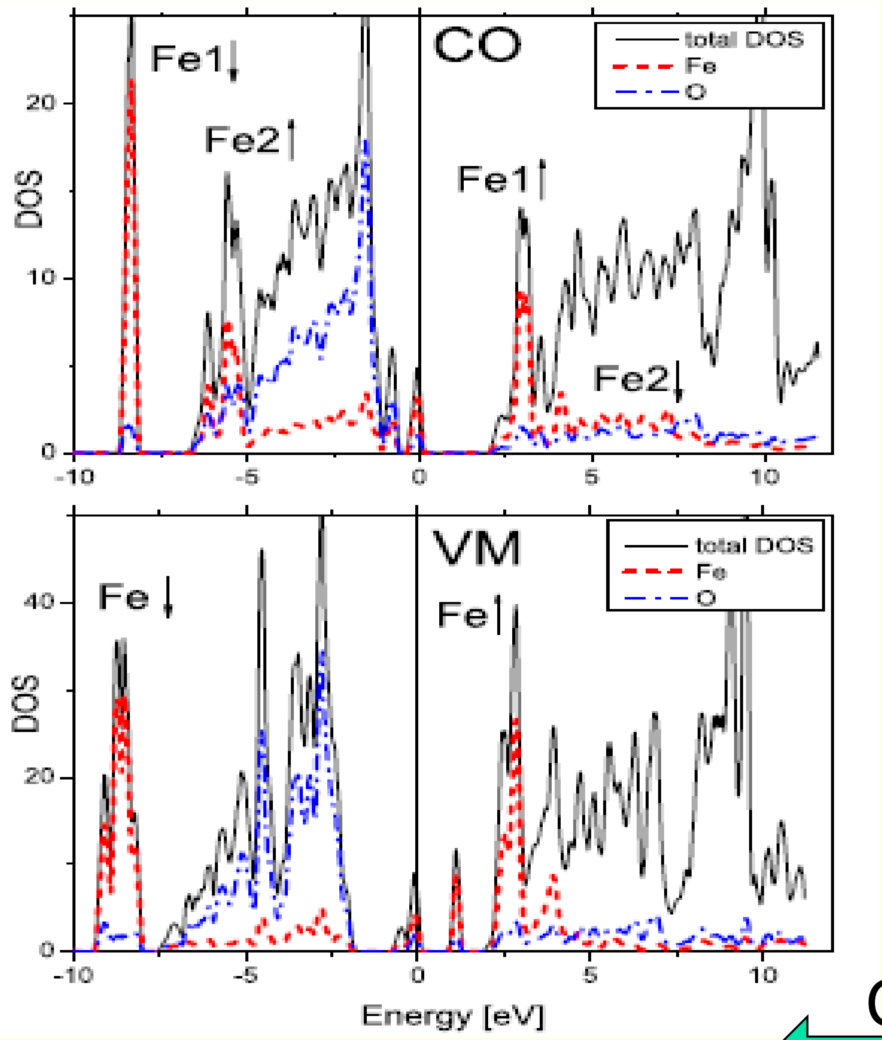


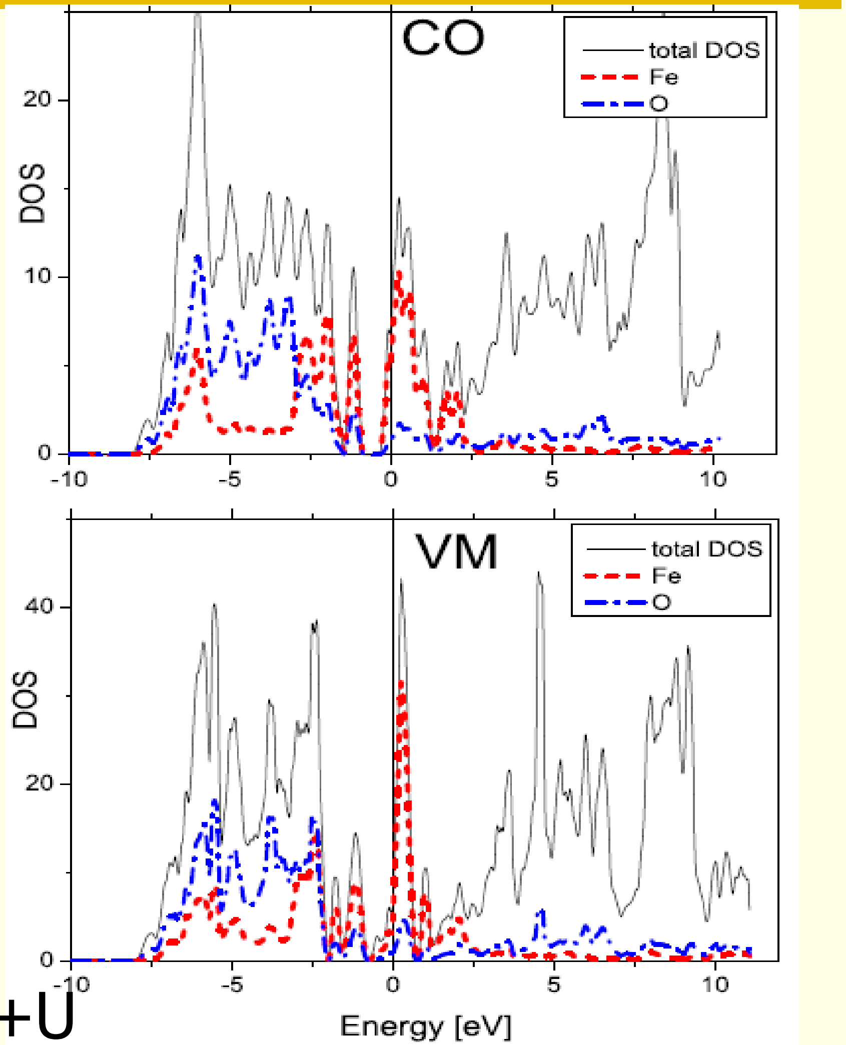
- Fe^{2+} and Fe^{3+} form chains along b
- contradicts Anderson charge-ordering conditions with minimal electrostatic repulsion (checkerboard like pattern)
- has to be compensated by orbital ordering and e^--lattice coupling

DOS: GGA+U vs. GGA

GGA+U GGA

single lower Hubbard-band in VM splits in CO with Fe^{3+} states lower than Fe^{2+}





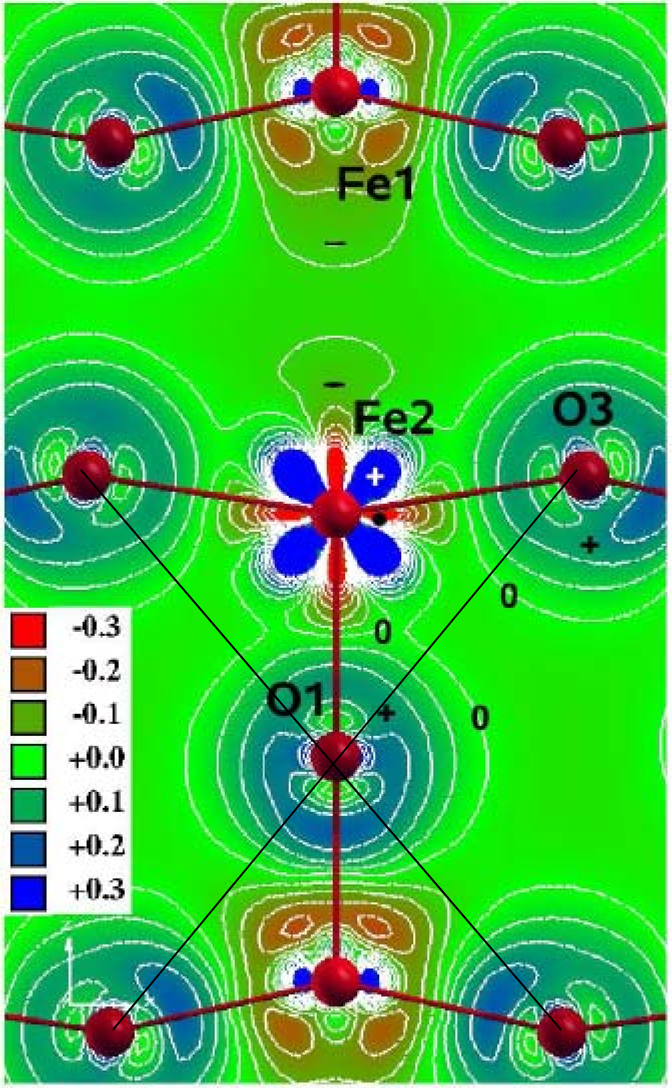
GGA+U

insulator

metal

Difference densities $\Delta\rho=\rho_{cryst}-\rho_{at}^{sup}$

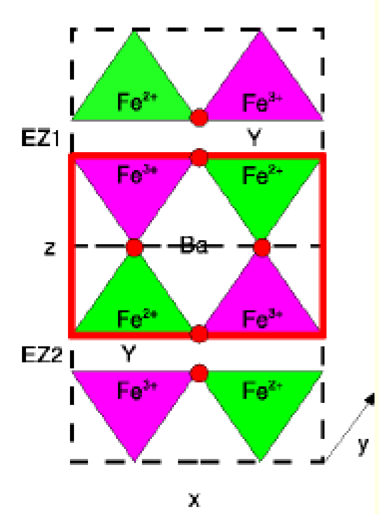
- CO phase

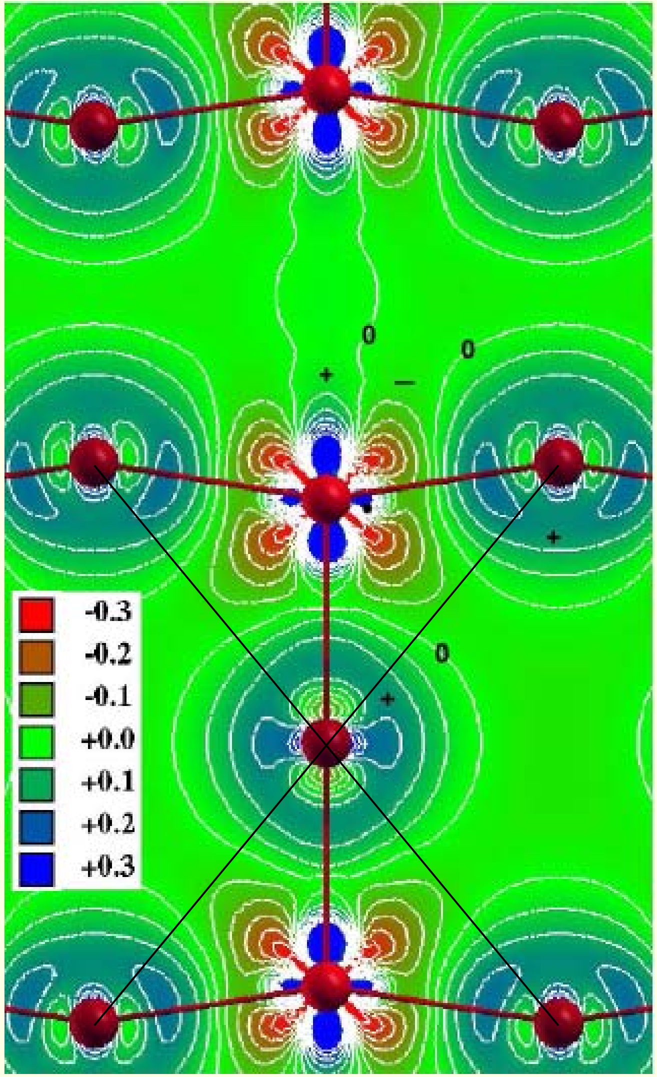


Fe^{2+}: d-xz
Fe^{3+}: d-x^2
O1 and O3: polarized
toward Fe^{3+}

VM phase

Fe: d-z^2 Fe-Fe interaction
O: symmetric





Mössbauer spectroscopy

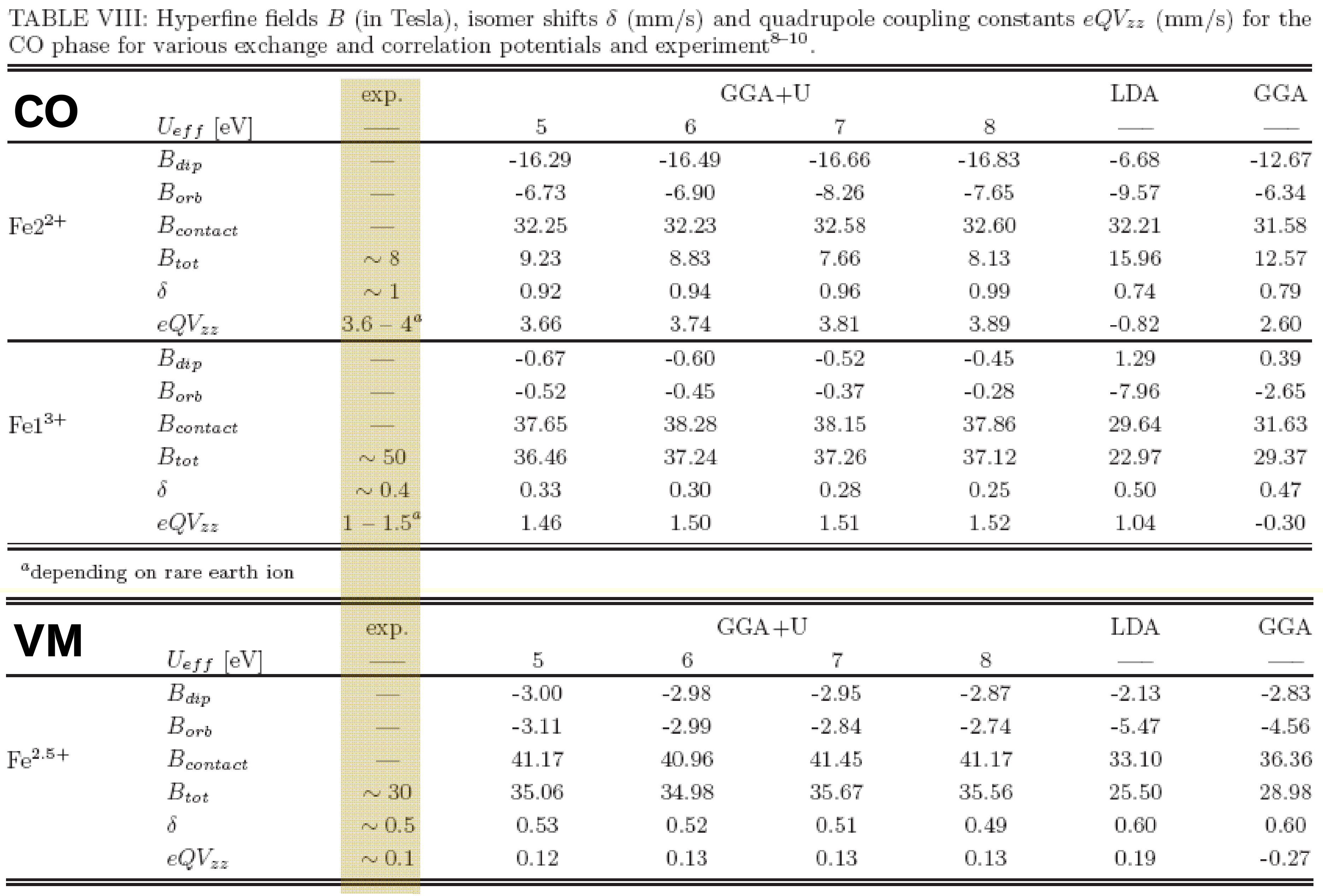


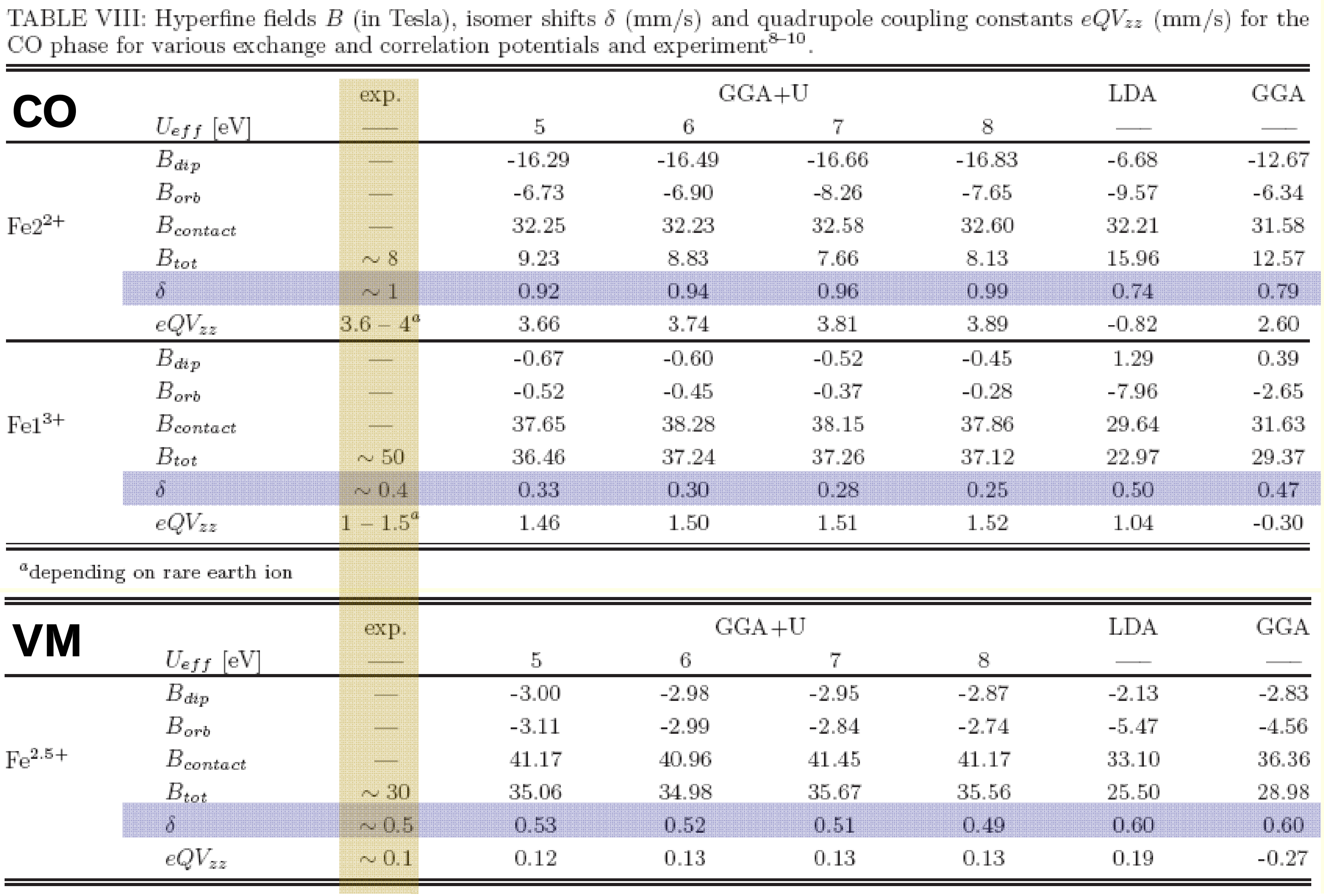
TABLE VIII: Hyperfine fields B (in Tesla), isomer shifts δ (mm/s) and quadrupole coupling constants eQV_{zz} (mm/s) for the CO phase for various exchange and correlation potentials and experiment[8–10].

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

Isomer shift: charge transfer too small in LDA/GGA



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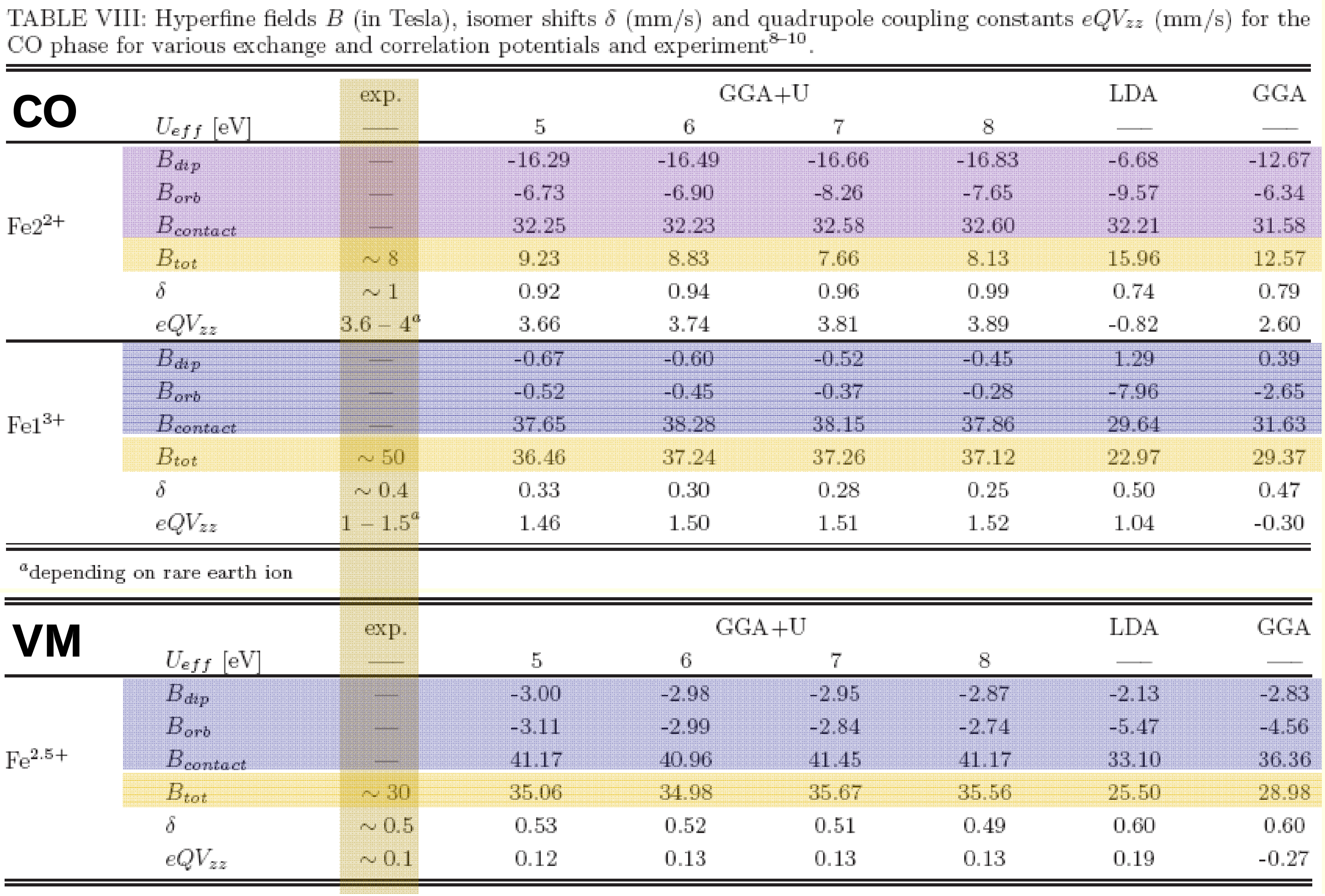
Hyperfine fields: Fe^{2+} has large B_{orb} and B_{dip}



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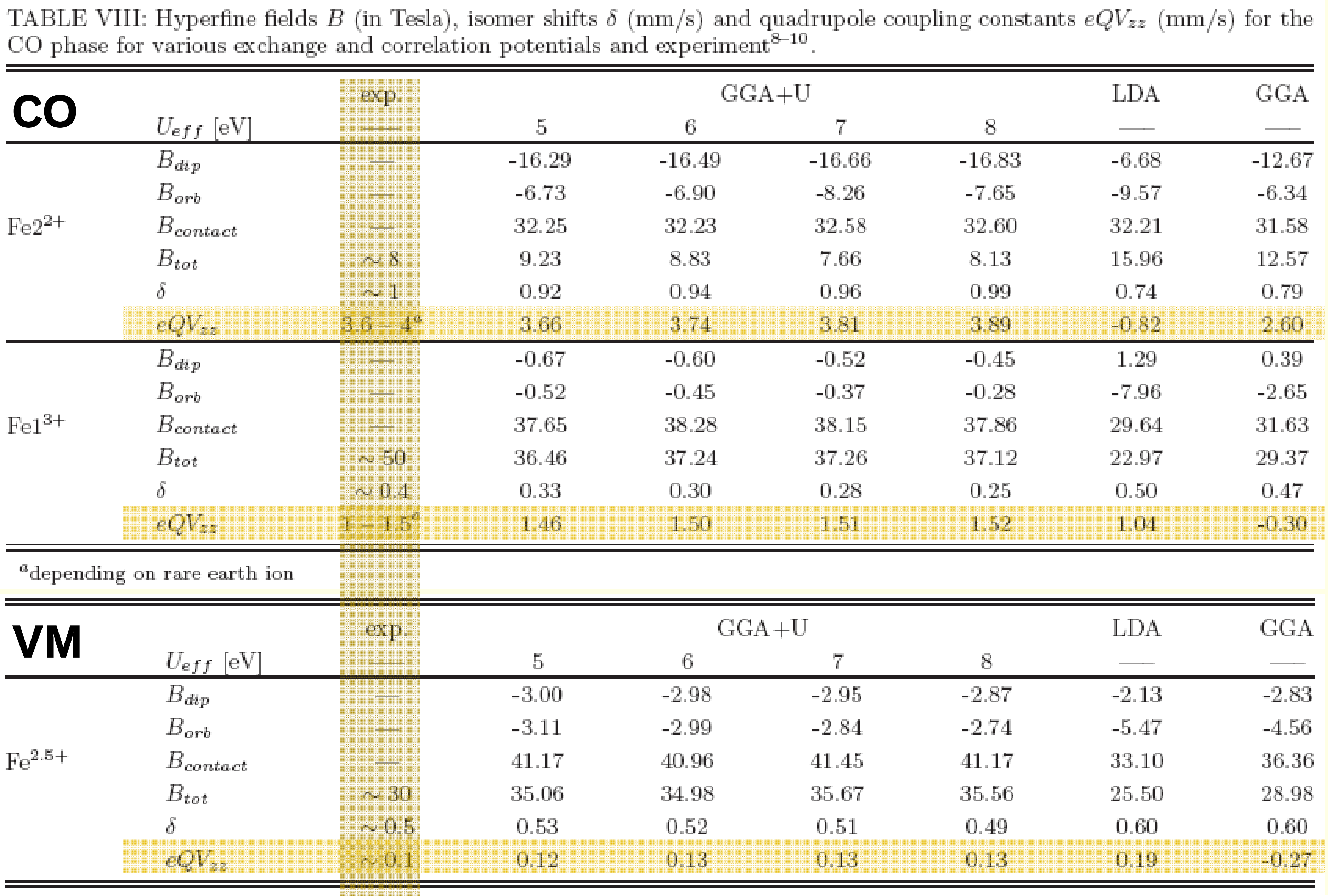
EFG: Fe^{2+} has too small anisotropy in LDA/GGA



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conversion of exp. data to EFGs

- Mössbauer:
  - $\Delta = \{e\,Q\,V_{zz}(1+\eta^2/3)^{1/2}\} / 2\,;$ $\Delta = (E_\gamma\,\Delta_\nu) / c$
  - $\Delta_\nu = (e\,Q\,c\,V_{zz}) / 2\,E_\gamma$ $Q(^{57}Fe)=0.16\ b;\ E_\gamma = 14410\ eV$
  - $Vzz\ [10^{21}\ V/m^2] = 6 * \Delta_\nu\ [mm/s]$
- NMR:
  - $\nu_Q = (3\,e\,Q\,V_{zz}) / \{2\,h\,I\,(2\,I - 1)\}$ I .. nuclear spin quantum n.
  - $V_{zz}\ [10^{21}\ V/m^2] = 4.135\ 10^{19}\ \nu_Q\,[MHz] / Q\ [b]$ $Q(^{49}Ti)=0.247\ b$