Hyperfine interactions

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Some slides were provided by Stefaan Cottenier (Gent)

Kohn-Sham equations

LDA, GGA

$$E = T_o[\rho] + \int V_{ext}\rho(\vec{r})d\vec{r} + \frac{1}{2}\int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}' - \vec{r}|}d\vec{r}d\vec{r}' + E_{xc}[\rho]$$

vary ρ

1-electron equations (Kohn Sham)

$$\{-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + V_C(\rho(\vec{r})) + V_{xc}(\rho(\vec{r}))\}\Phi_i(\vec{r}) = \varepsilon_i\Phi_i(\vec{r})$$

-Z/r

$$\int \frac{\rho(\vec{r})}{|\vec{r}' - \vec{r}|}d\vec{r}$$

$$\frac{\partial E_{xc}(\rho)}{\partial \rho}$$

$$\rho(\vec{r}) = \sum_{\varepsilon_i \le E_F} |\Phi_i|^2$$

$$E_{xc}^{LDA} \propto \int \rho(r)\ \varepsilon_{xc}^{hom.}[\rho(r)]\ dr$$

$$E_{xc}^{GGA} \propto \int \rho(r)\ F[\rho(r), \nabla\rho(r)]\ dr$$

LDA, **GGA** treats both, exchange and correlation effects, but approximately

New (better ?) functionals are still an active field of research

Kohn-Sham equations

$$E = T_o[\rho] + \int V_{ext}\rho(\vec{r})d\vec{r} + \frac{1}{2}\int \ldots$$

nuclear point charges interacting with electron charge distribution

vary ρ

1-electron equations (Kohn Sham)

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-Z/r

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LDA, **GGA**: treats both, exchange and correlation effects, but approximately

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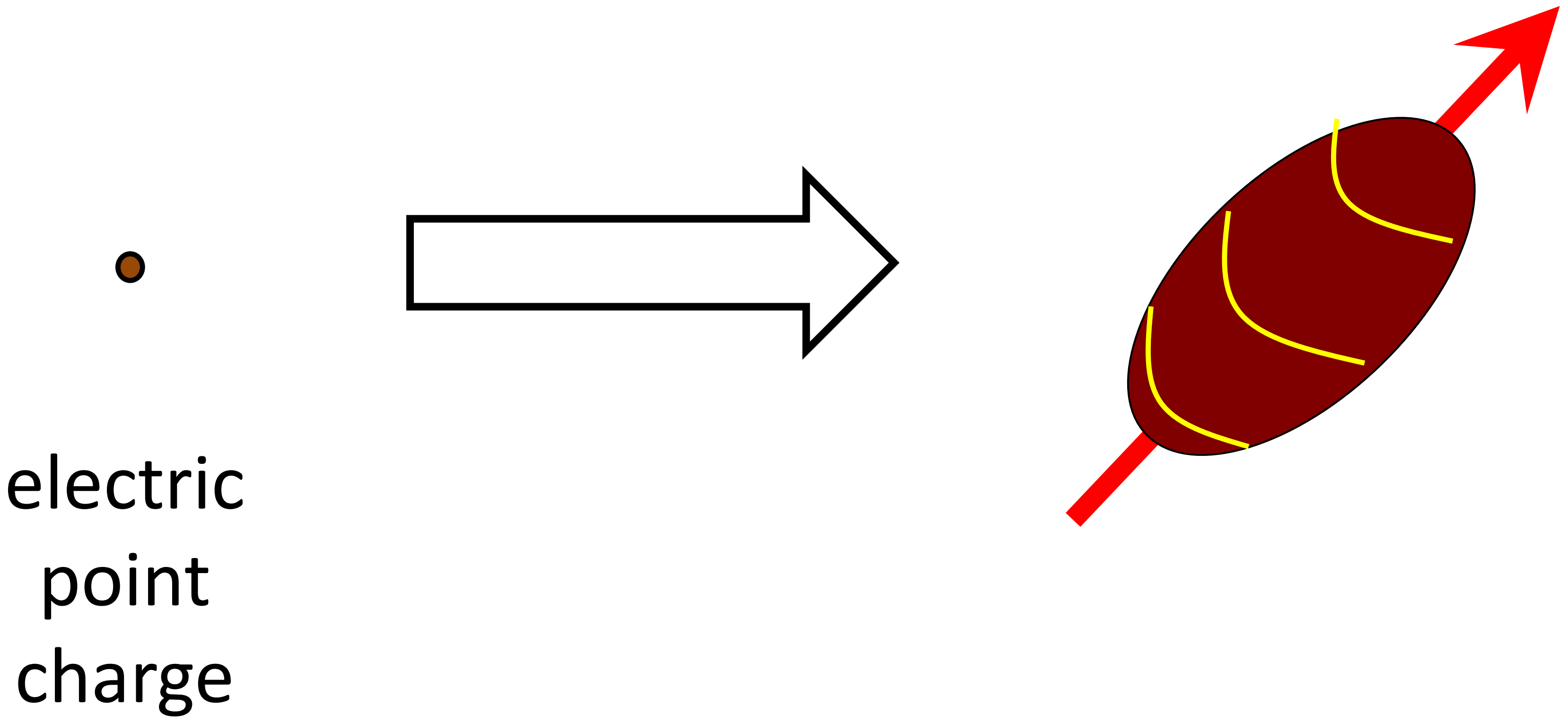
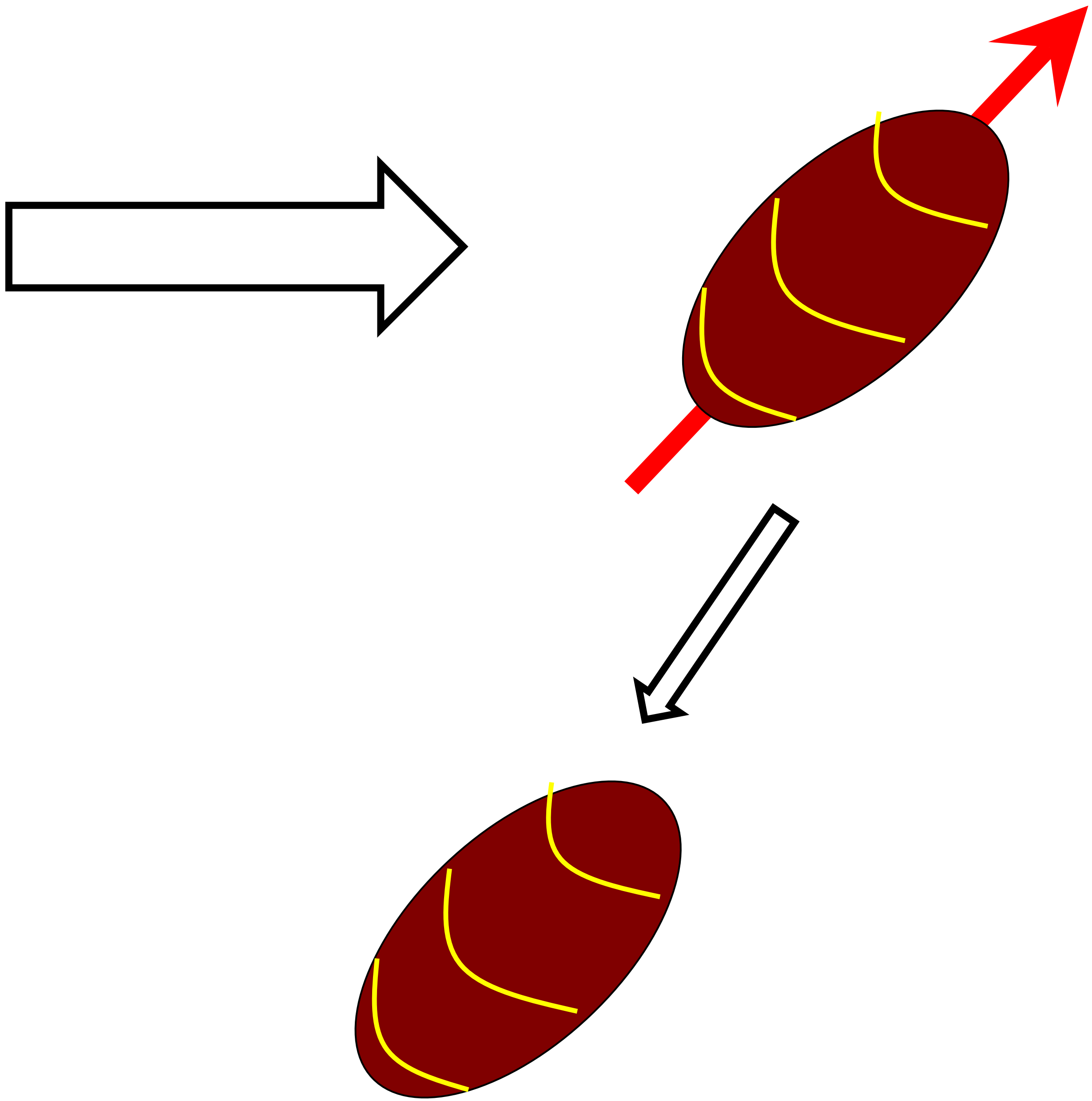
Definition :

hyperfine interaction

=

all aspects of the
nucleus-electron interaction
which go beyond
an electric point charge for a nucleus.

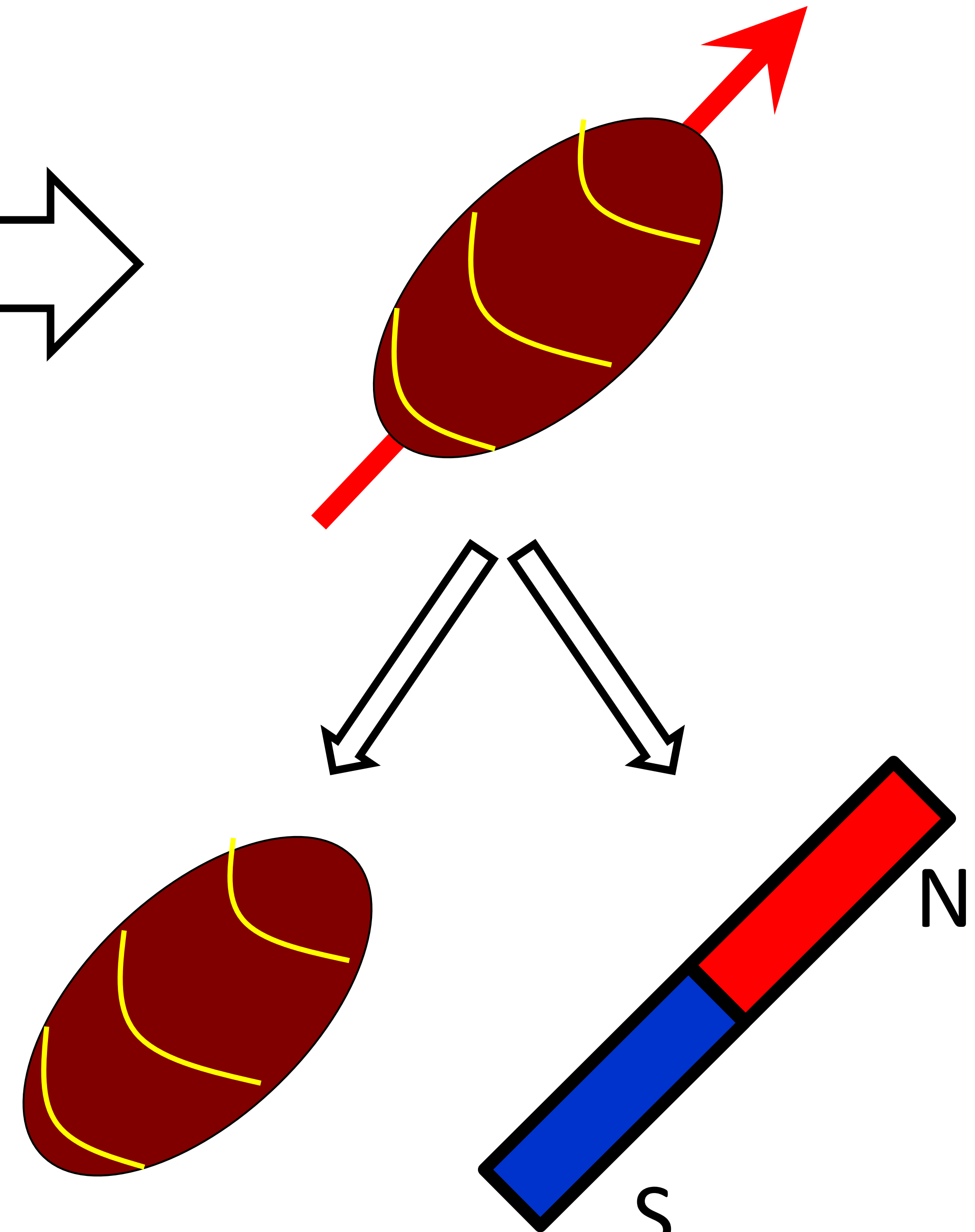

electric
point
charge



electric
~~point~~
charge

- volume
- shape

~~electric~~
point
~~charge~~



- volume
- shape
- magnetic moment

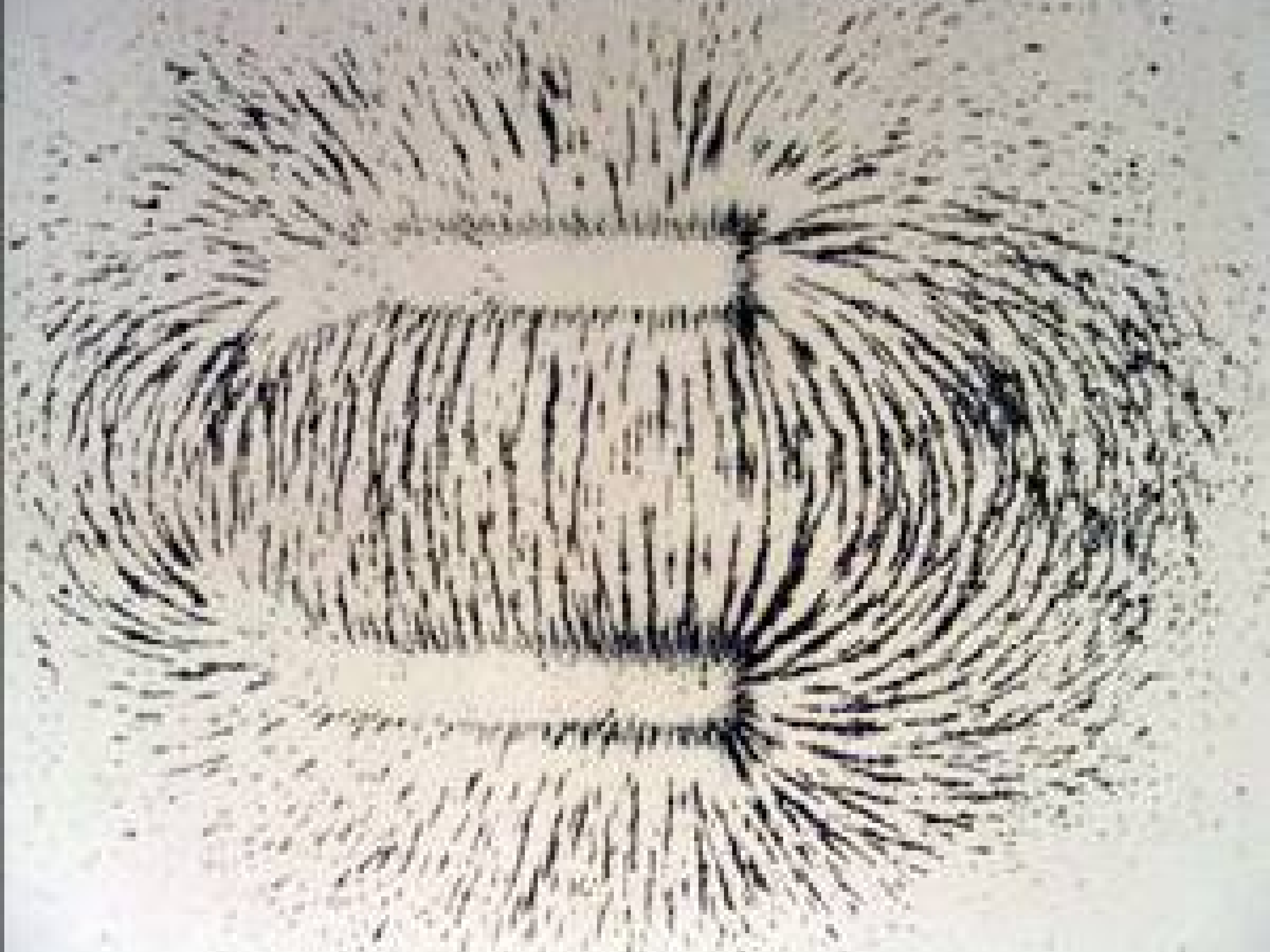
How to measure hyperfine interactions ?

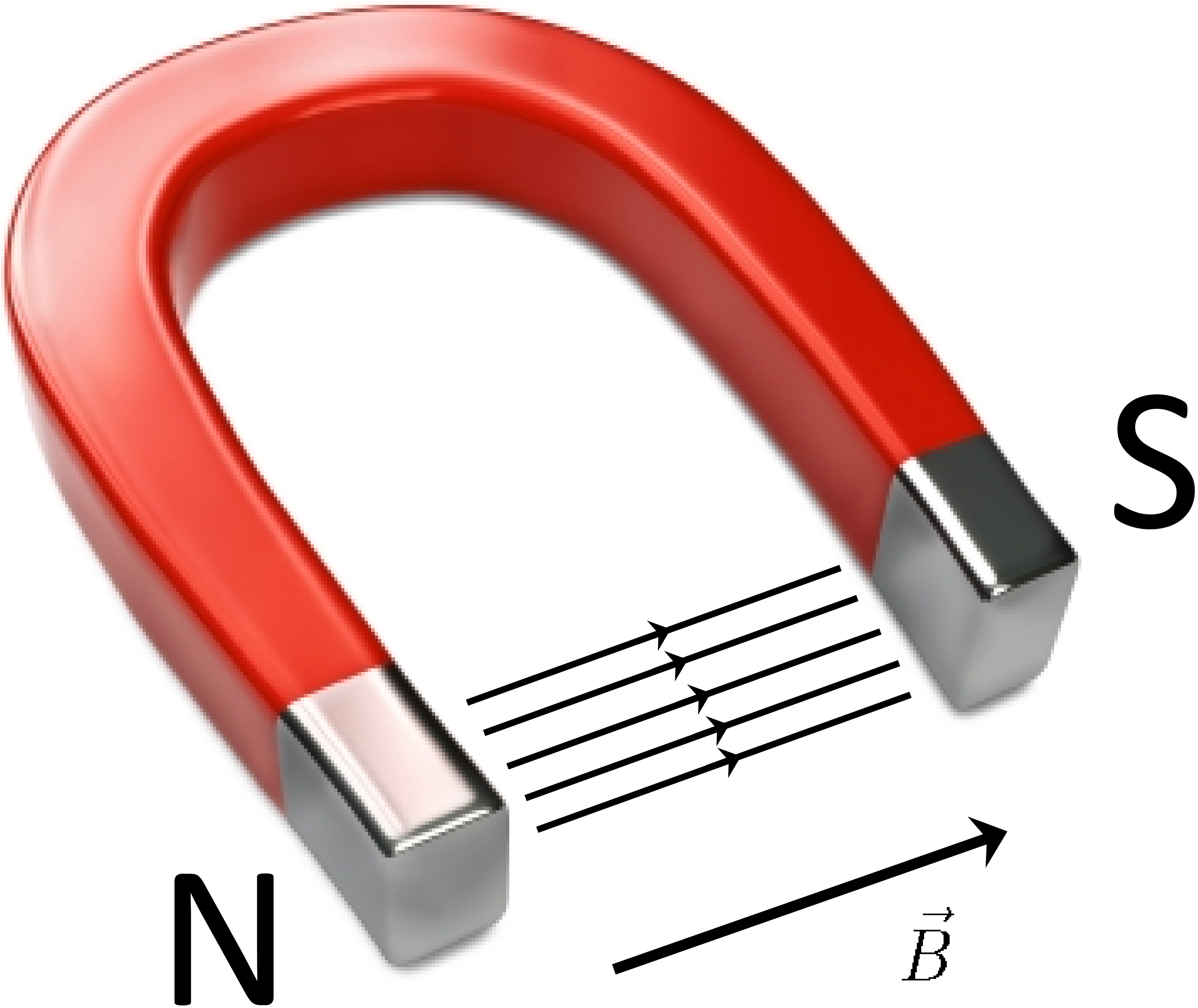
- NMR
- NQR
- Mössbauer spectroscopy
- TDPAC
- Laser spectroscopy
- LTNO
- NMR/ON
- PAD
- …

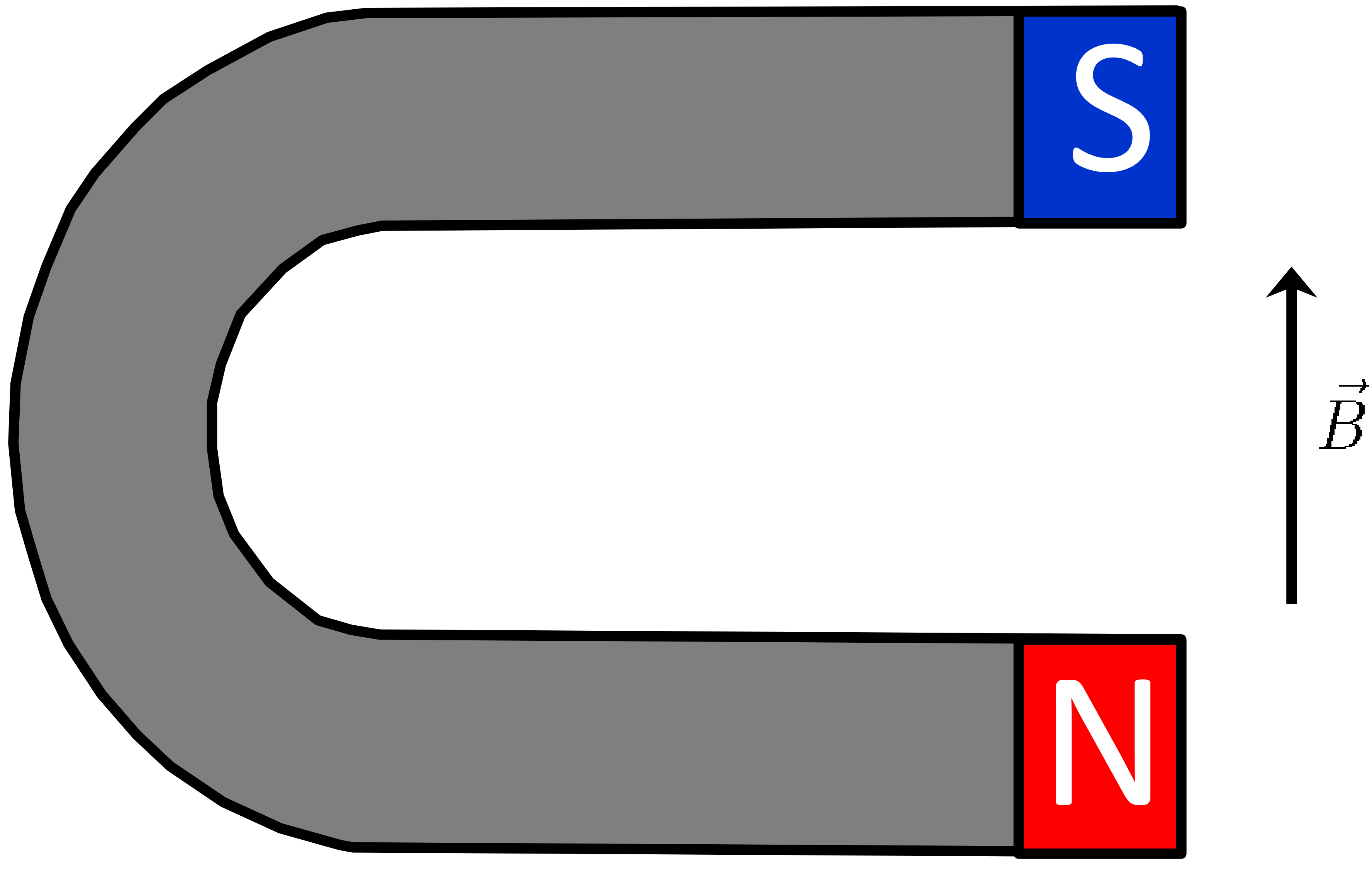
This talk:
- Hyperfine physics
- How to calculate HFF with WIEN2k

Content

- Definitions
- magnetic hyperfine interaction
- electric quadrupole interaction
- isomer shift
- summary




S
N
$\vec{B}$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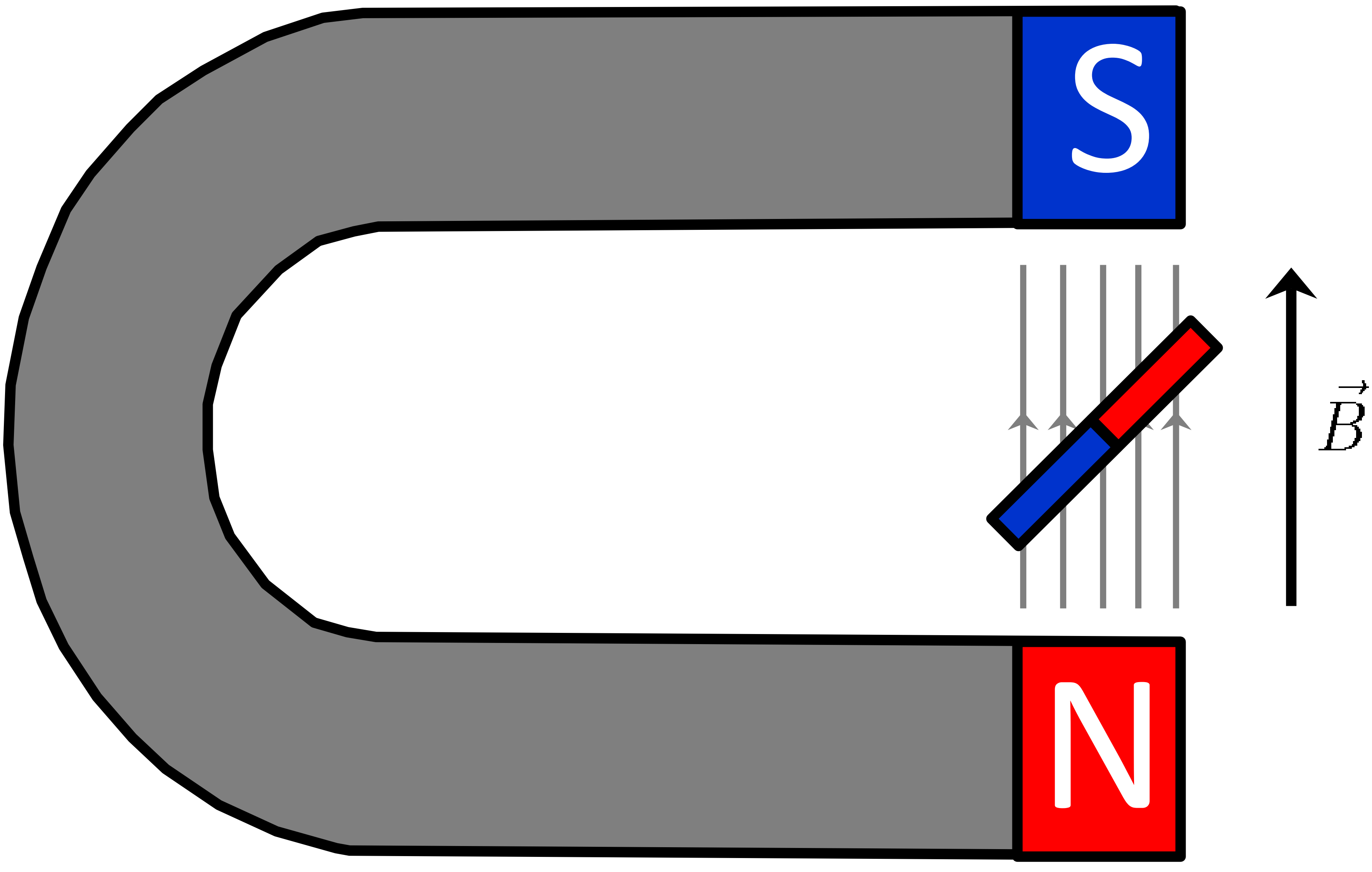
N
$\vec{B}$


S
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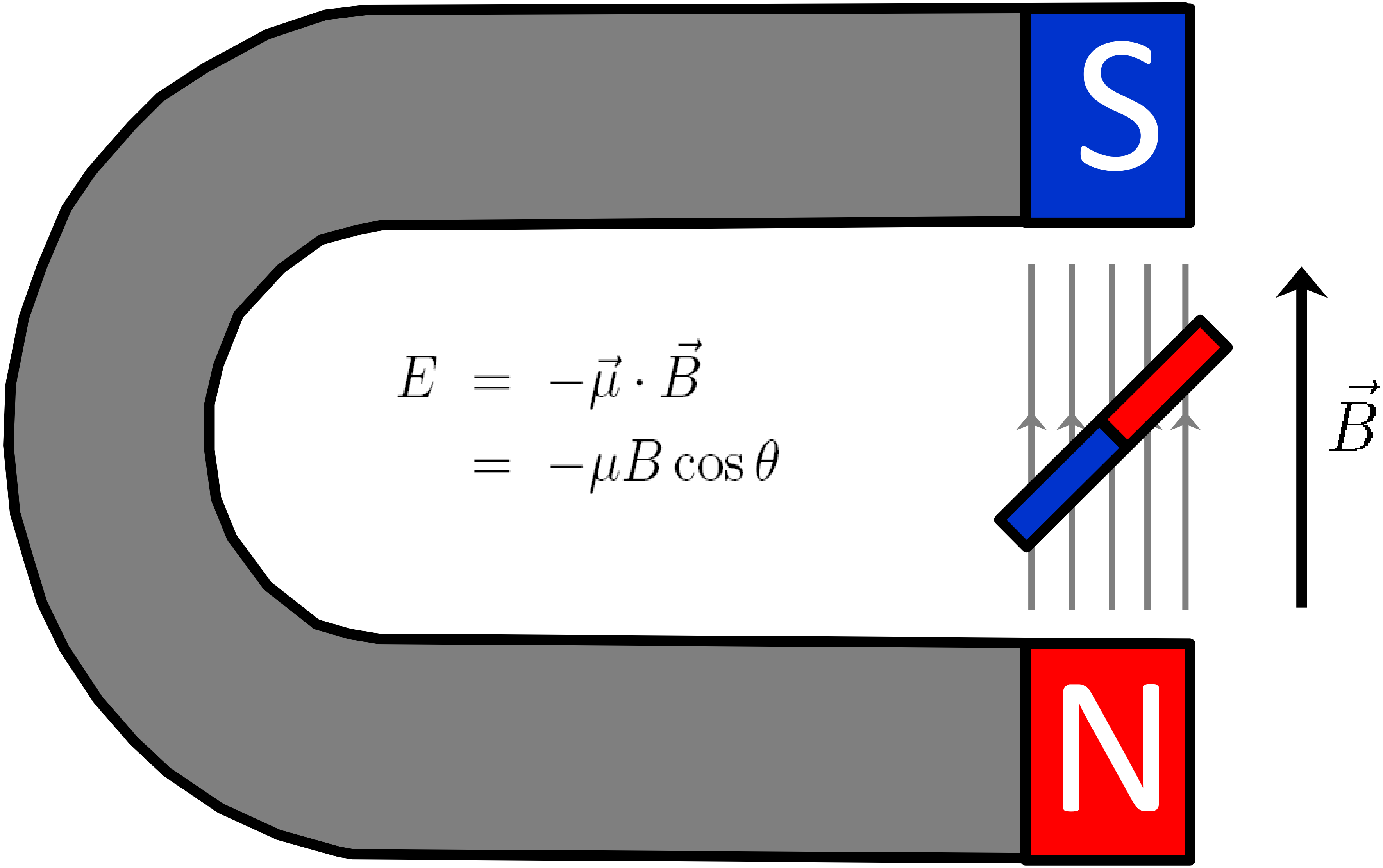
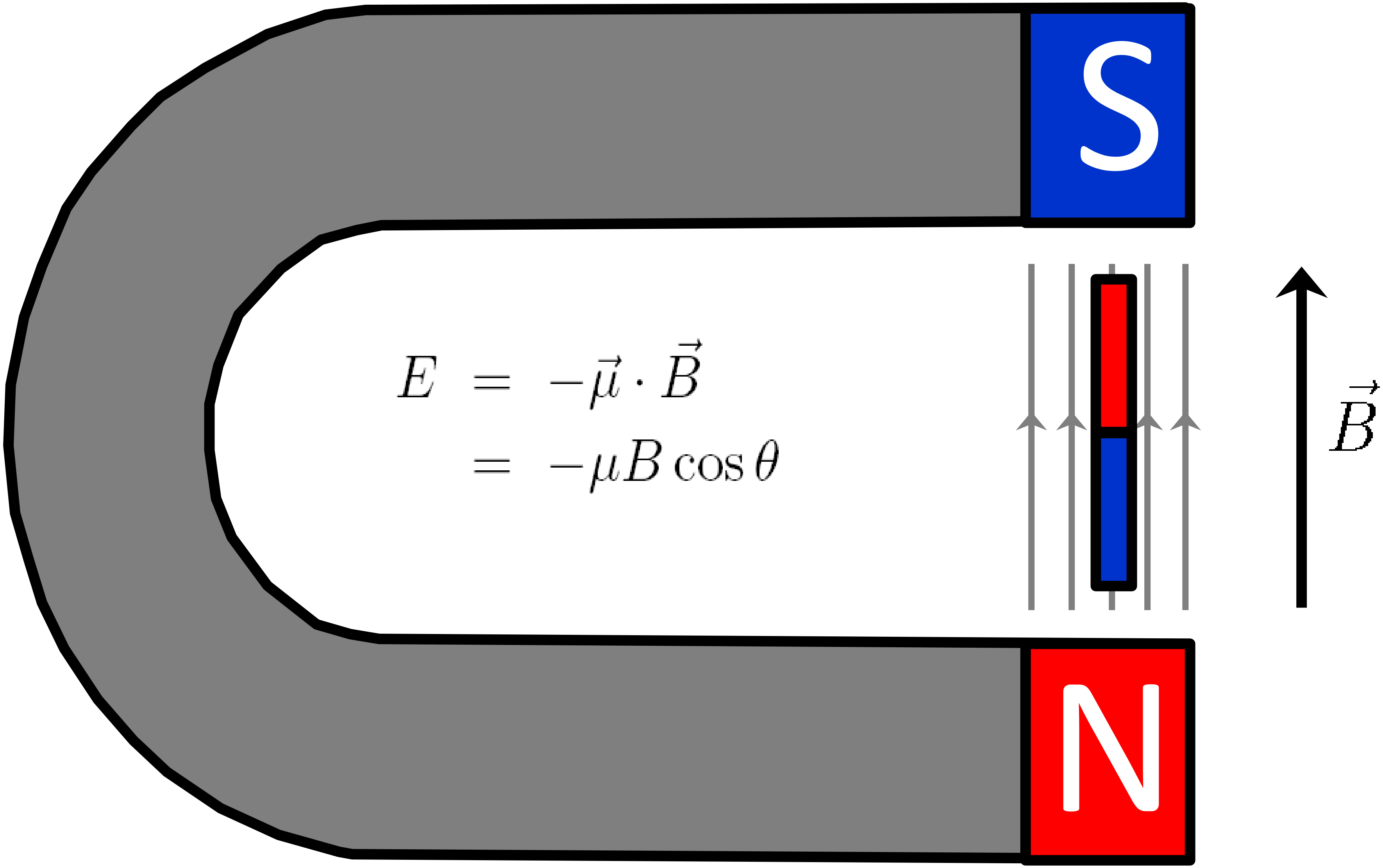

S
N
$E = -\vec{\mu} \cdot \vec{B}$
$= -\mu B \cos\theta$
$\vec{B}$



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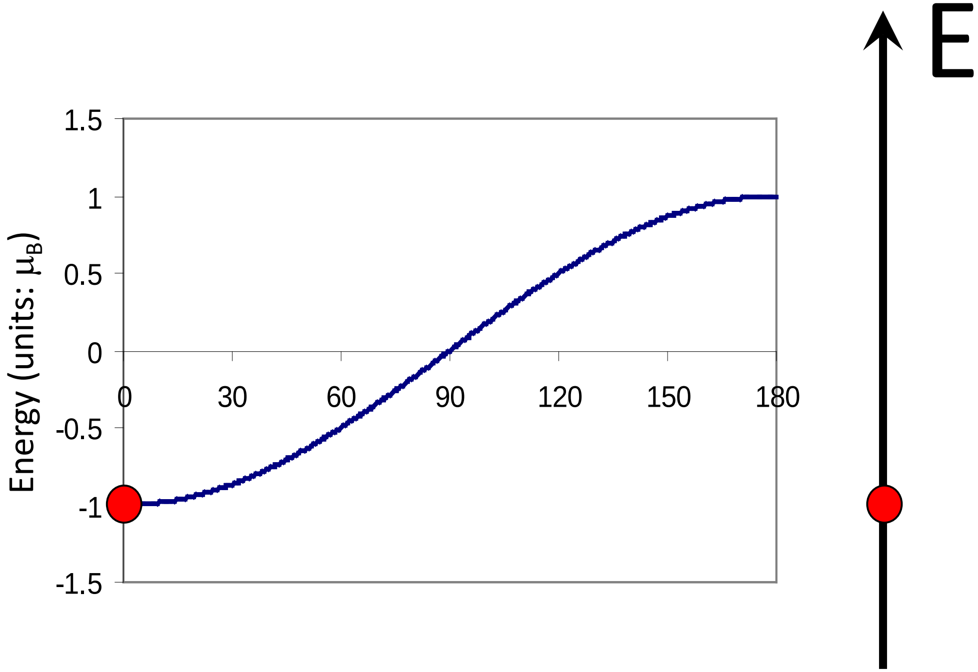

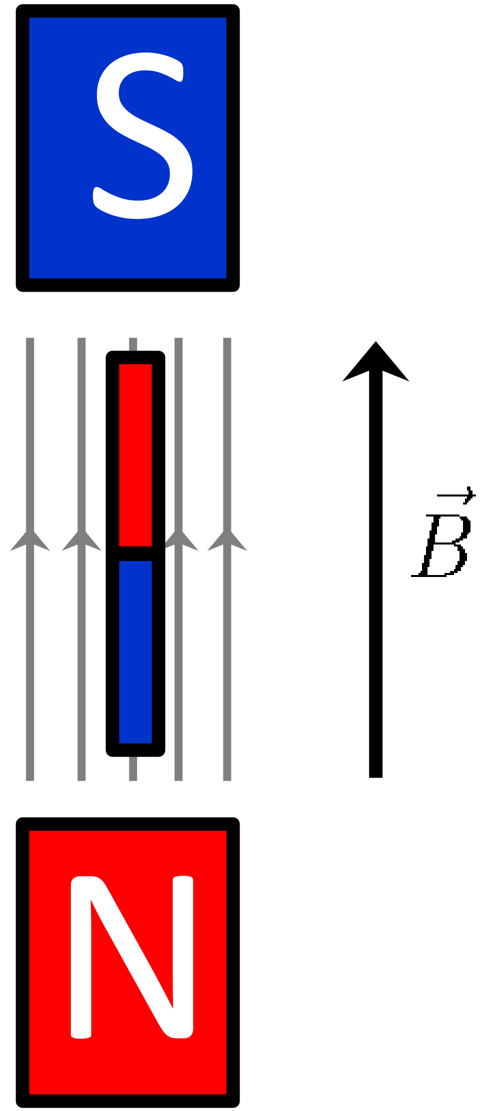

$$
\begin{aligned}
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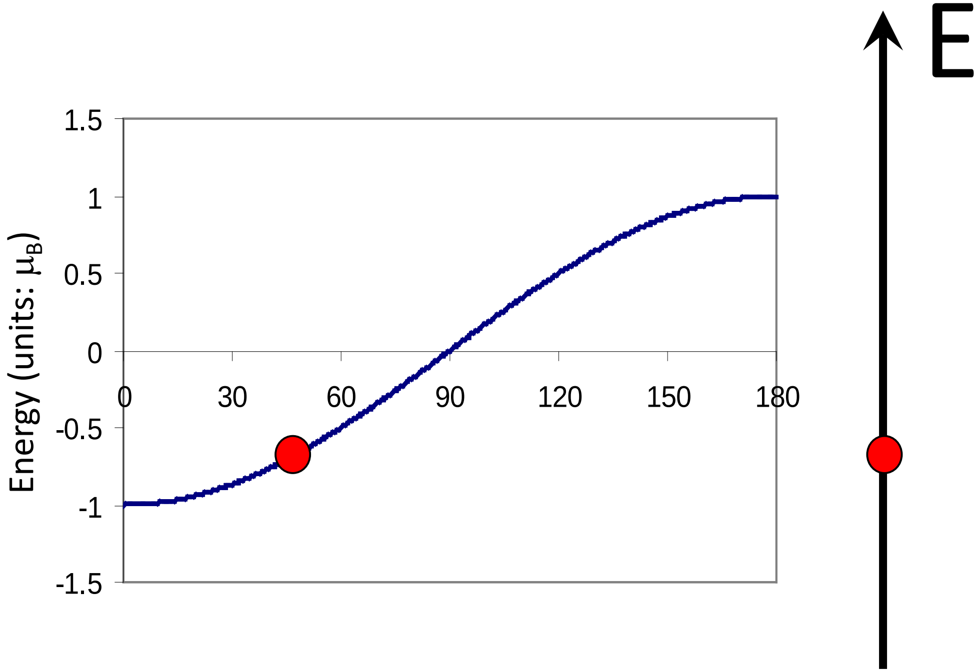

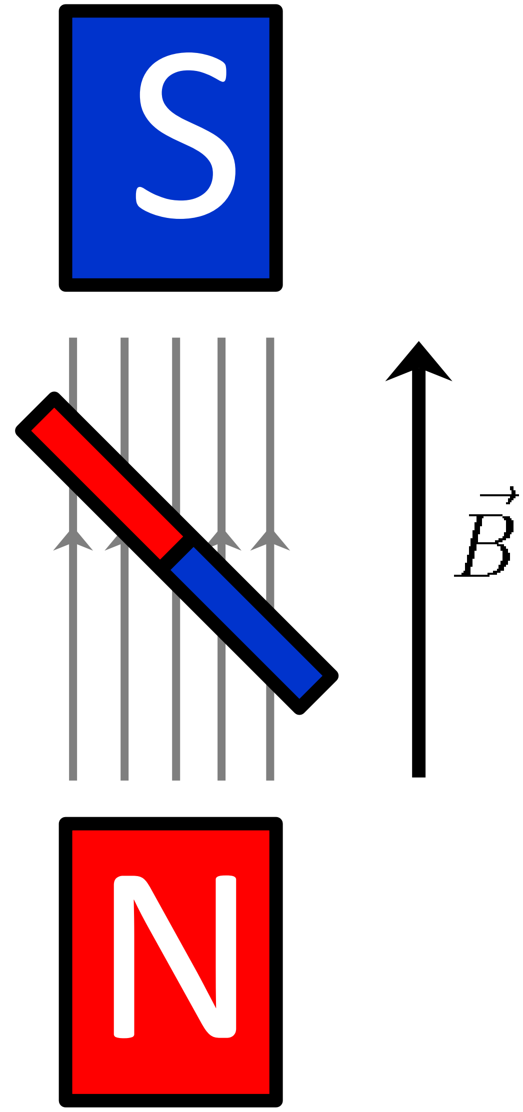

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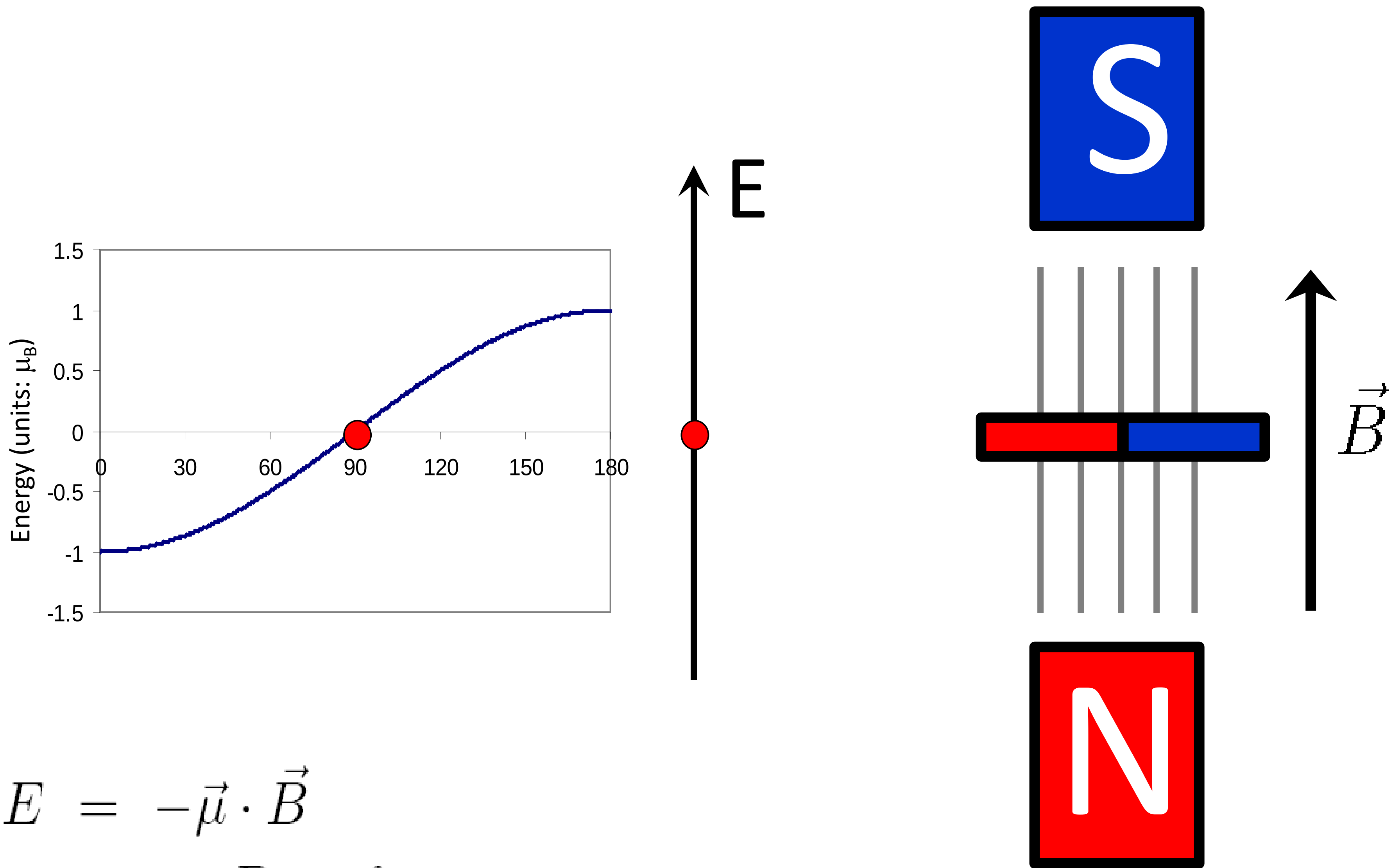
$$



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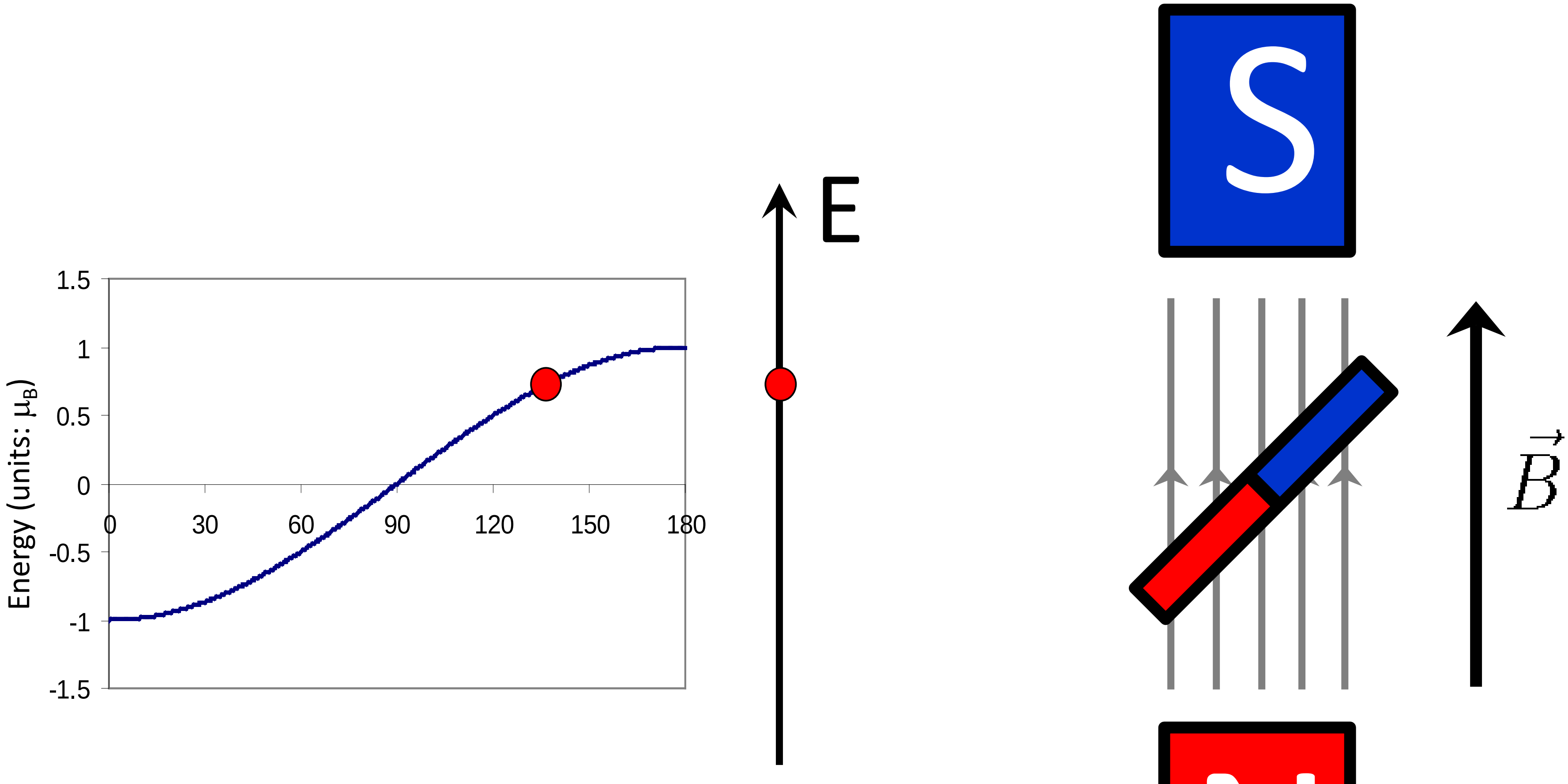

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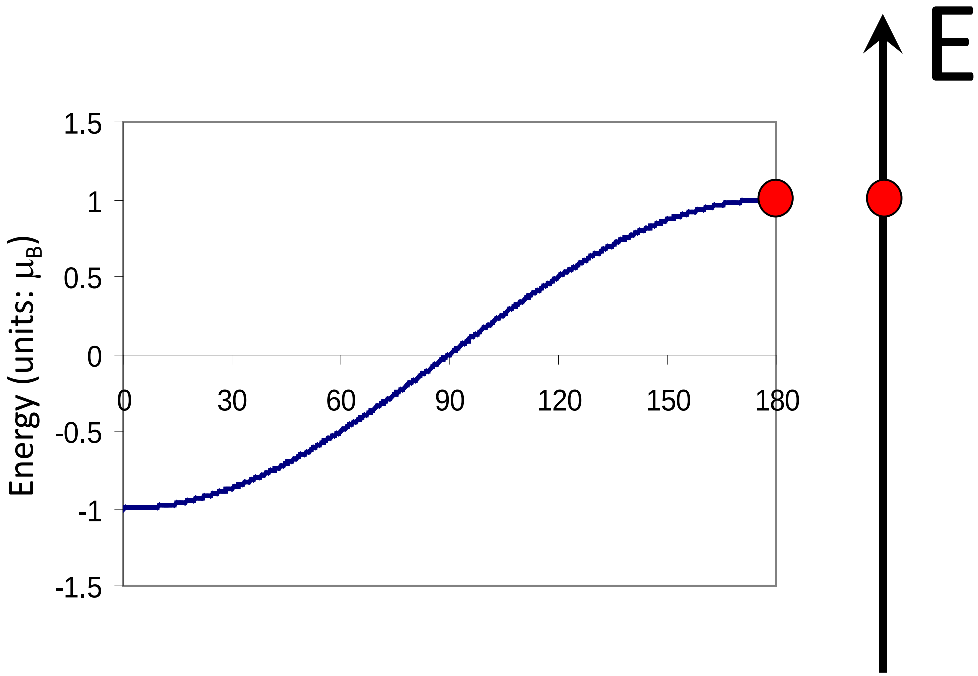
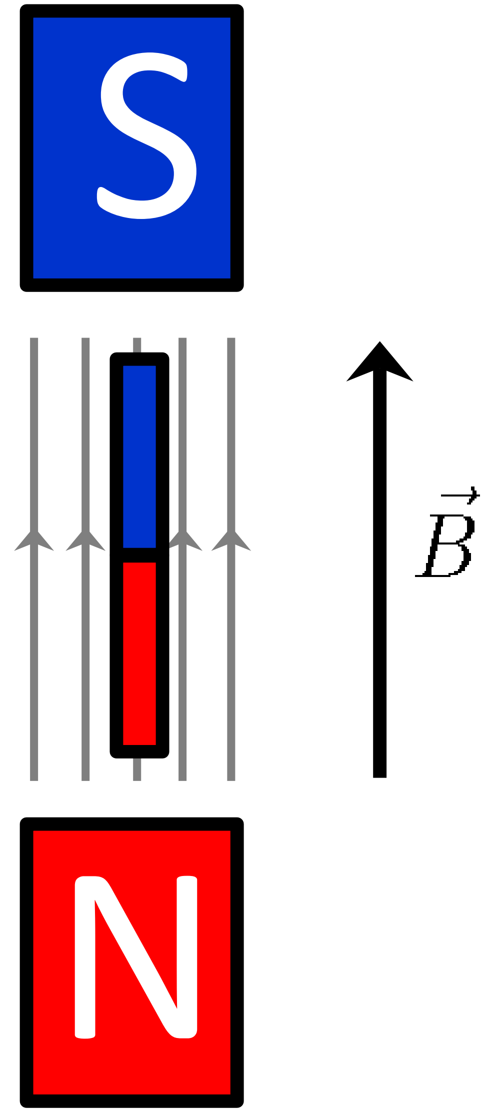
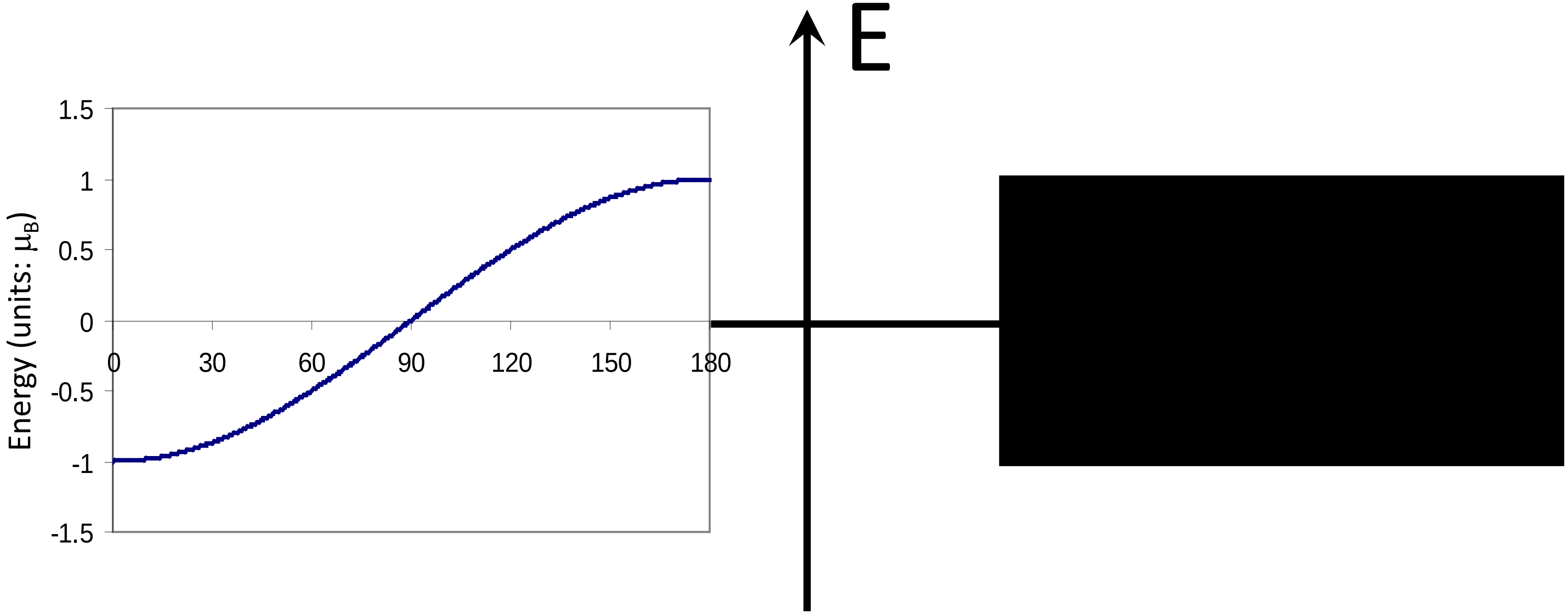




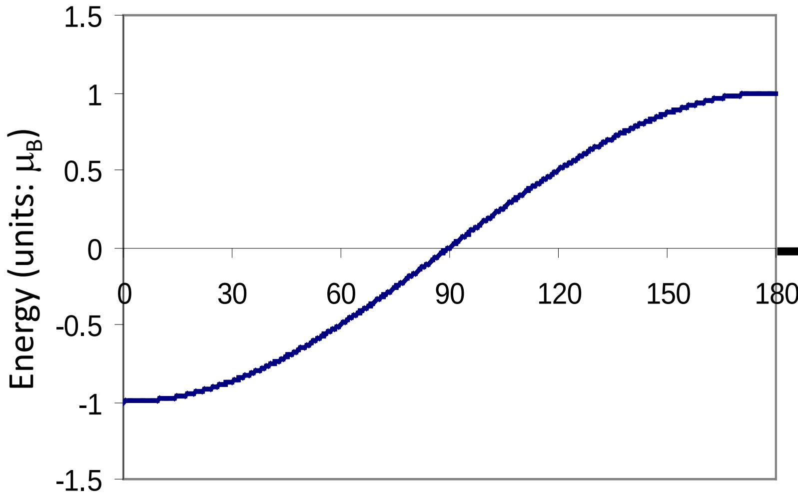
$$\begin{aligned} E &= -\vec{\mu} \cdot \vec{B} \\ &= -\mu B \cos\theta \end{aligned}$$

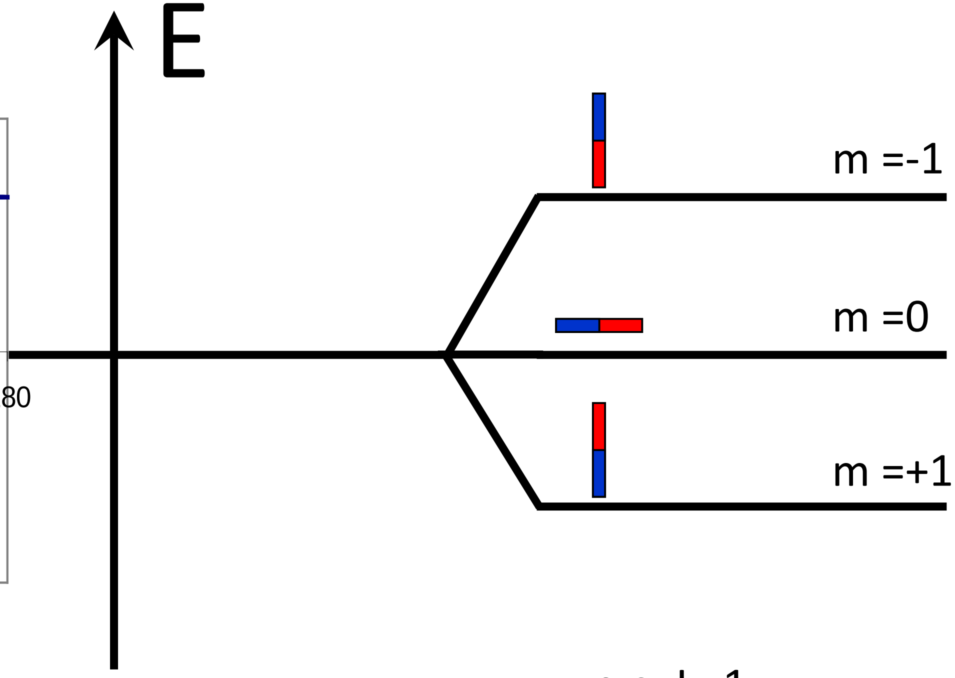


$$
\begin{aligned}
E &= -\vec{\mu}\cdot\vec{B} \\
&= -\mu B\cos\theta
\end{aligned}
$$

Classical

Quantum (=quantization)





$$
\begin{aligned}
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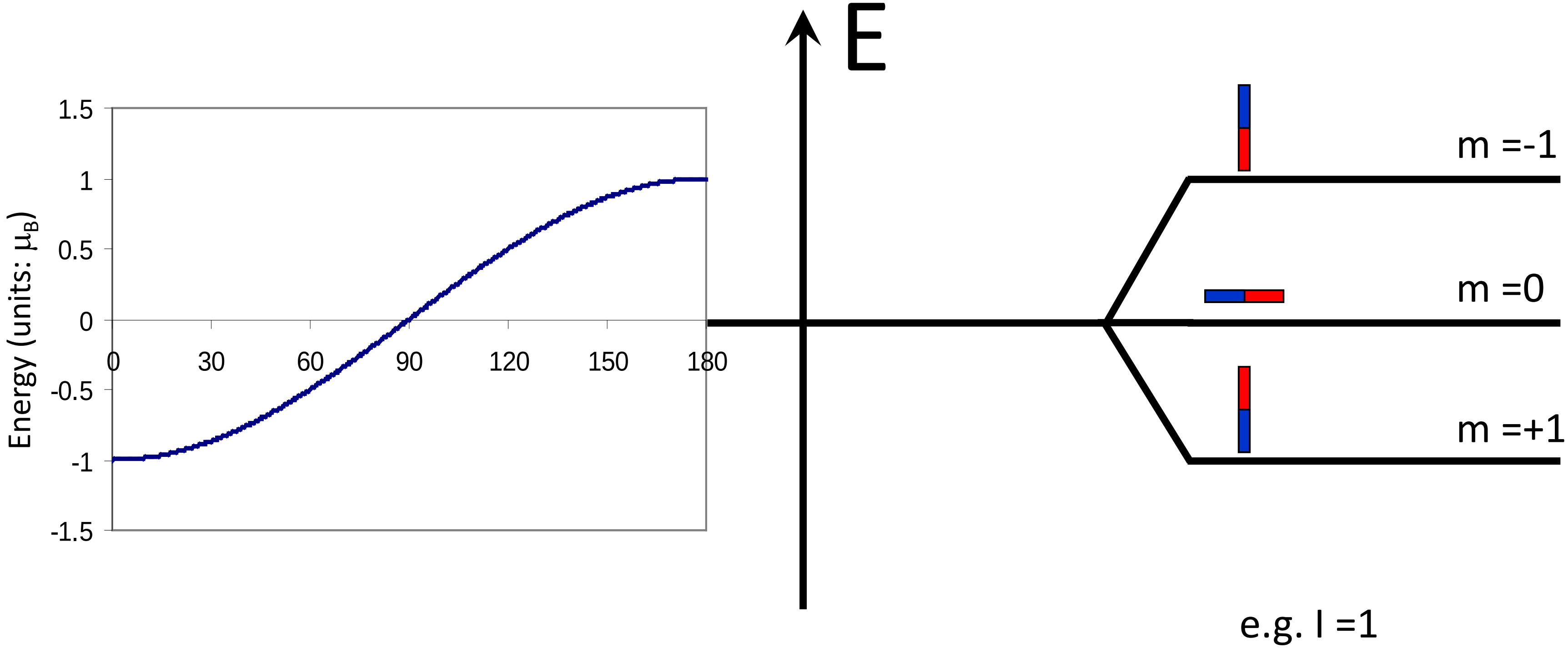
&= -\mu B\cos\theta
\end{aligned}
$$

$$
\hat{\boldsymbol{\mu}}_I = \frac{\mu}{I\,\hbar}\,\hat{\boldsymbol{I}}
$$

Classical

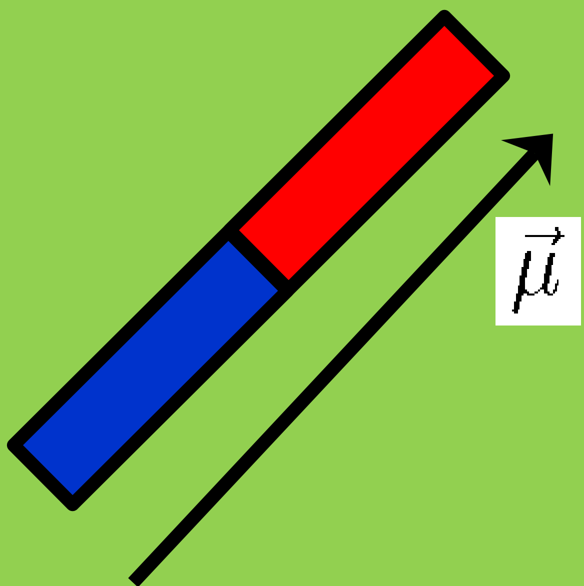
Quantum
(=quantization)



Hamiltonian : $$\hat{H} = -\frac{\mu\, B}{I\,\hbar}\,\hat{I}_z$$

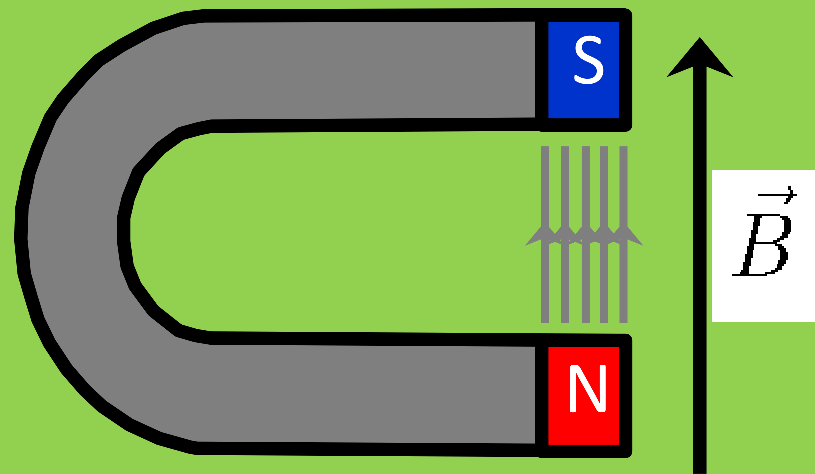
nuclear property

(vector)



electron property

(vector)



interaction energy (dot product) :

$$E = -\vec{\mu} \cdot \vec{B}$$

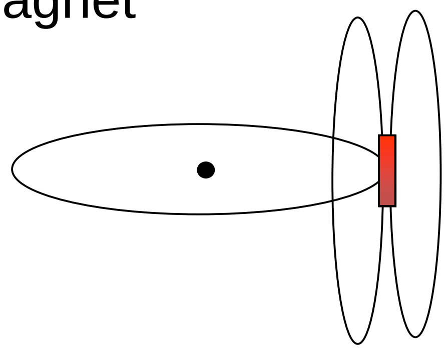
Source of magnetic fields at a nuclear site in an atom/solid

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

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

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

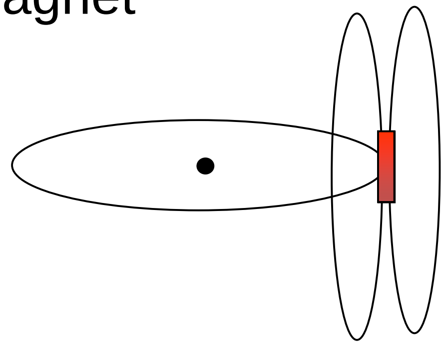
- B_{dip} = electron as bar magnet



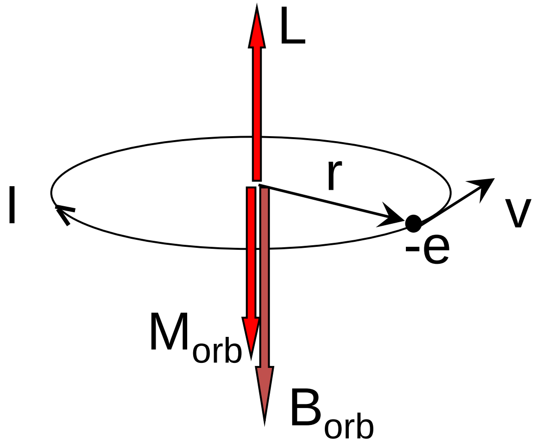
Source of magnetic fields at a nuclear site in an atom/solid

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

- B_{dip} = electron as bar magnet



- B_{orb} = electron as current loop



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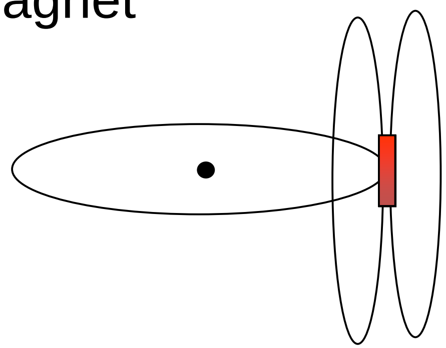

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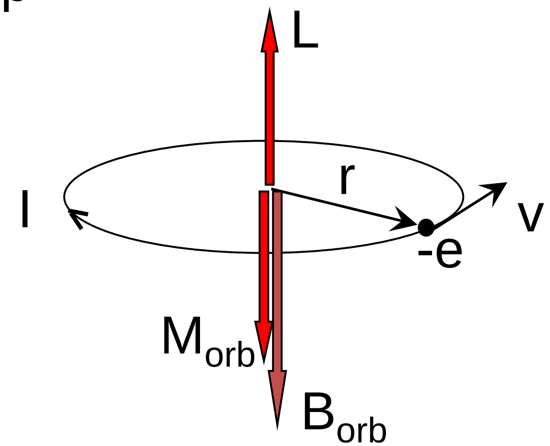
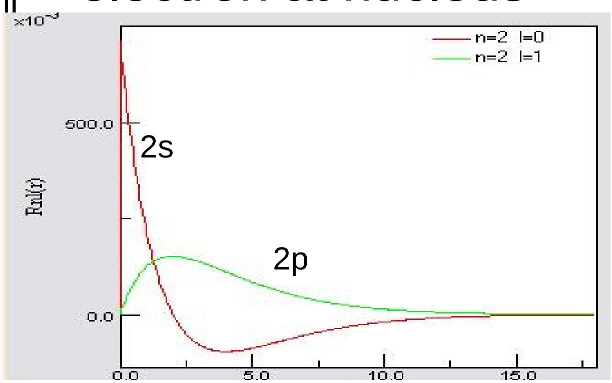


- B_{Fermi} = electron at nucleus

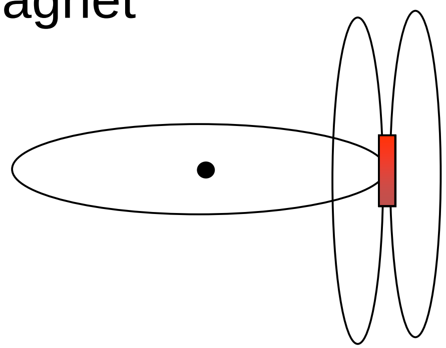


$$-\frac{2\mu_B\mu_0}{3}\left(|\psi_{e,\uparrow}(\mathbf{0})|^2 - |\psi_{e,\downarrow}(\mathbf{0})|^2\right)$$

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

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

- B_{dip} = electron as bar magnet



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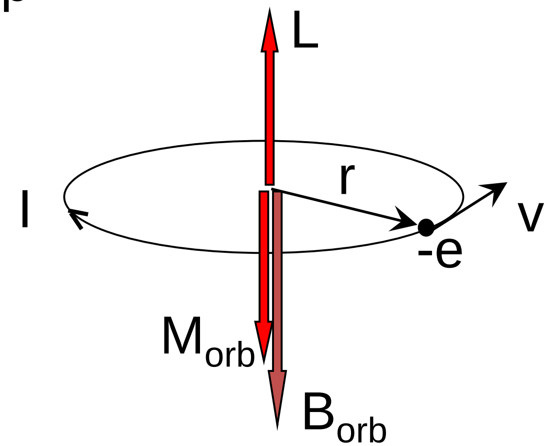

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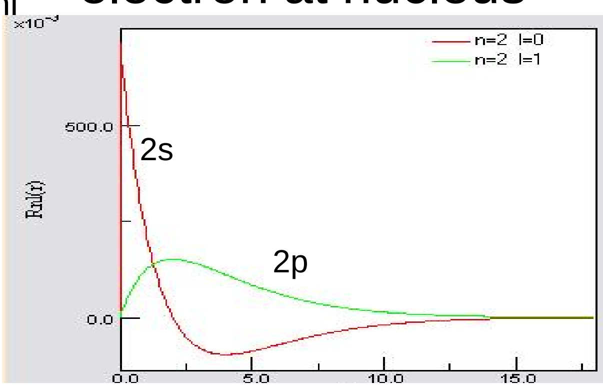
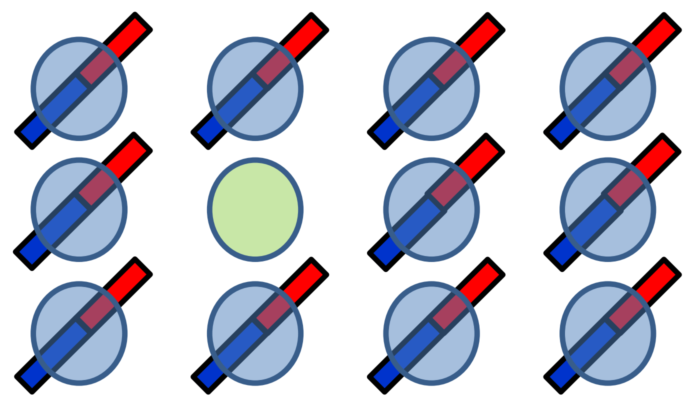


$$-\frac{2\mu_B\mu_0}{3}\left(|\psi_{e,\uparrow}(\mathbf{0})|^2 - |\psi_{e,\downarrow}(\mathbf{0})|^2\right)$$

- B_{lat} = neighbours as bar magnets



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)

Mössbauer spectroscopy:

- Isomer shift: $\delta = \alpha\ (\rho_0^{Sample} - \rho_0^{Reference})$; α=-.291 au^{3}mm s^{-1}
  - *proportional to the electron density ρ 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*

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

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

Verwey transition in $YBaFe_2O_5$

Charged ordered

Fe^{2+} Fe^{3+}

Valence mixed

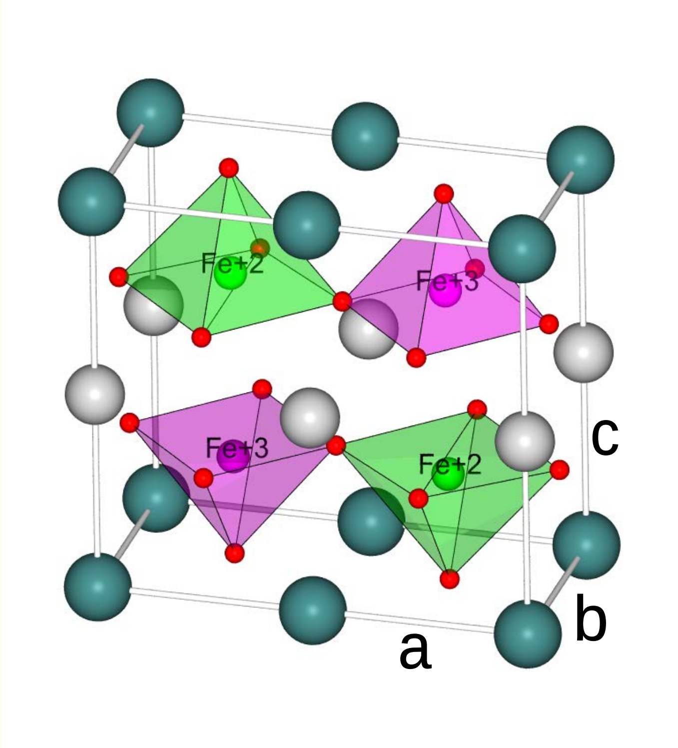
$Fe^{2.5+}$

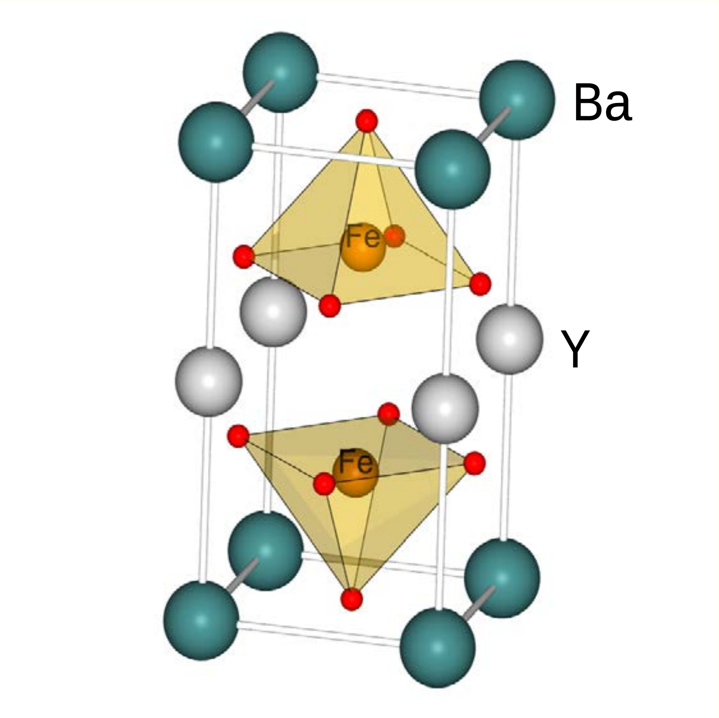
CO structure: Pmma

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

VM structure: Pmmm

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





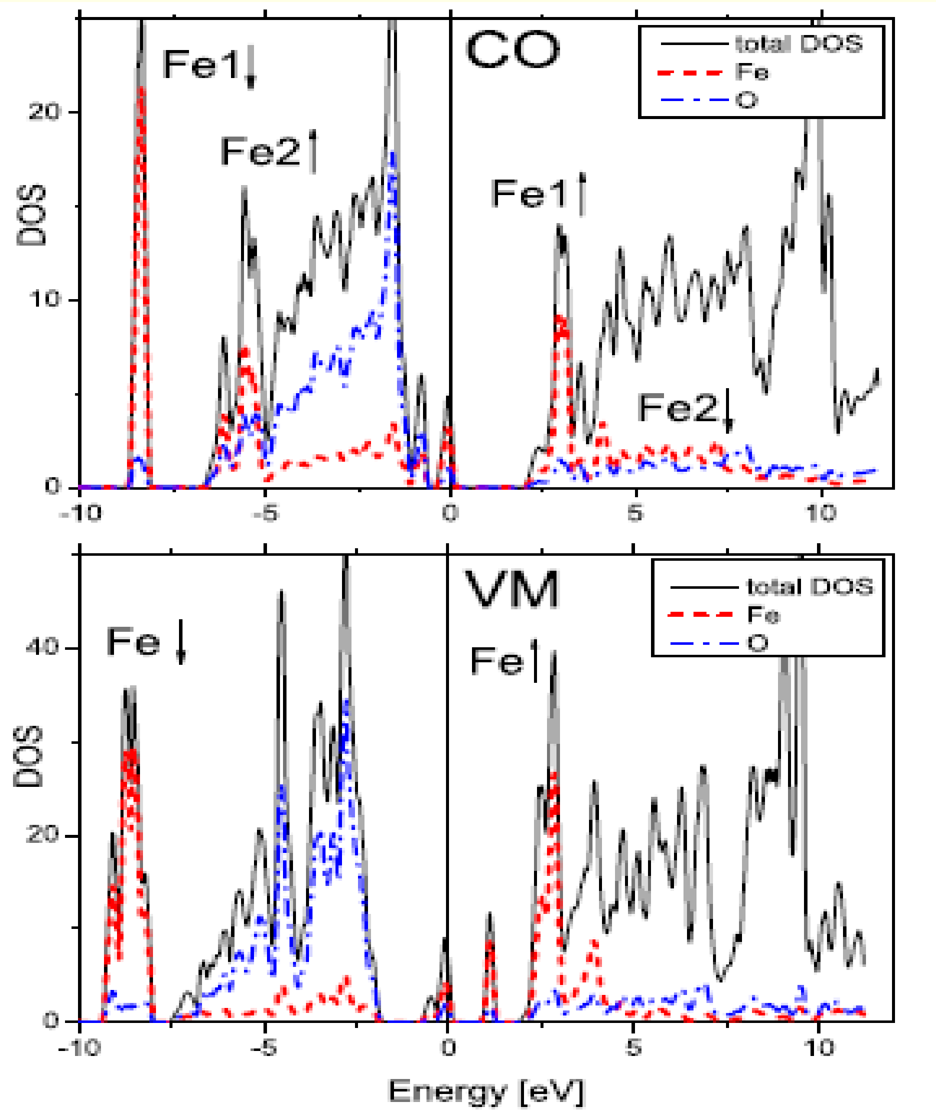
- Fe^{2+} and Fe^{3+} chains along b

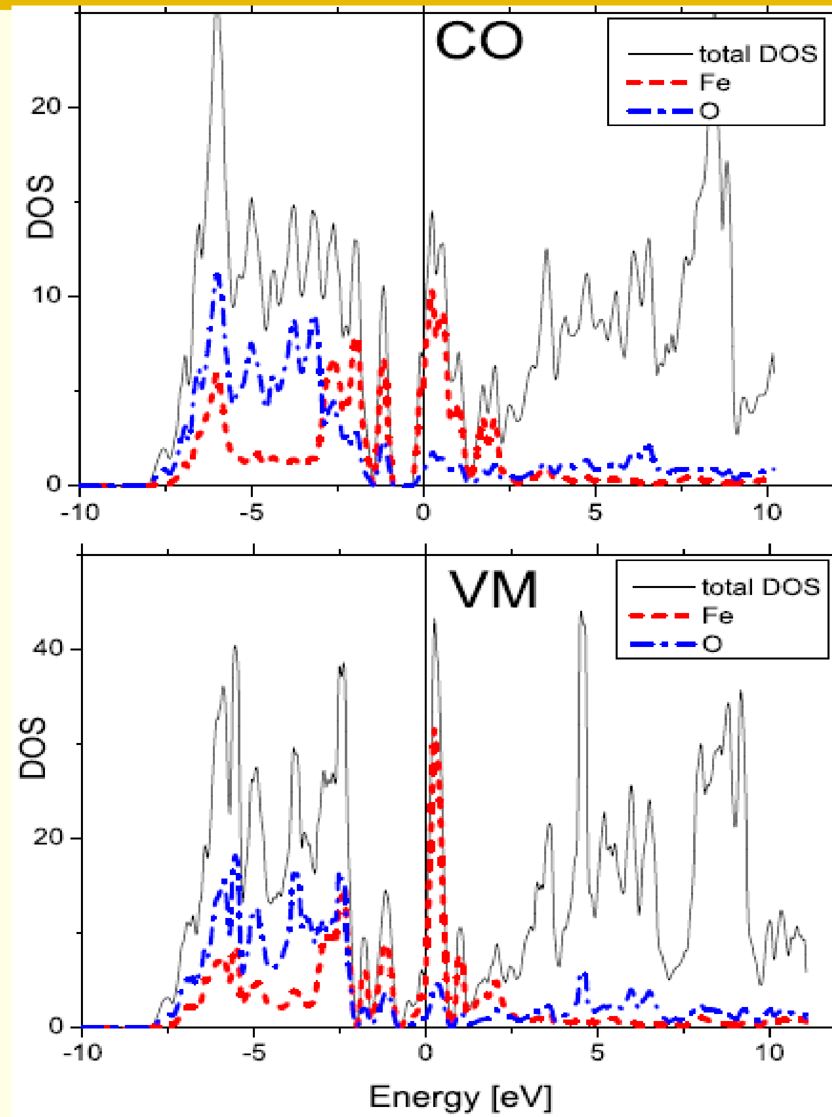
$Fe^{2.5+}$

DOS: GGA+U vs. GGA

GGA+U GGA

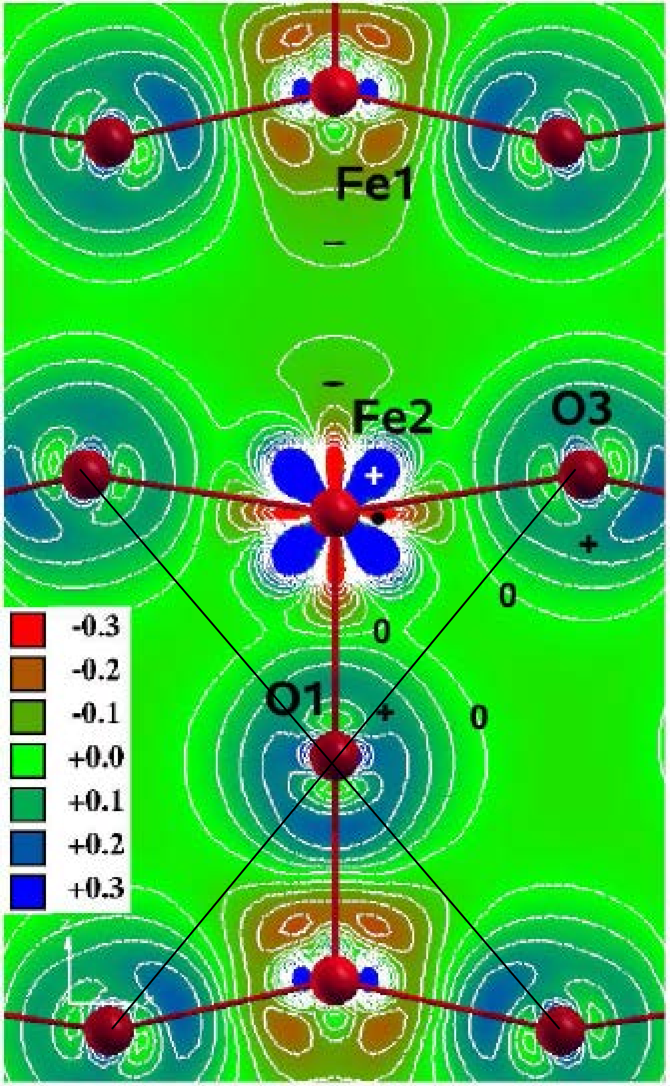
single lower Hubbard-band in VM splits in CO with Fe^{3+} states lower than Fe^{2+}



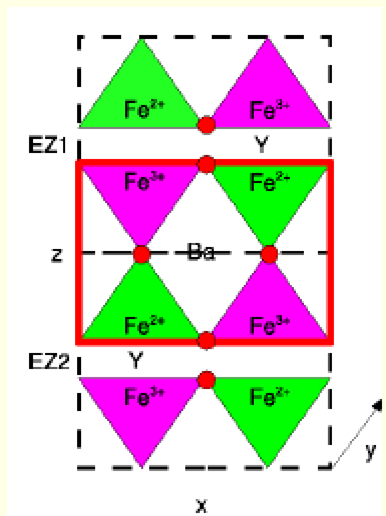


Difference densities $\Delta\rho=\rho_{cryst}-\rho_{at}^{sup}$

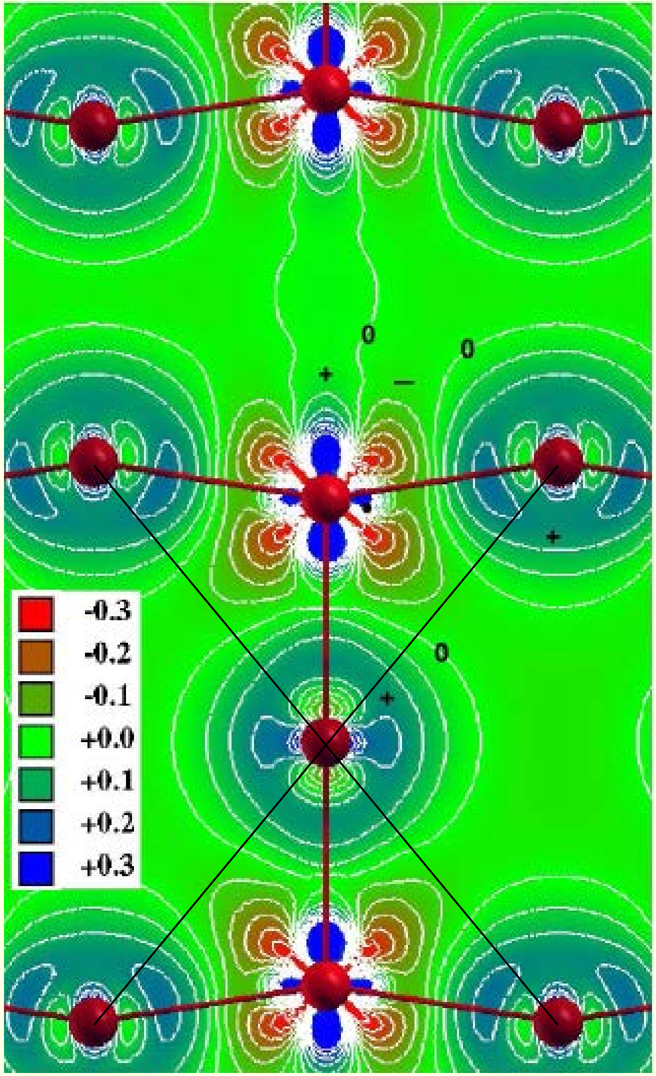
- CO phase



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

$YBaFe_2O_5$ HFF, IS and EFG with GGA+U, LDA/GGA

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	—	—
$Fe2^{2+}$	B_{dip}	—	-16.29	-16.49	-6.68	-12.67
	B_{orb}	—	-6.73	-6.90	-9.57	-6.34
	$B_{contact}$	—	32.25	32.23	32.21	31.58
	B_{tot}	~ 8	9.23	8.83	15.96	12.57
	δ	~ 1	0.92	0.94	0.74	0.79
	eQV_{zz}	$3.6 - 4$[a]	3.66	3.74	-0.82	2.60
$Fe1^{3+}$	B_{dip}	—	-0.67	-0.60	1.29	0.39
	B_{orb}	—	-0.52	-0.45	-7.96	-2.65
	$B_{contact}$	—	37.65	38.28	29.64	31.63
	B_{tot}	~ 50	36.46	37.24	22.97	29.37
	δ	~ 0.4	0.33	0.30	0.50	0.47
	eQV_{zz}	$1 - 1.5$[a]	1.46	1.50	1.04	-0.30

[a] depending on rare earth ion

HFF(Fe^{2+})

HFF(Fe^{3+})

VM

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

HFF($Fe^{2.5+}$)

Content

- Definitions
- magnetic hyperfine interaction
- electric quadrupole interaction
- isomer shift
- summary

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

$$E = V_0 Z$$

direction independent constant

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

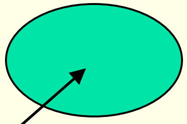
electric field x
nuclear dipol moment (=0)

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

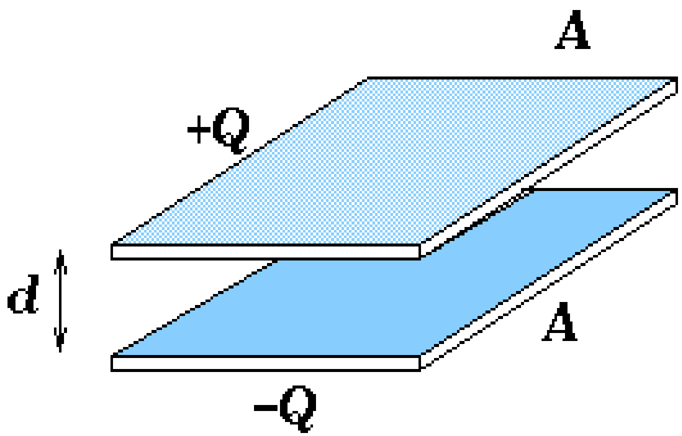
electric fieldgradient x
nuclear quadrupol moment Q

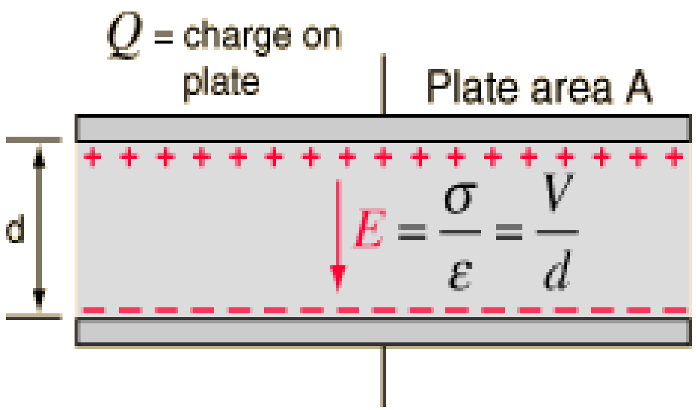
$$+ \dots$$

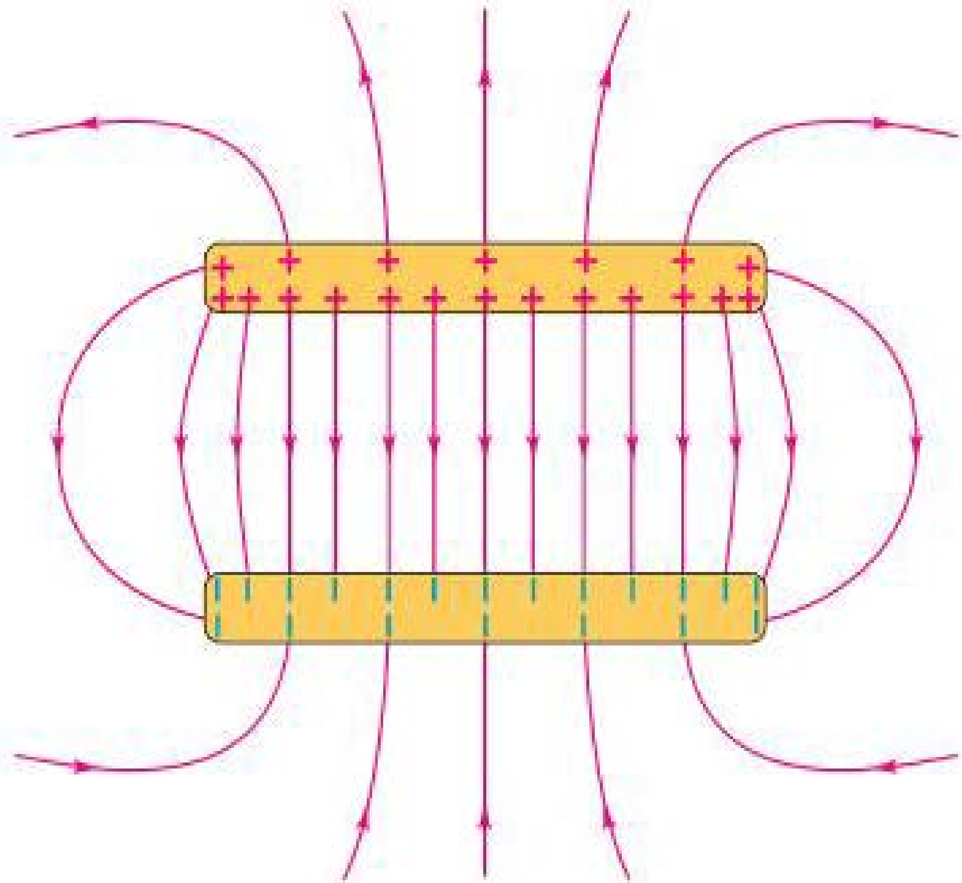
higher terms neglected



nucleus with charge Z, but not a sphere

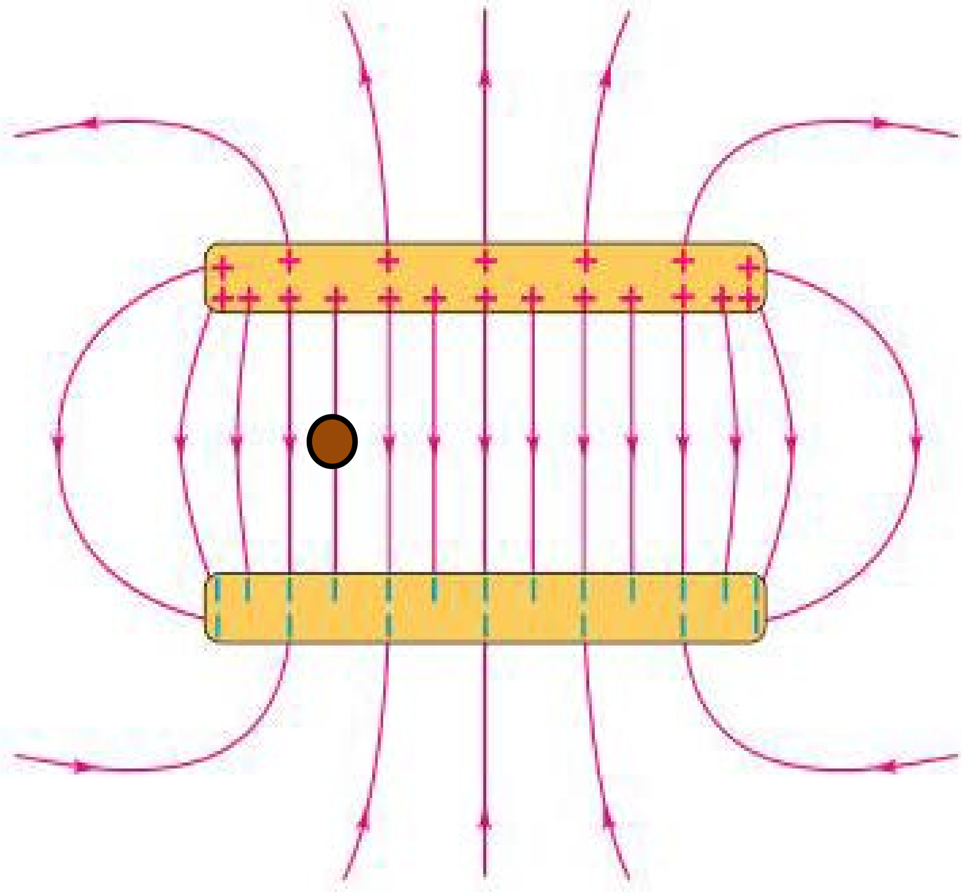

A
+Q
d
A
−Q


Q = charge on plate
Plate area A
d
$E = \frac{\sigma}{\varepsilon} = \frac{V}{d}$



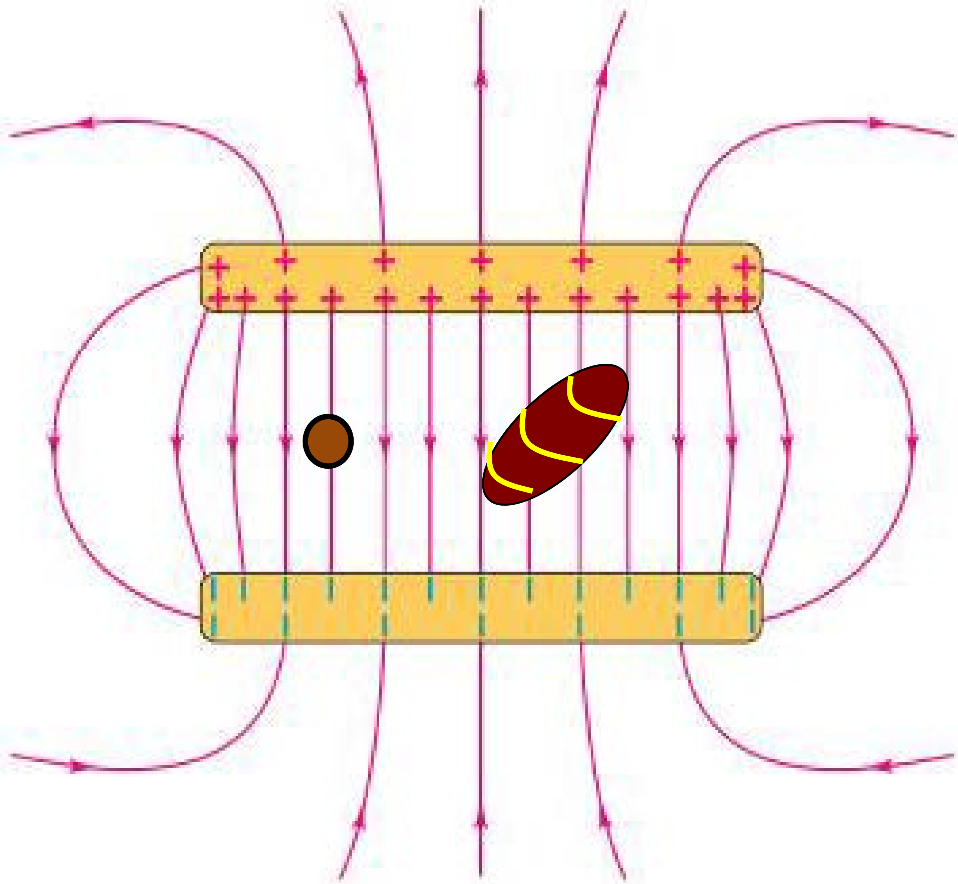
- Force on a point charge:

$$\vec{F} = Q\vec{E}$$



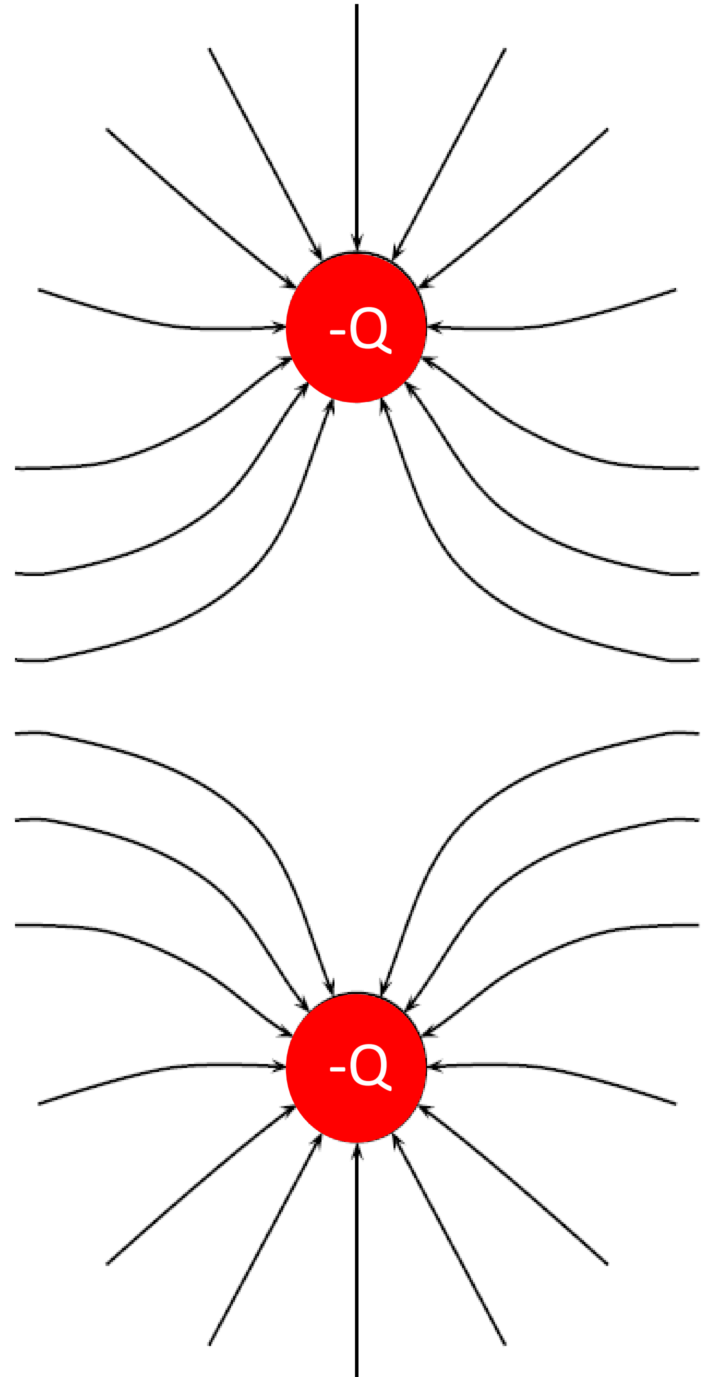
- Force on a point charge:

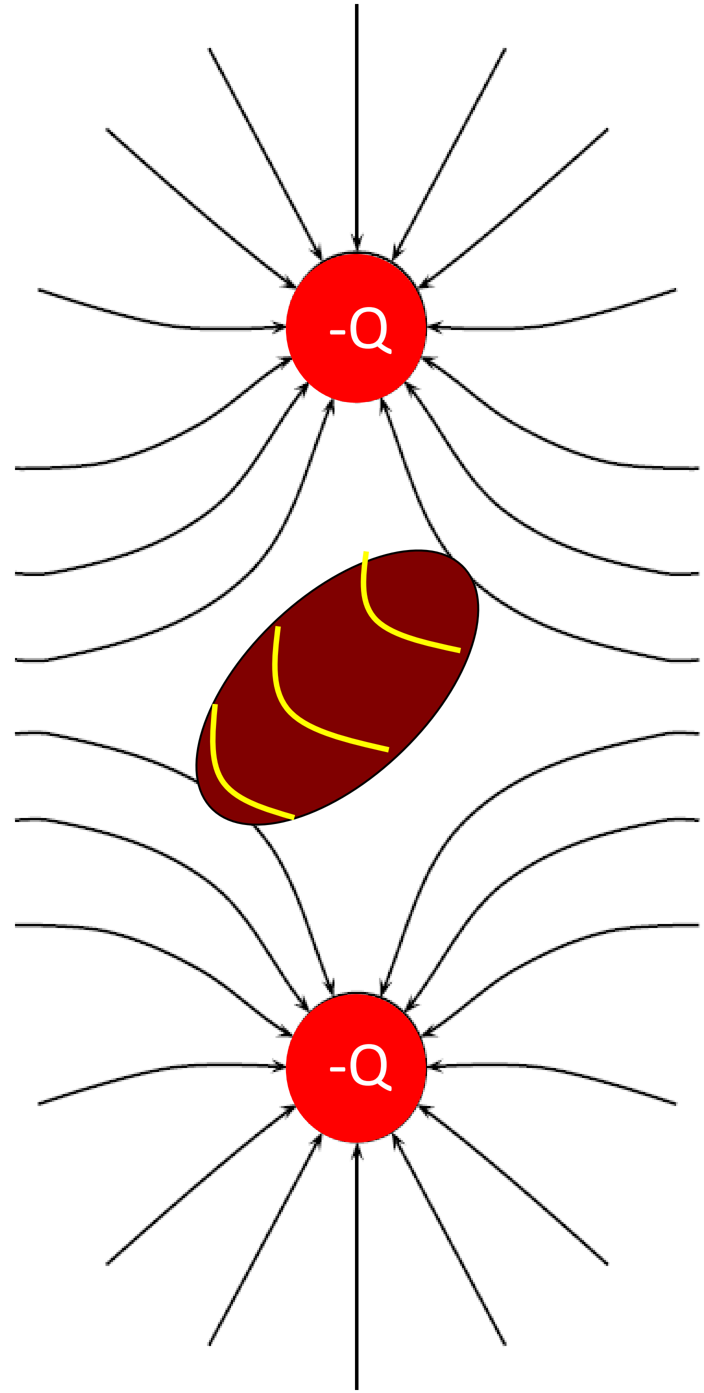
$$\vec{F} = Q\vec{E}$$



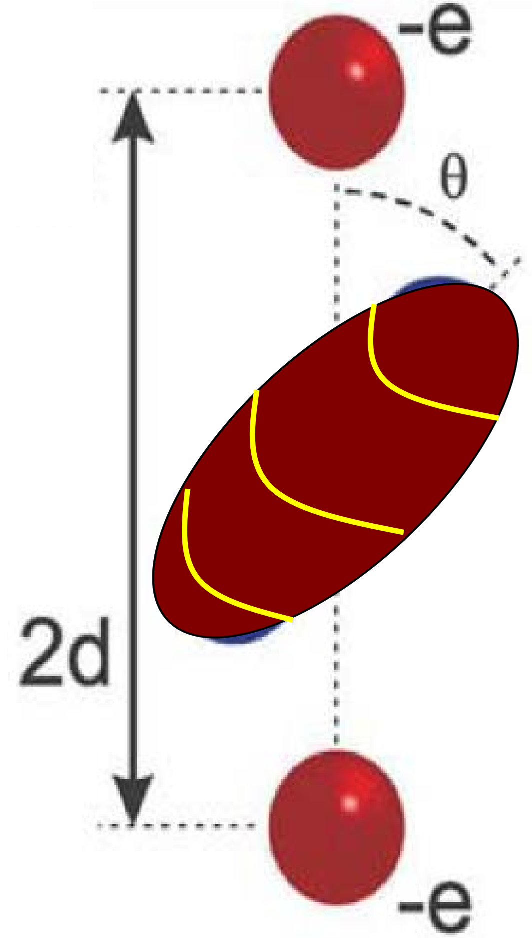
- Force on a general charge:

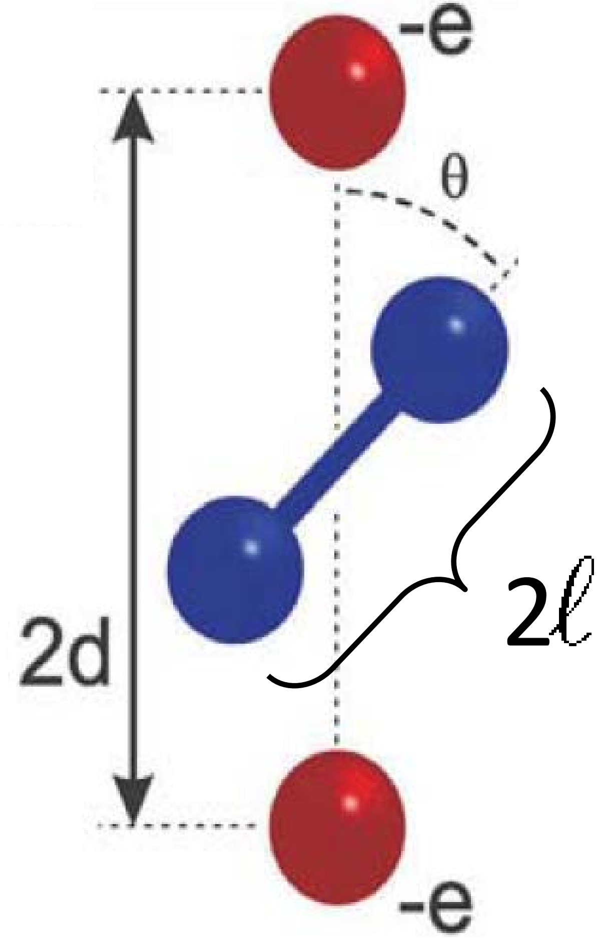
$$\vec{F} = \int \vec{E}\,dQ$$
$$= Q\vec{E}$$


-Q
-Q

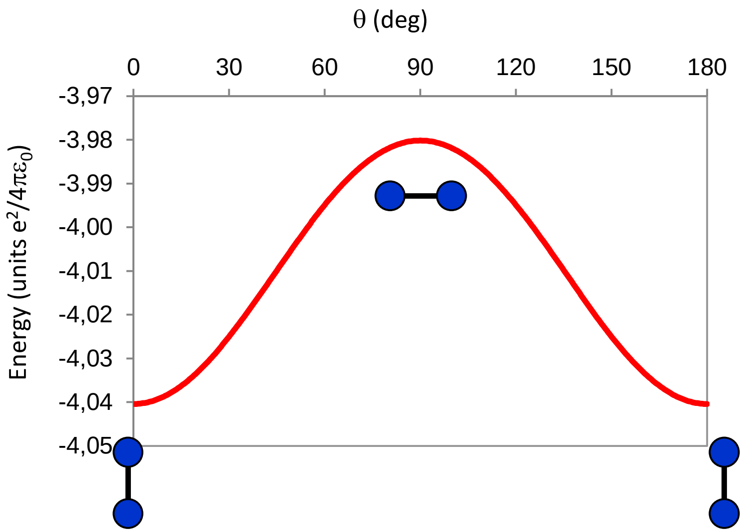


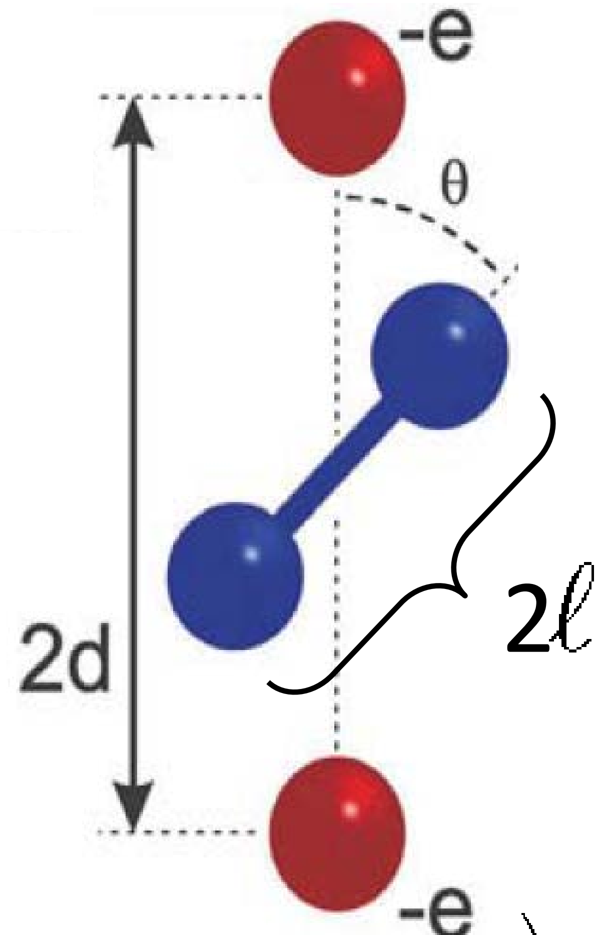
-Q
-Q


-e
θ
2d
-e



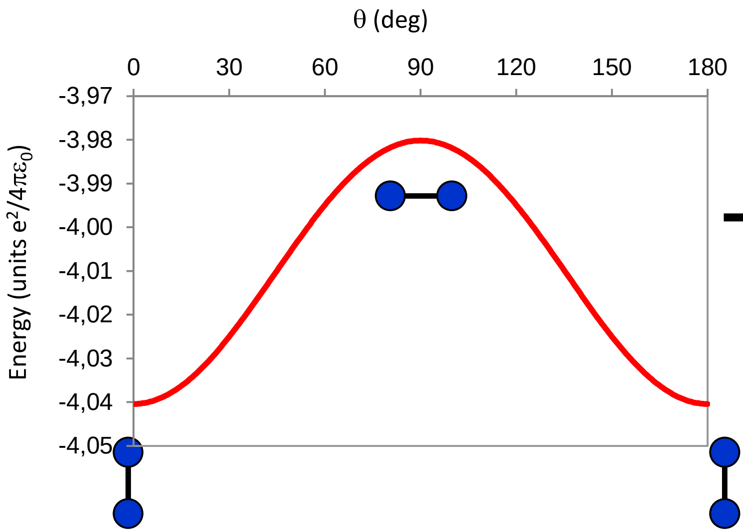
-e
θ
2ℓ
2d
-e



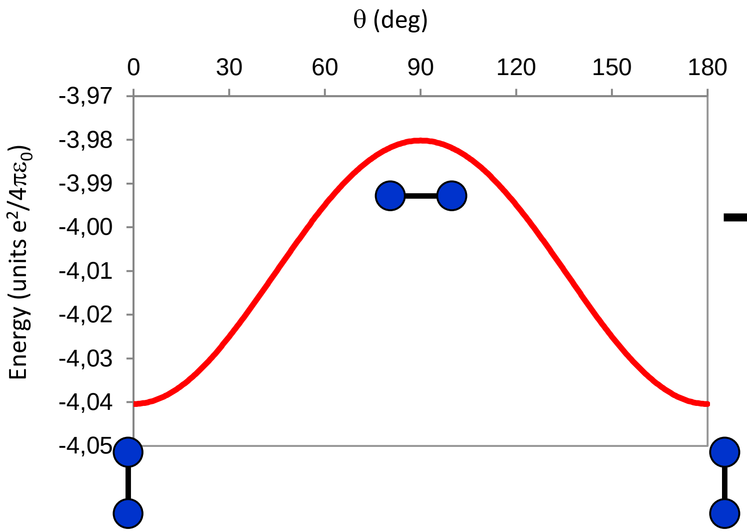


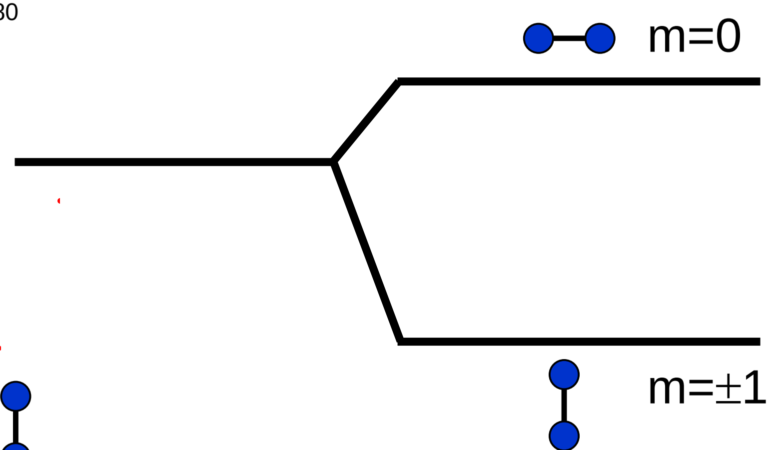
$$C = \mathrm{e}^2/(4\pi\varepsilon_0)$$

$$E_0(\theta) = -2C\left(\frac{1}{\sqrt{\ell^2\sin^2\theta + (d-\ell\cos\theta)^2}} + \frac{1}{\sqrt{\ell^2\sin^2\theta + (d+\ell\cos\theta)^2}}\right)$$


θ (deg)
0
30
60
90
120
150
180
-3,97
-3,98
-3,99
-4,00
-4,01
-4,02
-4,03
-4,04
-4,05
Energy (units $e^2/4\pi\varepsilon_0$)

[redacted]



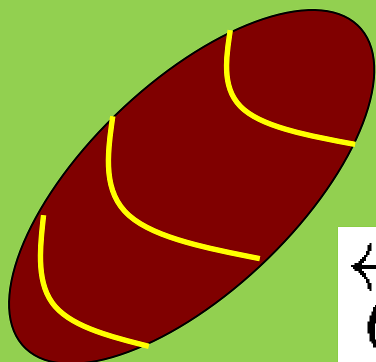


e.g. I = 1

$$H_{qq}^{nuc} = \frac{e\,Q\,V_{zz}}{4\,I(2I-1)\,\hbar^2}\left[(3I_z^2 - I^2) + \frac{\eta}{2}(I_+^2 + I_-^2)\right]$$

nuclear property

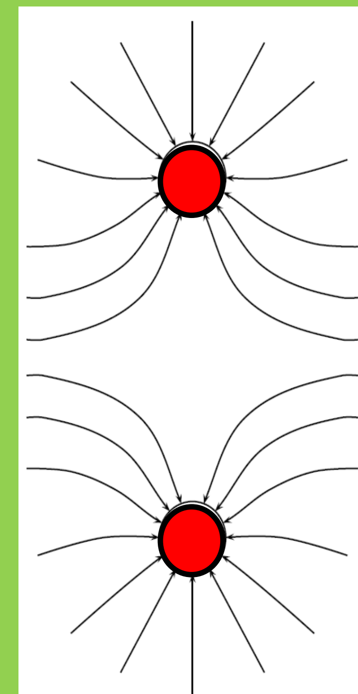
(tensor – rank 2)



$\overleftrightarrow{Q}$

electron property

(tensor – rank 2)



$\overleftrightarrow{V}$

interaction energy (dot product) :

$$E_Q \propto \overleftrightarrow{Q} \cdot \overleftrightarrow{V}$$

Electric field gradients (EFG)

- Nuclei with a nuclear quantum number $I \geq 1$ have an electrical quadrupole moment **Q**
- Nuclear quadrupole interaction (NQI) can aid to determine the distribution of the electronic charge surrounding such a nuclear site
- Experiments
  - *NMR*
  - *NQR*
  - *Mössbauer*
  - *PAC*

$$\boxed{\nu \approx eQ\Phi / h}$$

Nuclear electronic

Φ EFG traceless tensor

$$\Phi_{ij} = V_{ij} - \frac{1}{3}\delta_{ij}\nabla^2 V$$

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

with $\boxed{V_{xx} + V_{yy} + V_{zz} = 0}$ traceless

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

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

EFG V_{zz}

principal component

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

asymmetry parameter

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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and

P. Herzig
Institut für Physikalische Chemie, Universität Wien, A-1090 Vienna, Austria

(Received 5 December 1984)

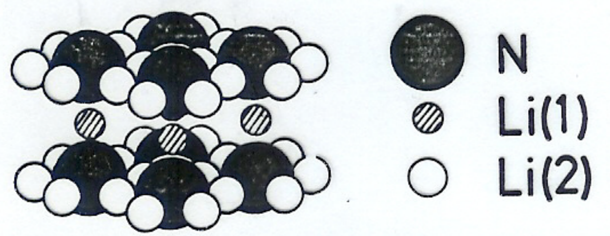


Fig. 1. Crystal structure of Li_3N with increased c dimension

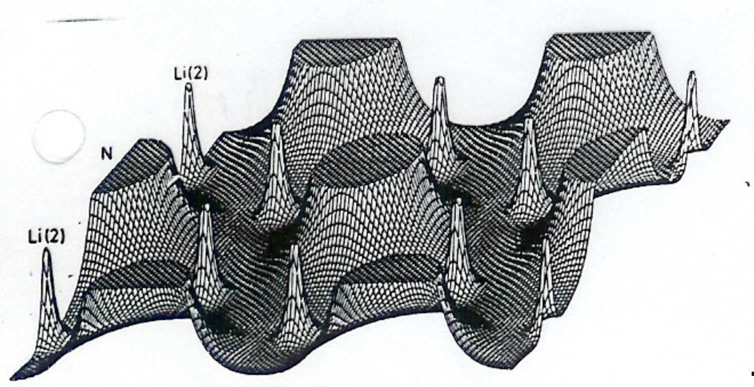


TABLE I. Electric field gradient Φ_{zz} in 10^{20} V m^{-2}.

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

<u>Sternheimer factor</u> to experimental value

Electronic structure of Li_3N

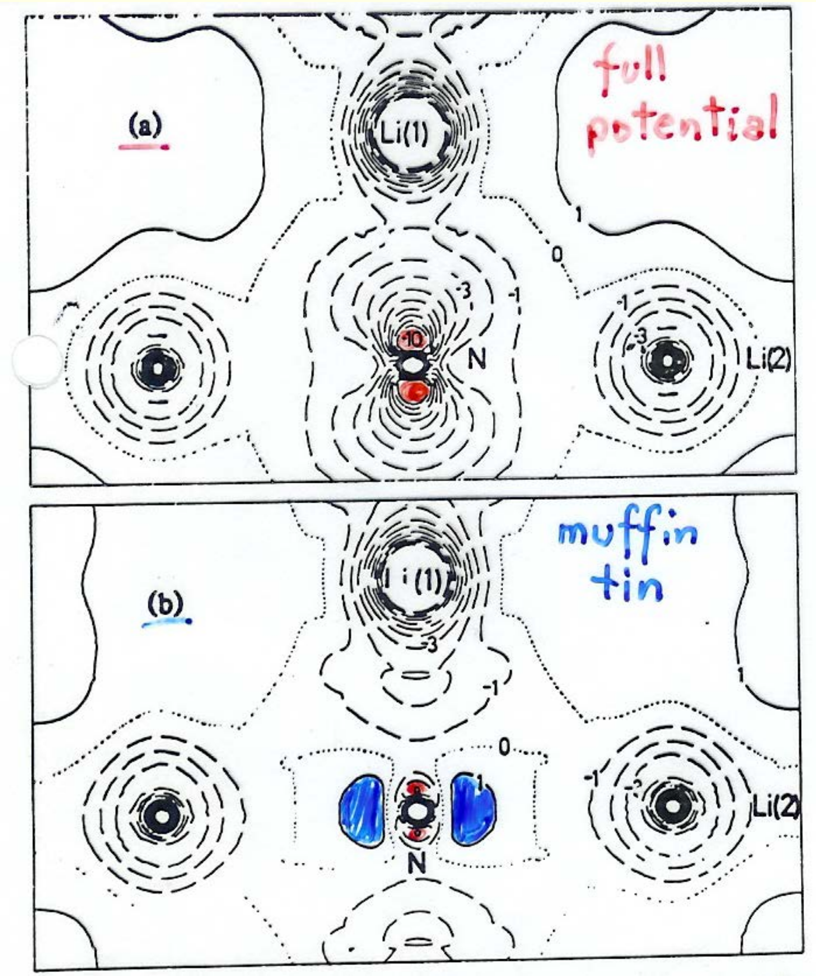
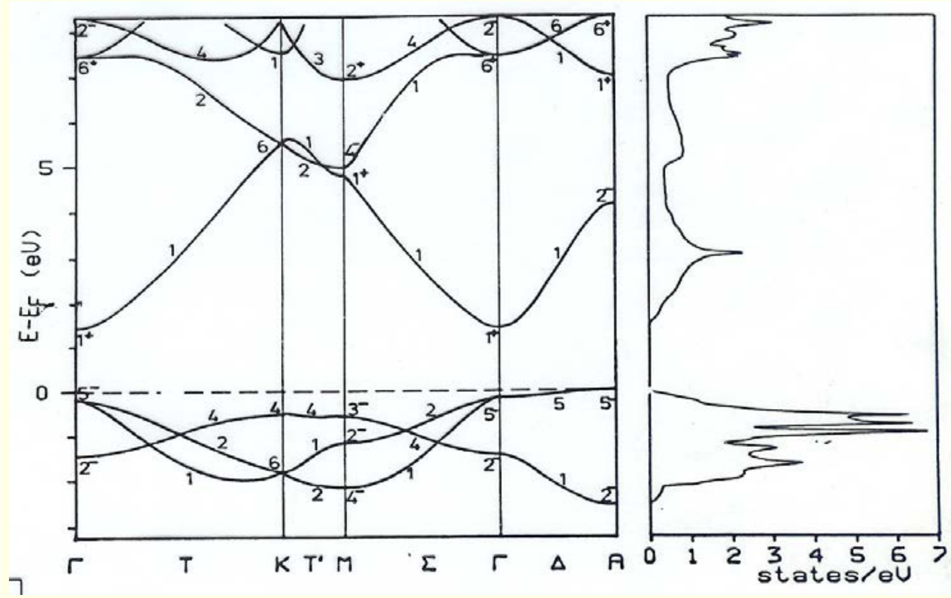


FIG. 1. Difference electron density of Li_3N in the $(1\bar{1}0)$ plane with respect to a superposition of Li^+ and N^{3-} ionic densities; contour intervals and numbers are in units of 0.01 $e\,\text{Å}^{-3}$: (a) GP-LAPW (present work), (b) MT-LAPW [taken from Fig. 5(b) of Ref. 10].



- The charge anisotropy around N differs strongly between
  - muffin-tin and
  - full-potential
- affecting the EFG.

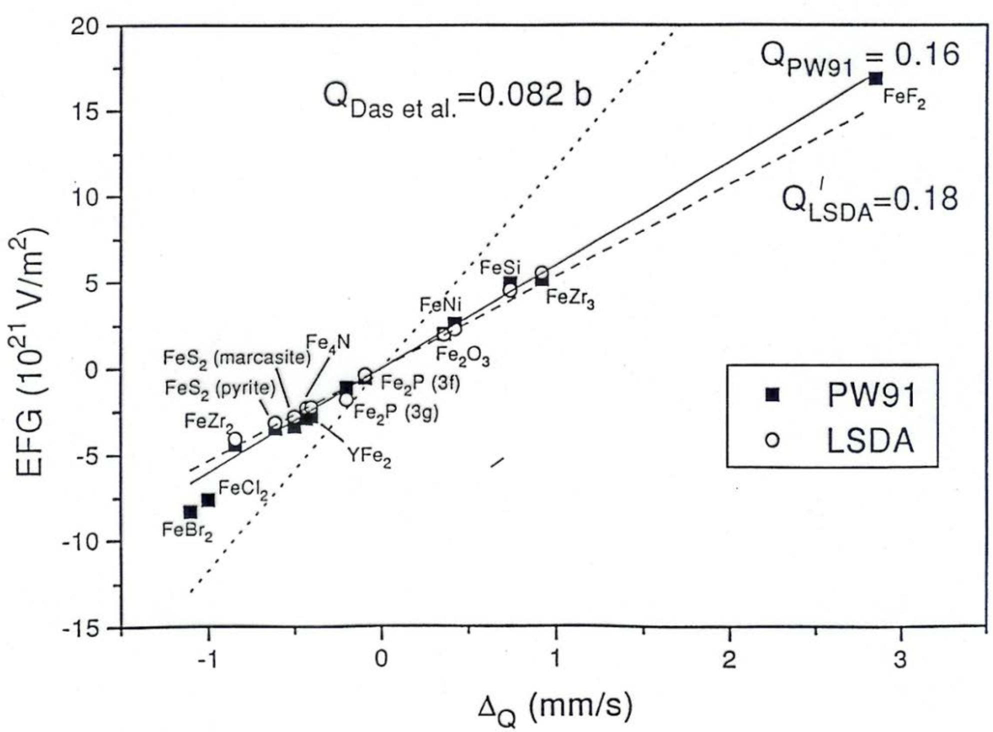
Nuclear quadrupole moment of ^{57}Fe

VOLUME 75, NUMBER 19 , 3545 PHYSICAL REVIEW LETTERS 6 NOVEMBER 1995

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

Philipp Dufek, Peter Blaha, and Karlheinz Schwarz
Institut für Technische Elektrochemie, Technische Universität Wien, A-1060 Vienna, Austria
(Received 17 July 1995)

Theoretical and experimental Fe-EFG in Fe-compounds



- 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:

EFG is a tensor of second derivatives of V_C at the nucleus:

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

$$V_c(r) = \int \frac{\rho(r')}{r - r'} dr' = \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r})$$

Cartesian LM-repr.

$$V_{zz} \propto V_{20}(r=0)$$

$$V_{yy} \propto -\tfrac{1}{2} V_{20} - V_{22}$$

$$V_{xx} \propto -\tfrac{1}{2} V_{20} + V_{22}$$

$$V_{zz} \propto \int \frac{\rho(r) Y_{20}}{r^3} dr \quad = V_{zz}^p + V_{zz}^d$$

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

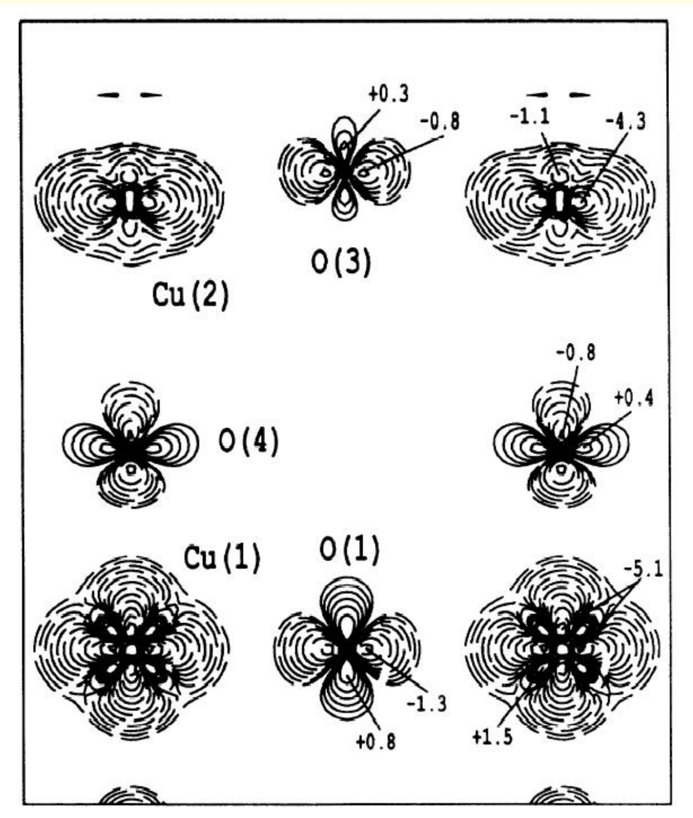
$$V_{zz}^d \propto \left\langle \frac{1}{r^3} \right\rangle_d \left[d_{xy} + d_{x^2-y^2} - \tfrac{1}{2}(d_{xz} + d_{yz}) - d_{z^2} \right]$$

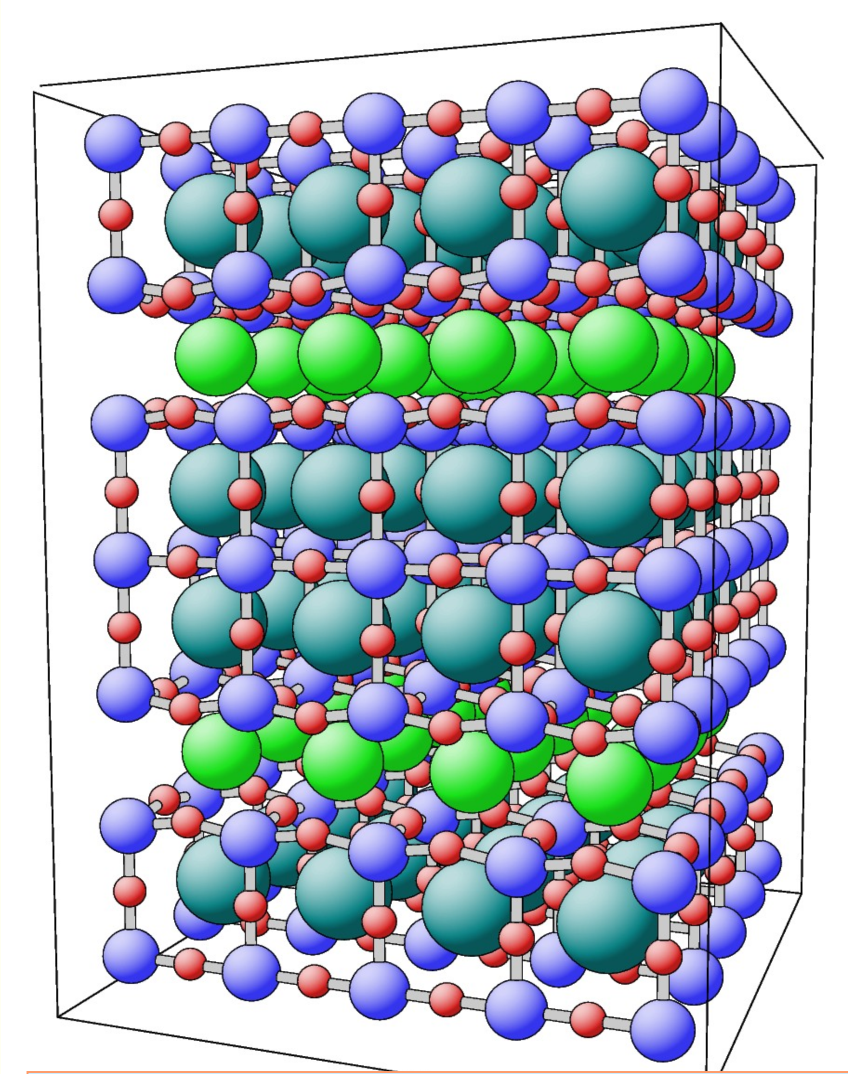
EFG is proportional to differences in orbital occupations

High temperature superconductor

- $YBa_2Cu_3O_7$
- Electronic structure
- Charge density, EFG

  EFG (electric field gradient)



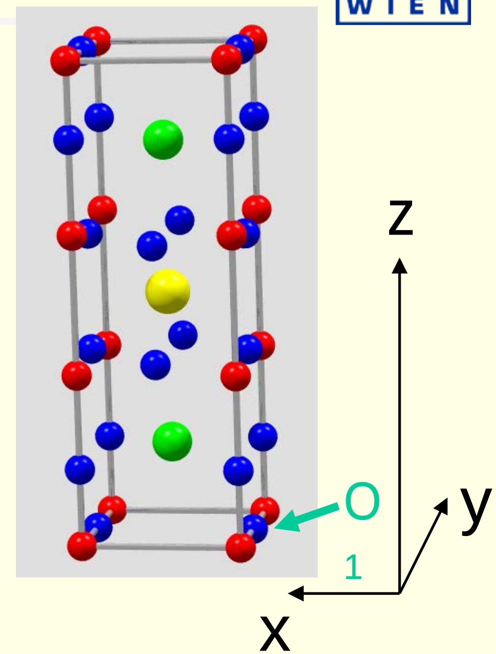


K.Schwarz, C.Ambrosch-Draxl, P.Blaha, Phys.Rev. B 42, 2051 (1990)

EFG at O sites in $YBa_2Cu_3O_7$

- Interpretation of the EFG (measured by NQR) 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**

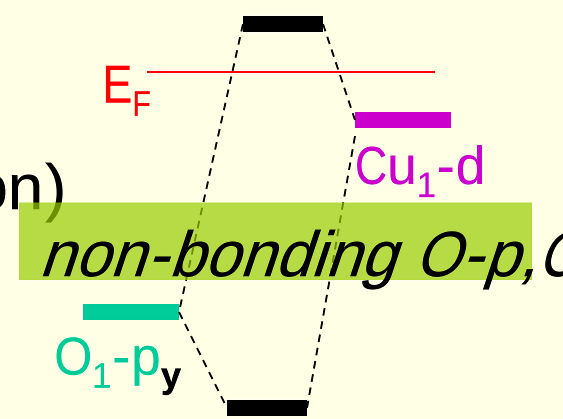


Asymmetry count

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

EFG (p-contribution)

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

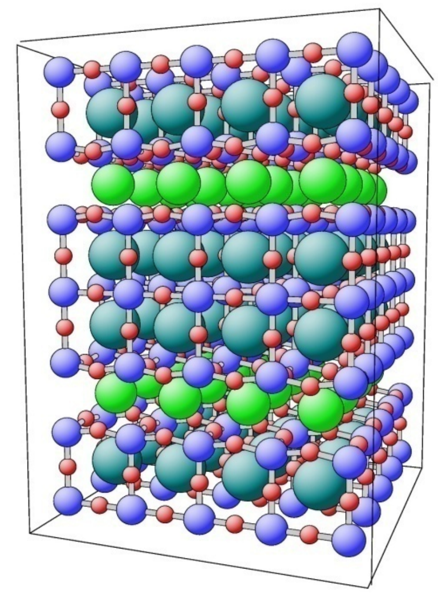


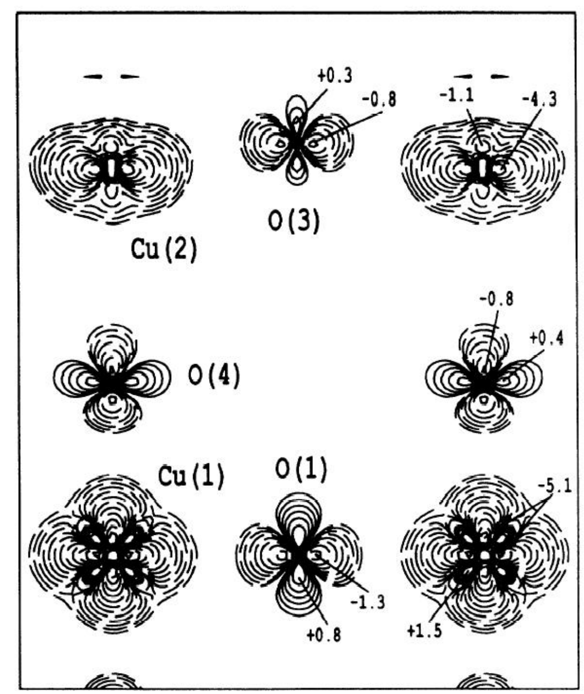
EFG is proportional to asymmetric charge distribution around given nucleus

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, P.Blaha, Phys.Rev. B46, 5849 (1992)

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

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

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

V^{p}_{zz} = 0.038 x 250 = 9.5 (10^{21} V/m^2)

V^{d}_{zz} = -.288 x 47 = -13.5

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

V^{d}_{zz} = -.14 x 47 = -6.6

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

How to do it in WIEN2k ?

Electric-field gradient

In regular scf file:

```
:EFGxxx
:ETAxxx
Main directions of the EFG
```

5 degrees of freedom

Full analysis printed in case.output2
if EFG keyword in case.in2 is put (UG 7.6)
(split into many different contributions)

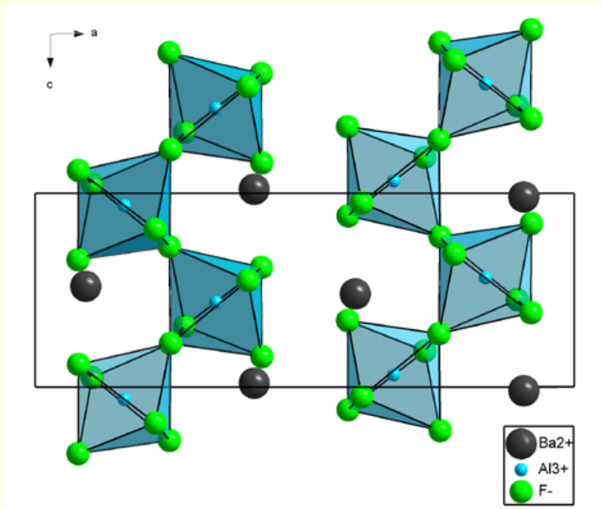
more info:

- Blaha, Schwarz, Dederichs, PRB 37 (1988) 2792
- EFG document in wien2k FAQ (Katrin Koch, SC)

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

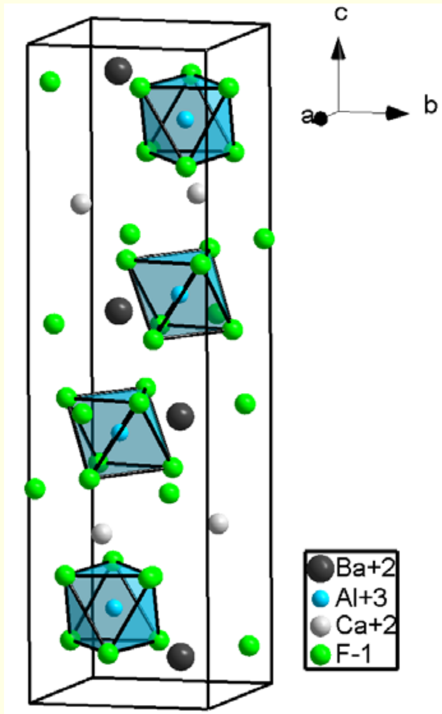


α-$BaAlF_5$

α-$CaAlF_5$, β-$CaAlF_5$,

β-$BaAlF_5$, γ-

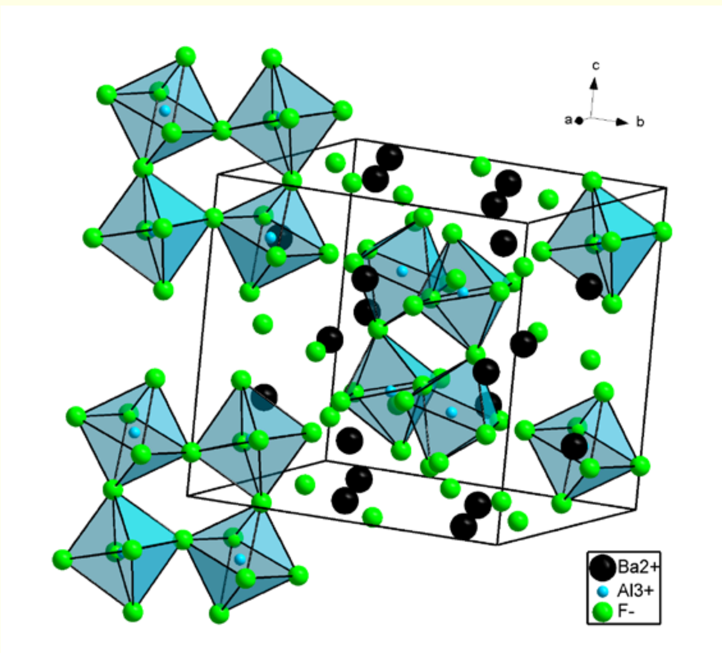
Isolated octahedra



α-$BaCaAlF_7$

Ca_2AlF_7, Ba_3AlF_9-Ib,

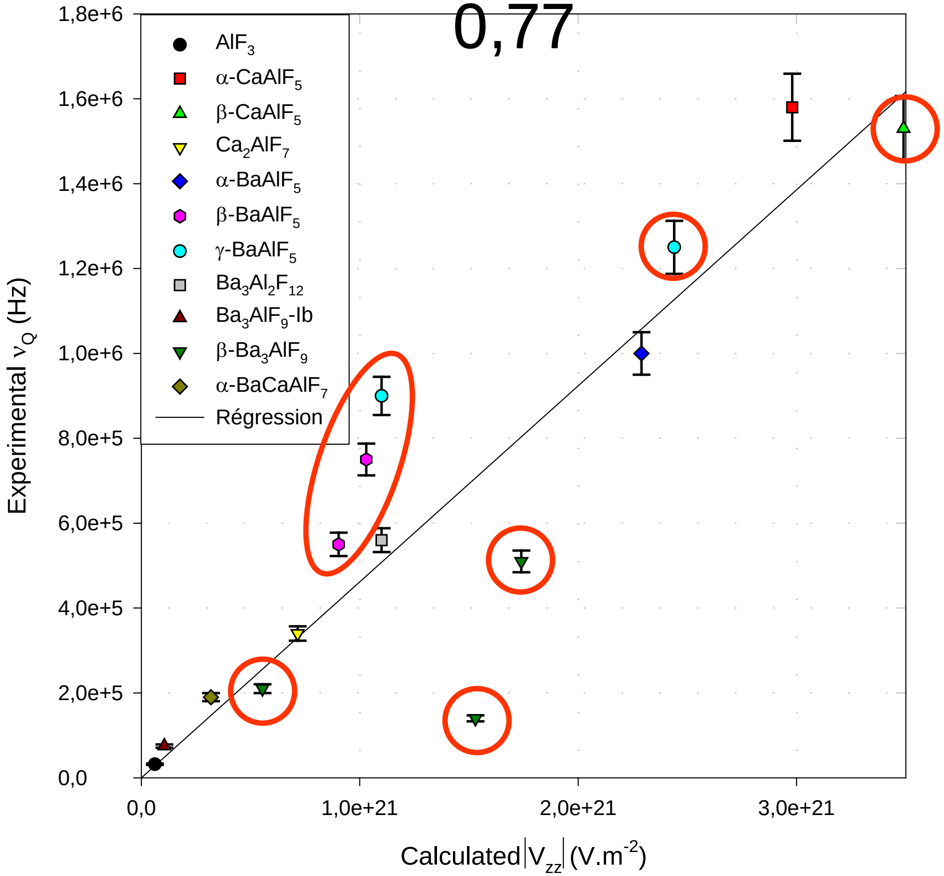
Rings formed by four octahedra sharing corners



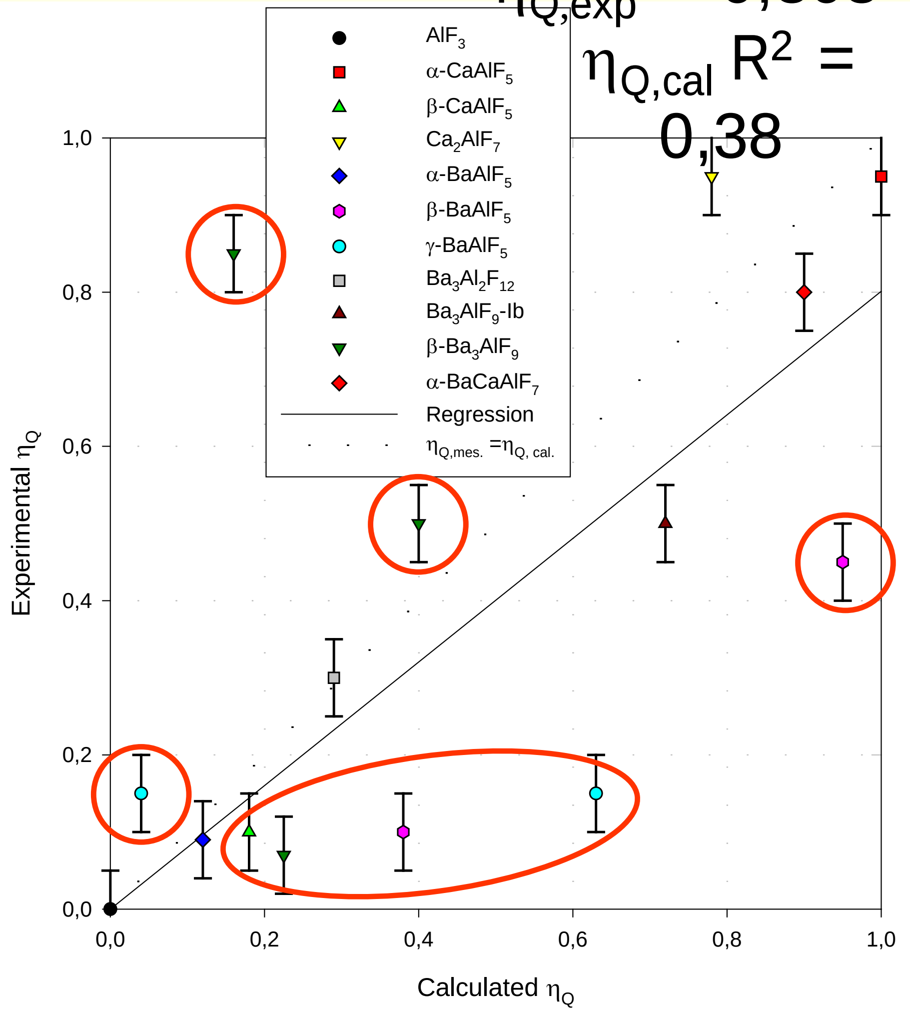
$Ba_3Al_2F_{12}$

ν_Q and η_Q calculations **using XRD data**

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

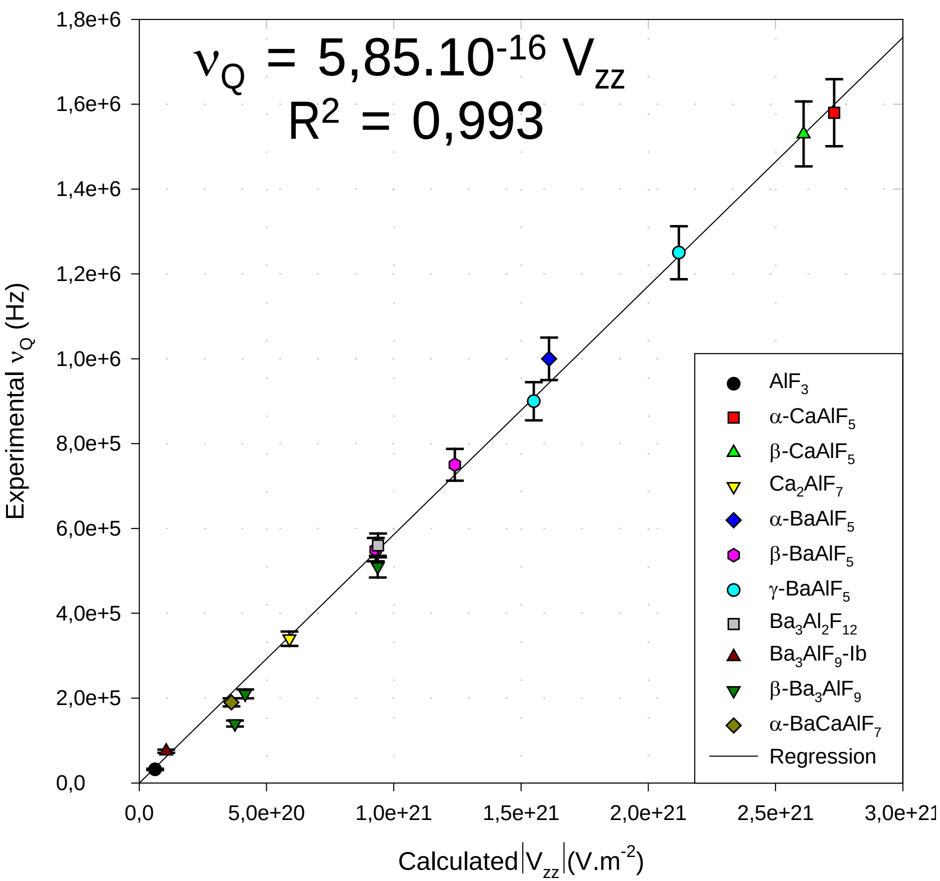


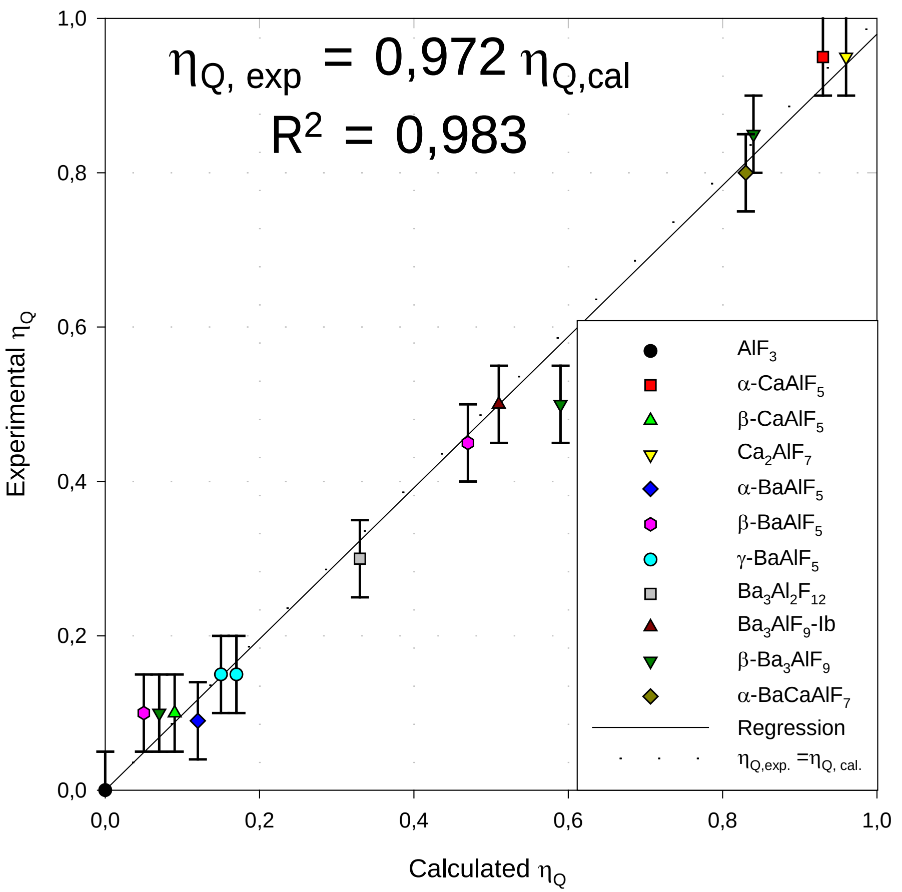
$\eta_{Q,exp}$ = 0,803 $\eta_{Q,cal}$ R^2 = 0,38



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

ν_Q and η_Q after structure optimization

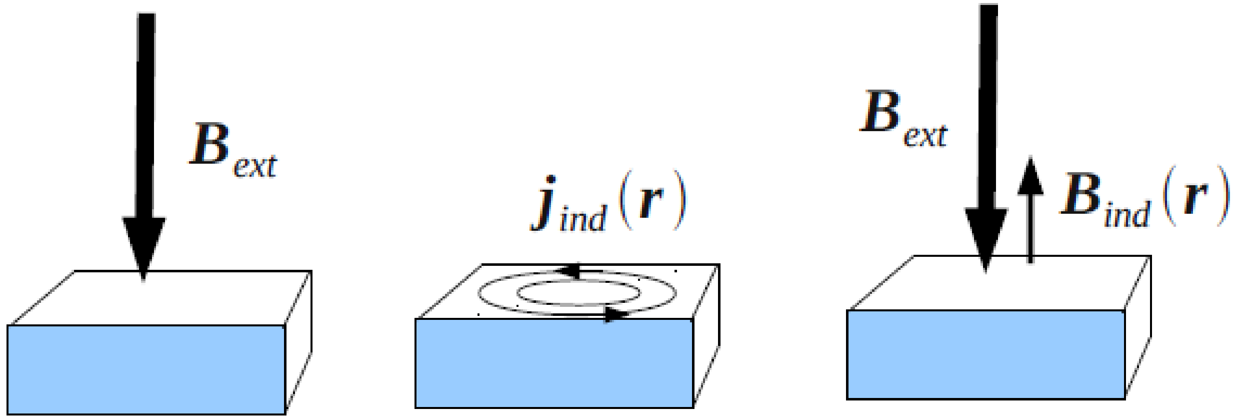




Very fine agreement between experimental and calculated values

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

NMR shielding, chemical shift:



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

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

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

chemical shift: $\delta(ppm) = \frac{\sigma_{ref} - \sigma}{\sigma_{ref}}\ x\ 10^6$

Content

- Definitions
- magnetic hyperfine interaction
- electric quadrupole interaction
- isomer shift
- summary

$YBaFe_2O_5$ HFF, IS and EFG with GGA+U, LDA/GGA

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

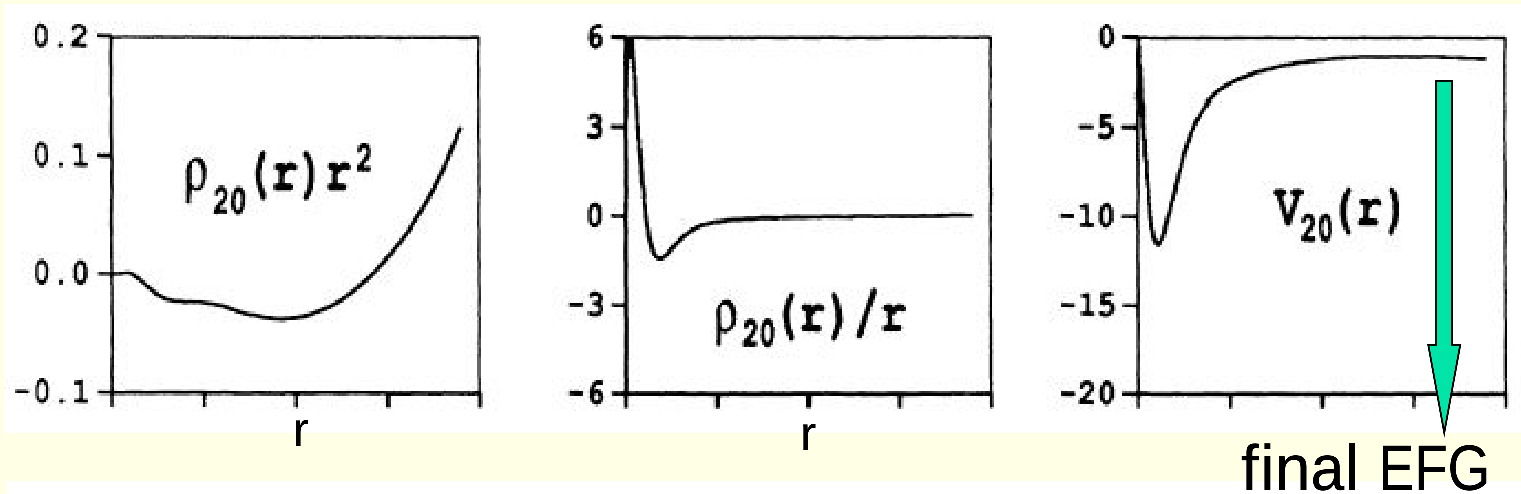
		exp.	GGA+U				LDA	GGA
	U_{eff} [eV]	—	5	6	7	8	—	—
$Fe^{2.5+}$	B_{dip}	—	-3.00	-2.98	-2.95	-2.87	-2.13	-2.83
	B_{orb}	—	-3.11	-2.99	-2.84	-2.74	-5.47	-4.56
	$B_{contact}$	—	41.17	40.96	41.45	41.17	33.10	36.36
	B_{tot}	~ 30	35.06	34.98	35.67	35.56	25.50	28.98
	δ	~ 0.5	0.53	0.52	0.51	0.49	0.60	0.60
	eQV_{zz}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

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

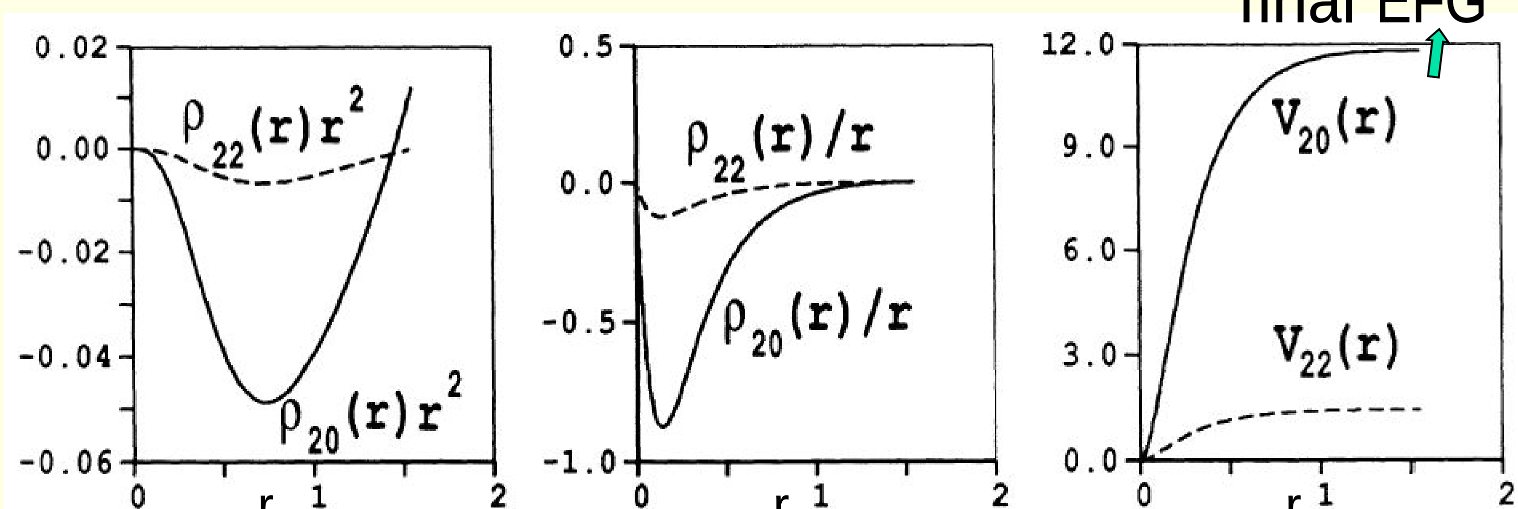
- EFG is determined by the non-spherical charge density inside sphere

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

- Cu(2)

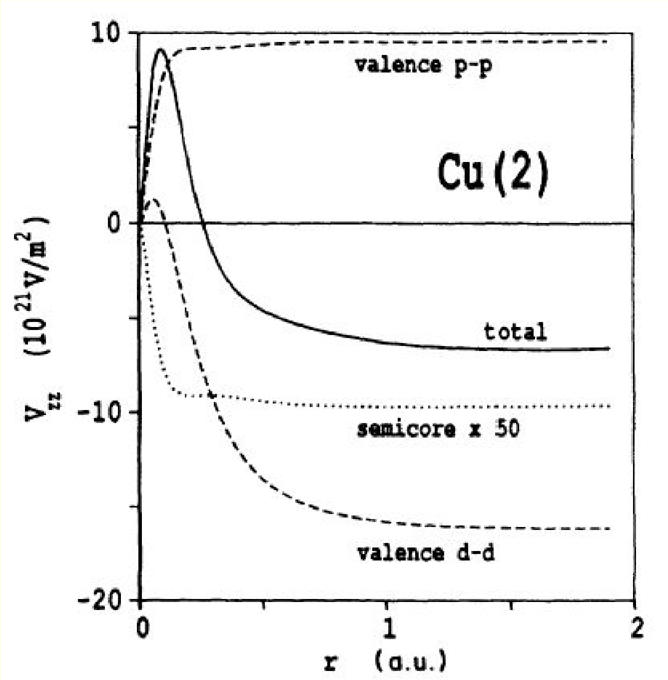


- O(4)



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.