Center for
Molecular
Modeling

UNIVERSITEIT
GENT

Department of
Materials Science
and Engineering

hyperfine interactions

(and how to do it in WIEN2k)

my talks on YouTube
http://goo.gl/P2b1Hs

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Kohn-Sham equations

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

nuclear point charges interacting with electron charge distribution

1-electron equations (Kohn Sham)

vary ρ

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

-Z/r

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

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

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

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

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

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

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

Slide by K. Schwarz

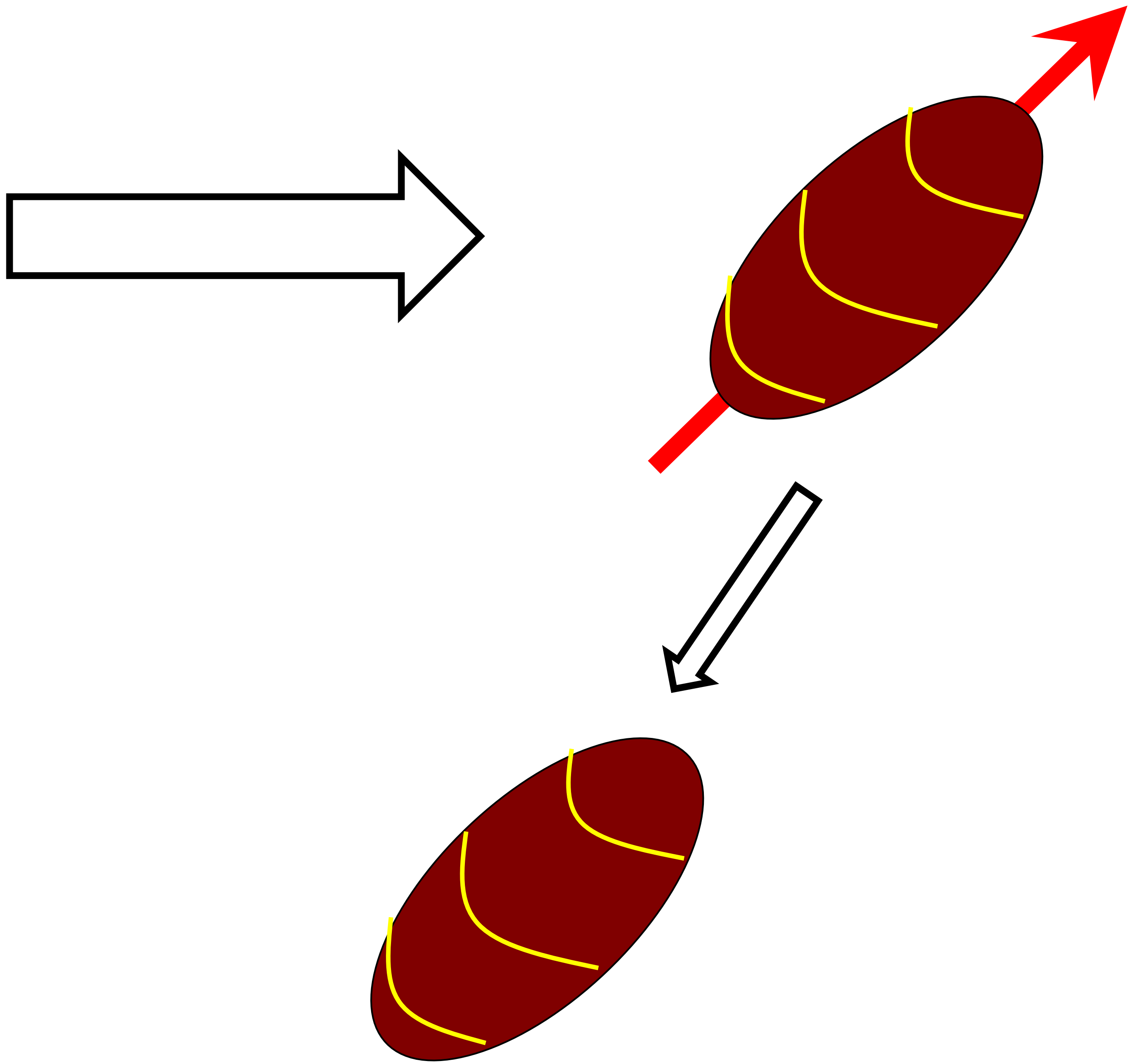
Definition :

hyperfine interaction

=

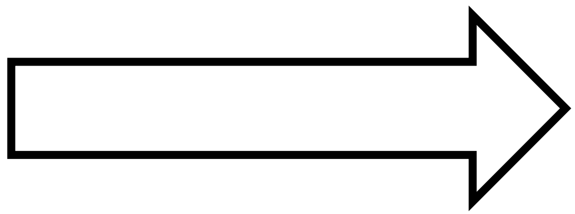
all aspects of the
nucleus-electron interaction
that go beyond
the nucleus as an electric point charge.

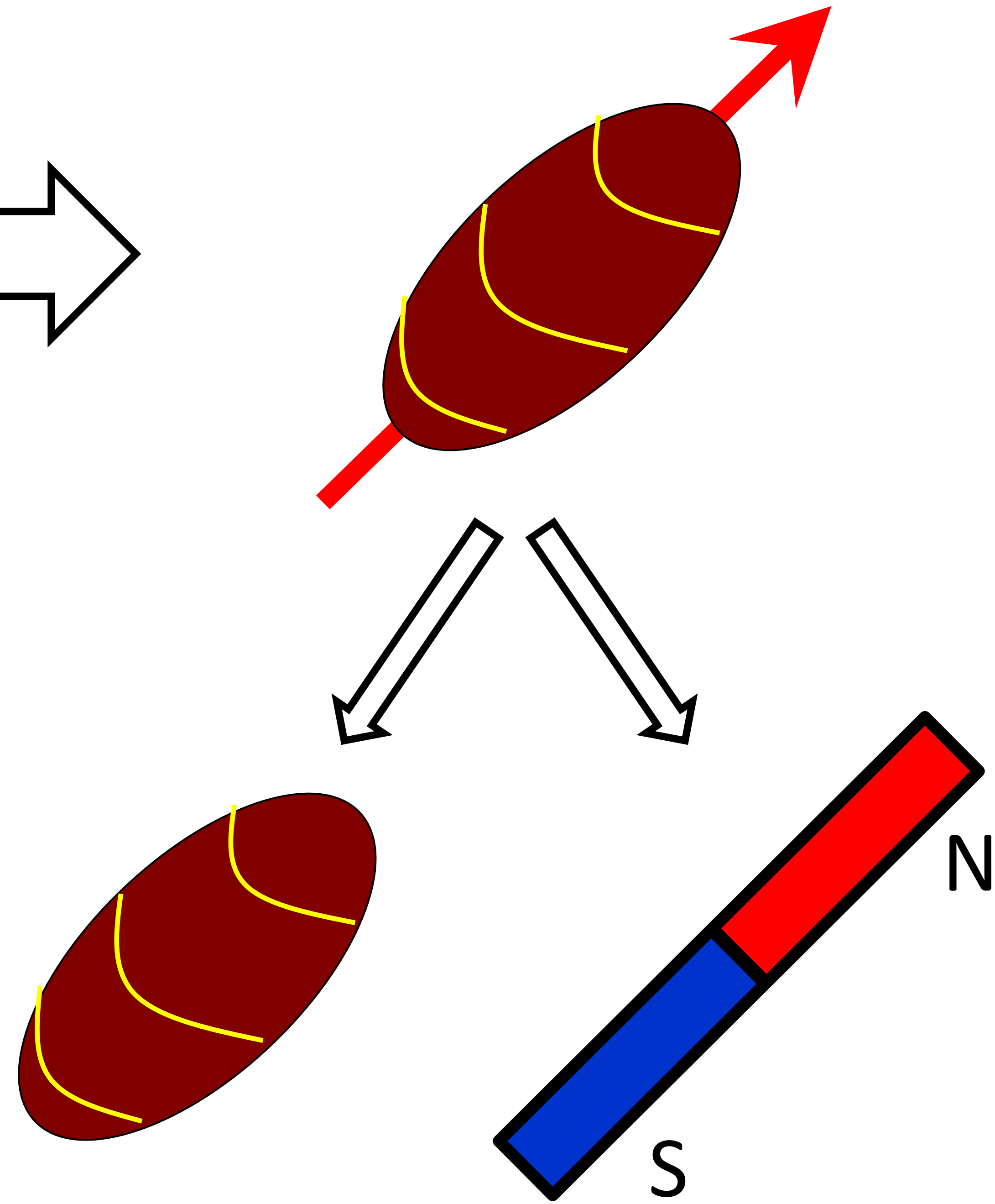
electric
~~point~~
charge



- volume
- shape

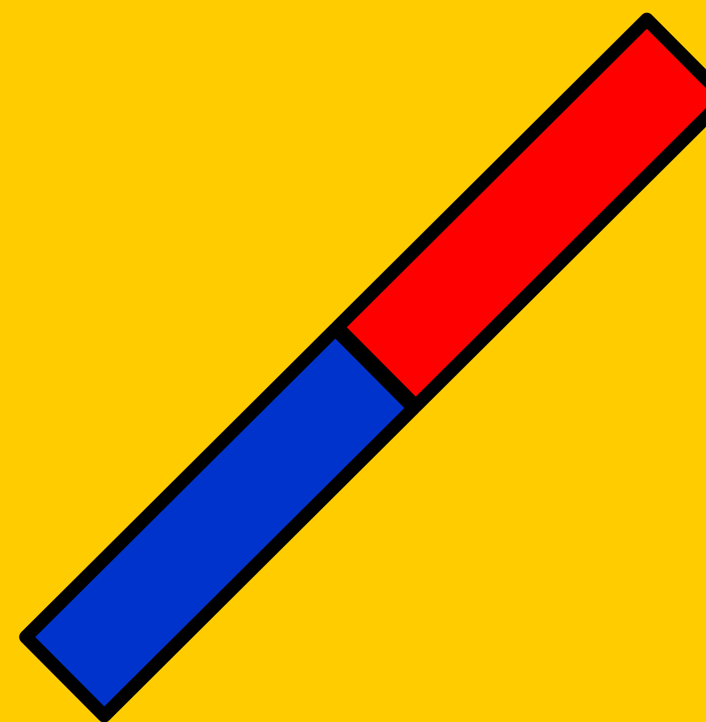
~~electric~~
point
~~charge~~

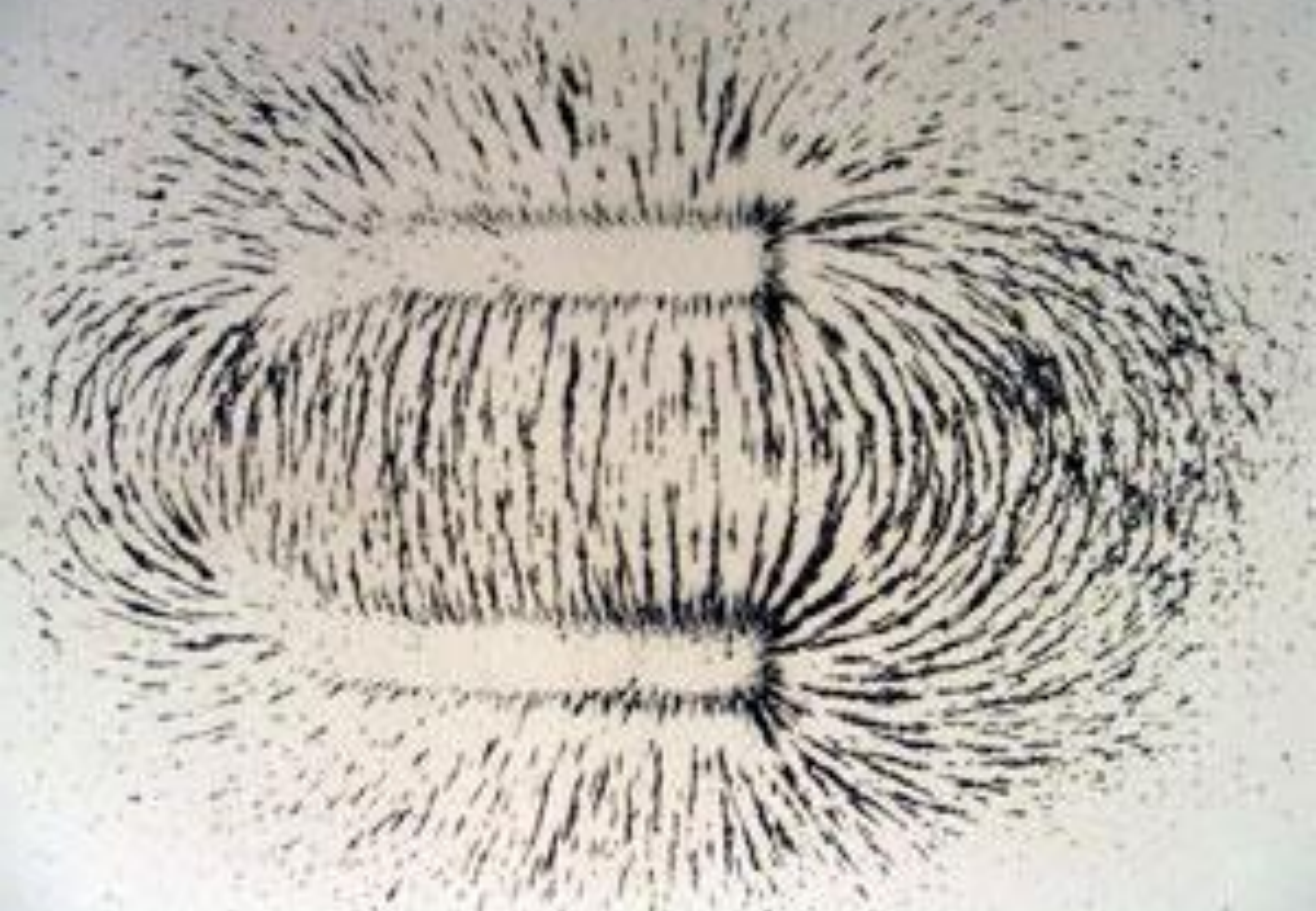


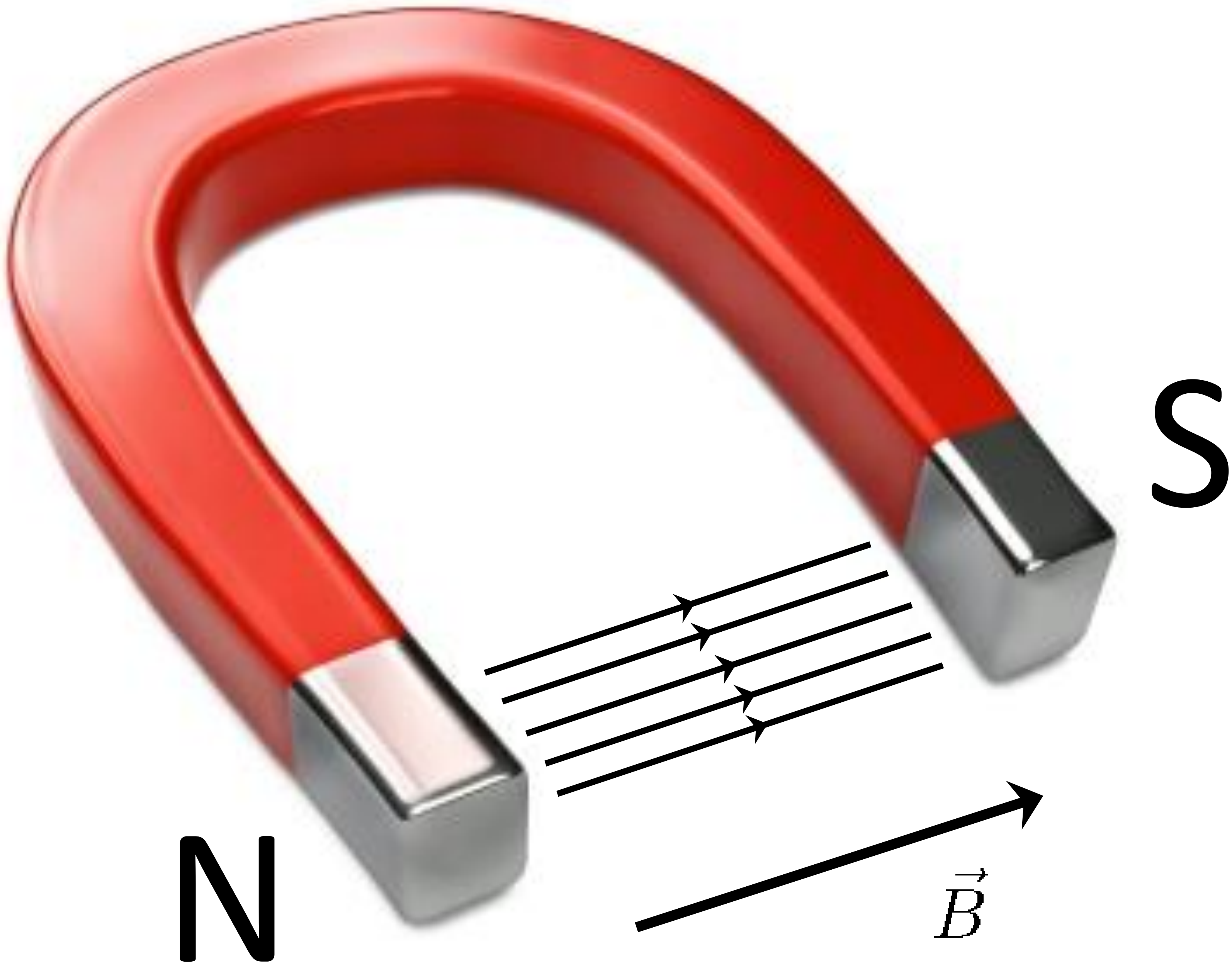


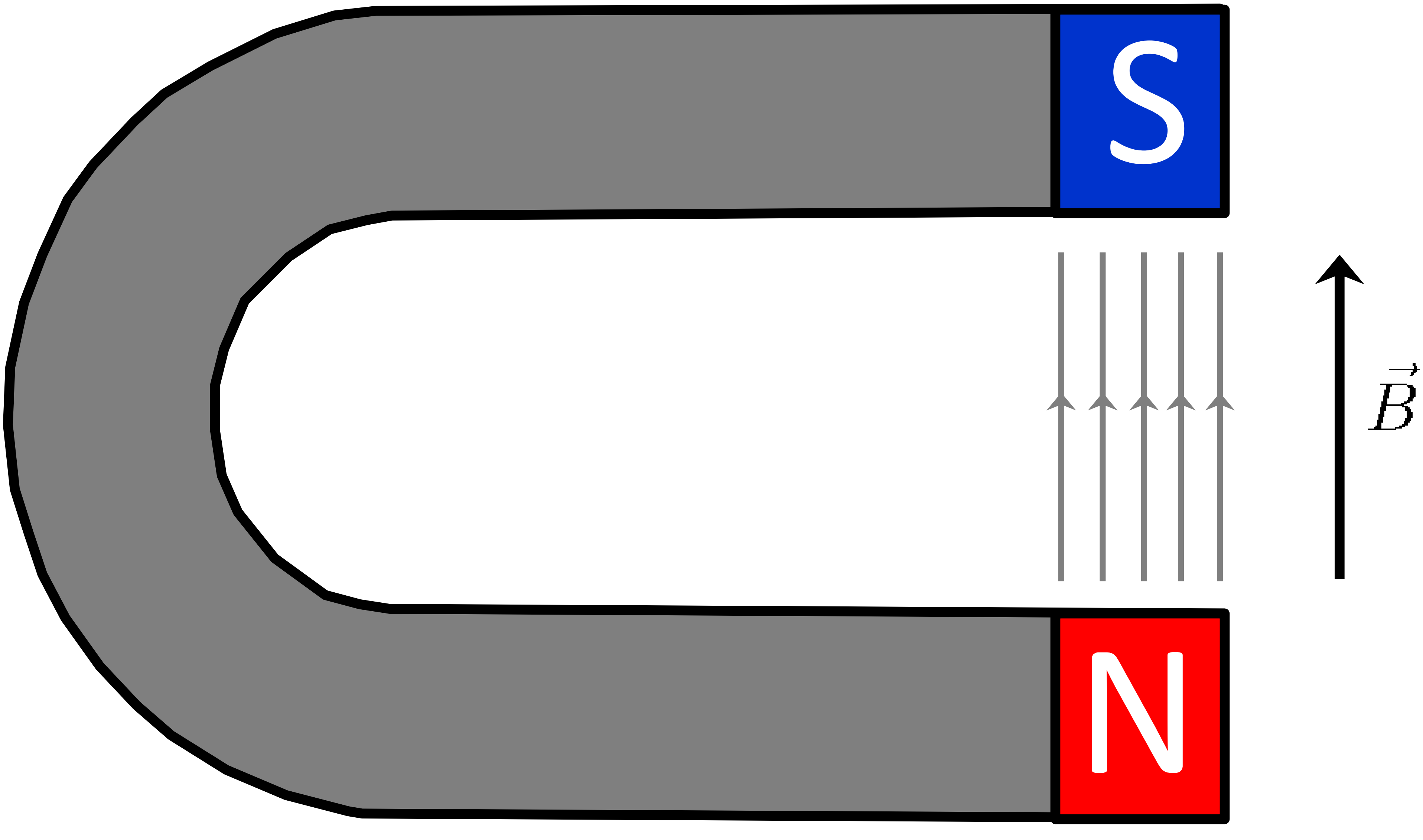
- volume
- shape
- magnetic moment

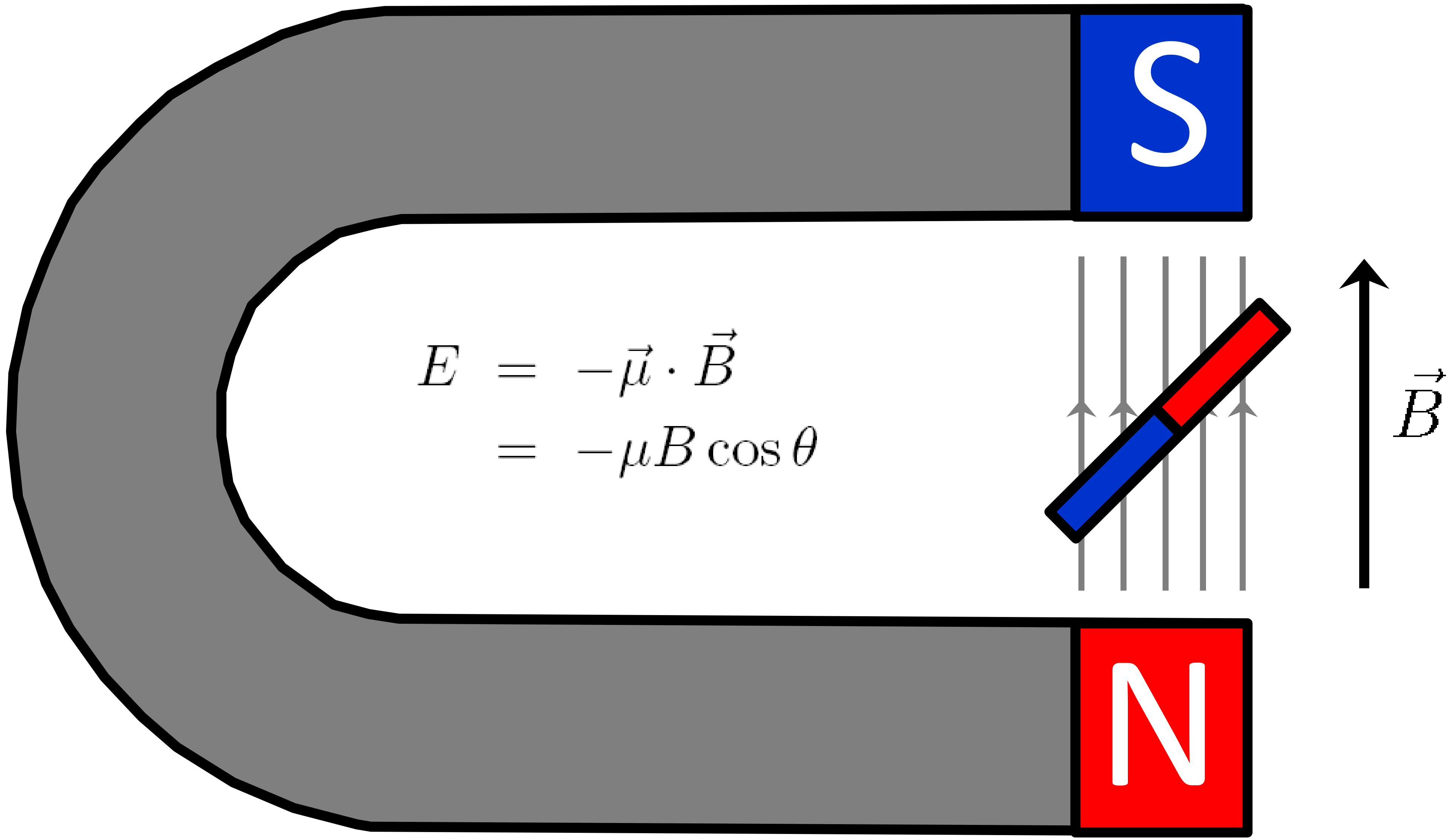
- magnetic hyperfine interaction
- electric quadrupole interaction
- isomer shift

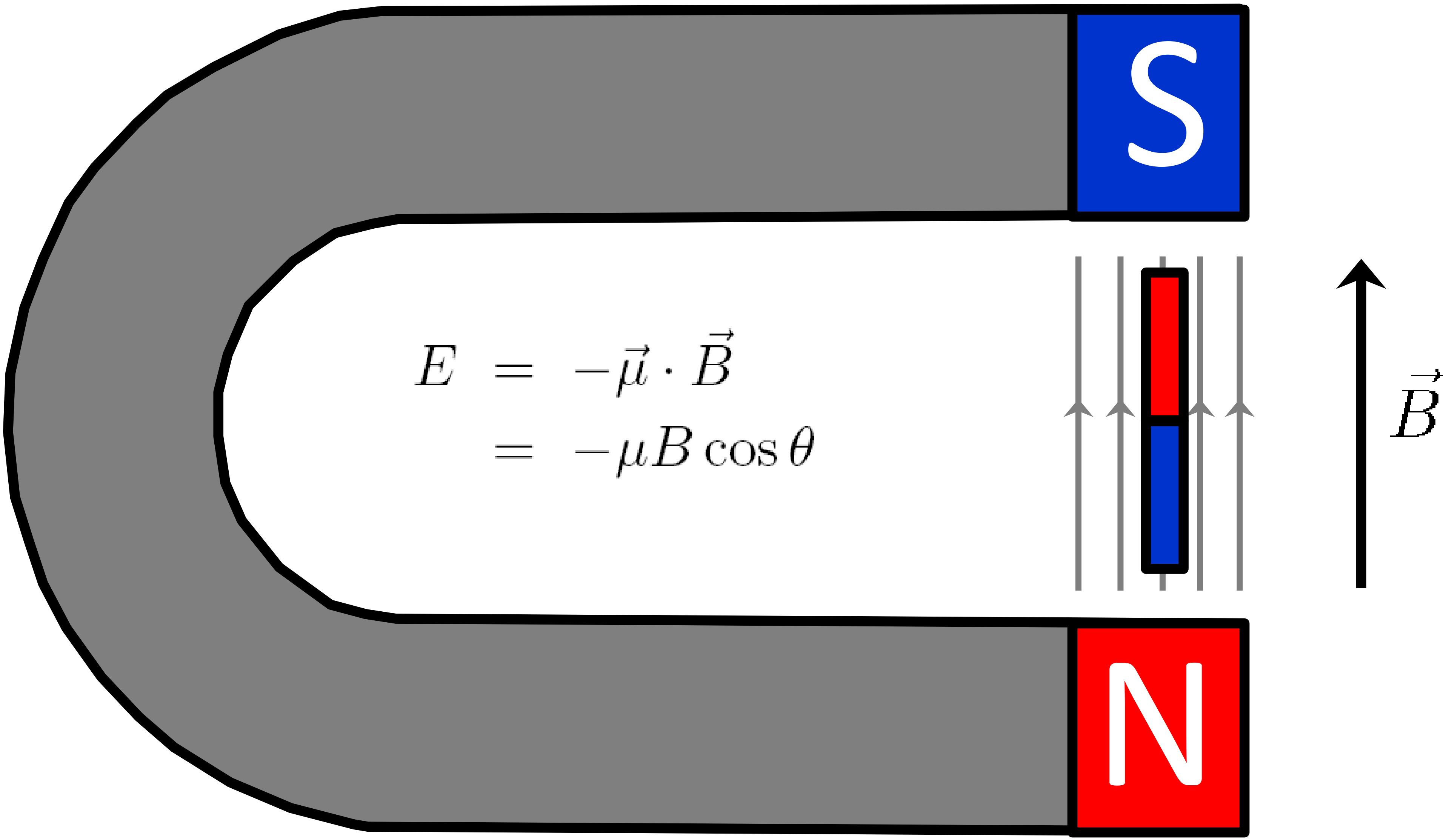





S
N
$\vec{B}$


S
N
$\vec{B}$


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


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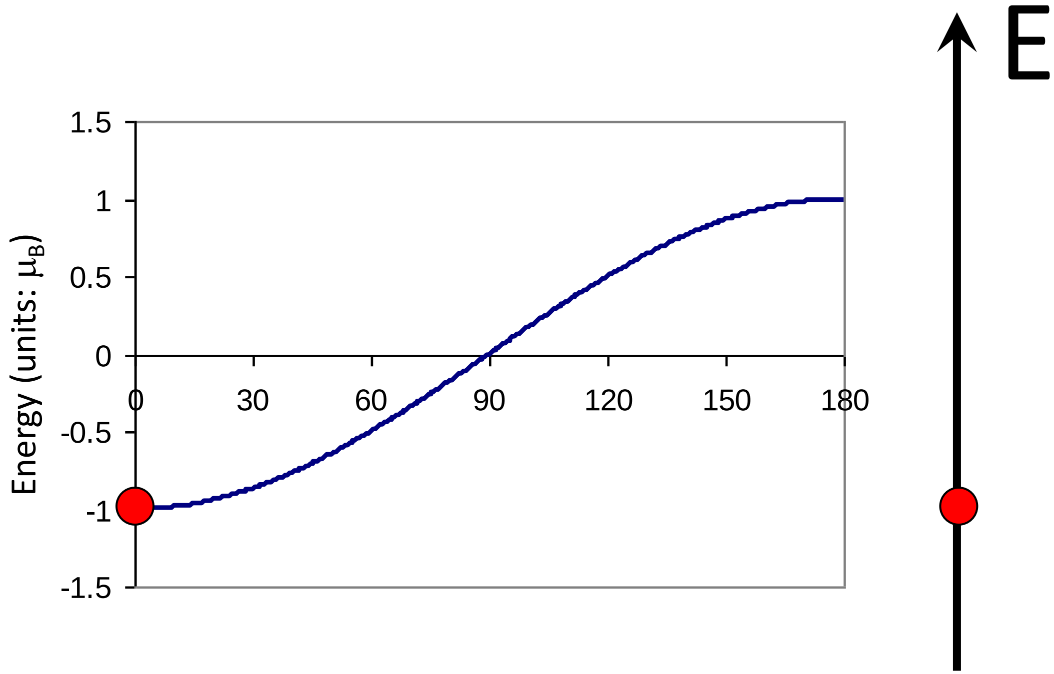
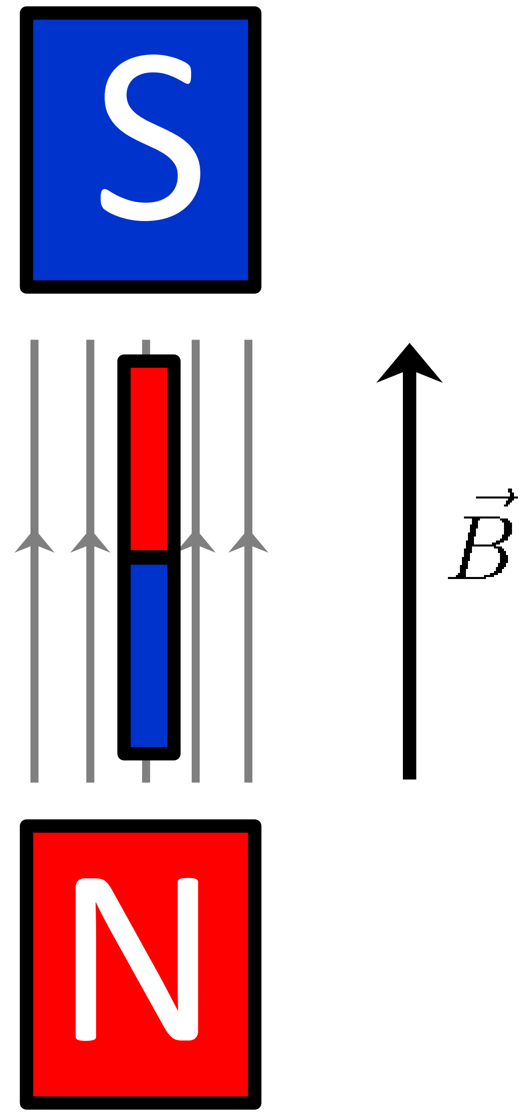
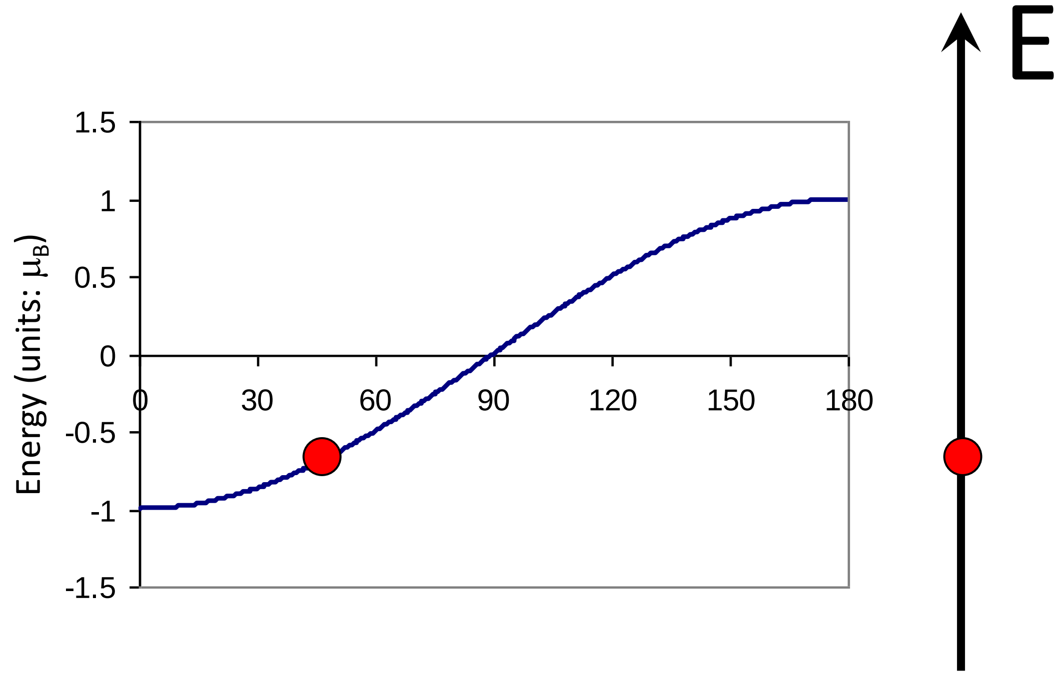
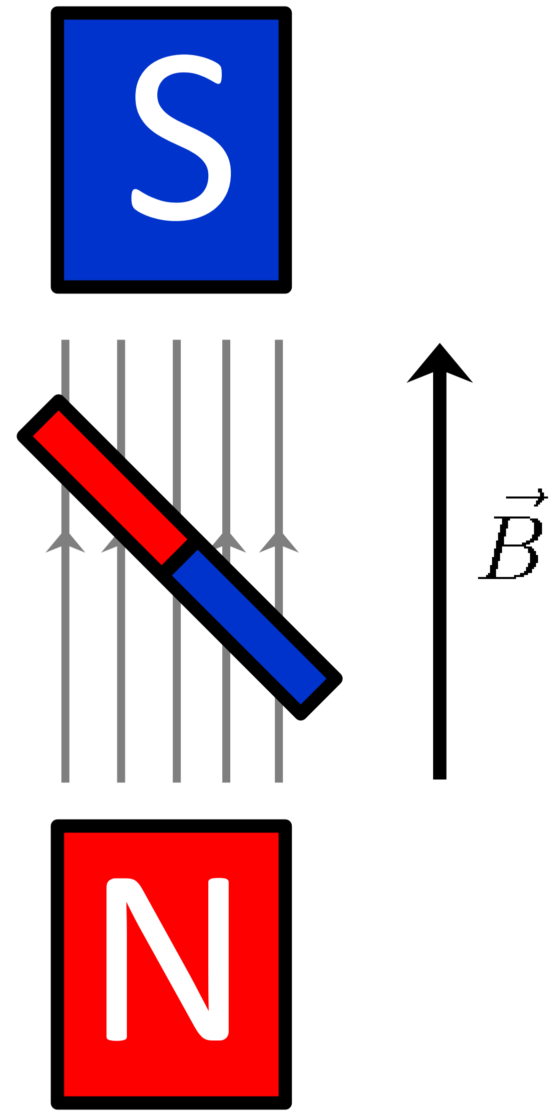
$\vec{B}$



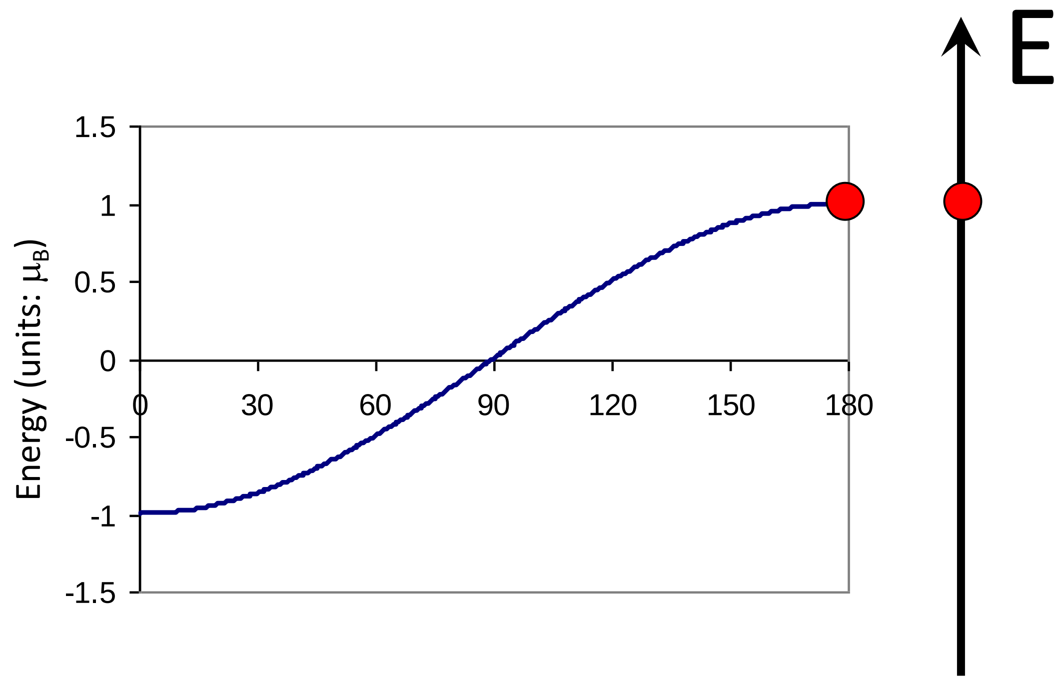


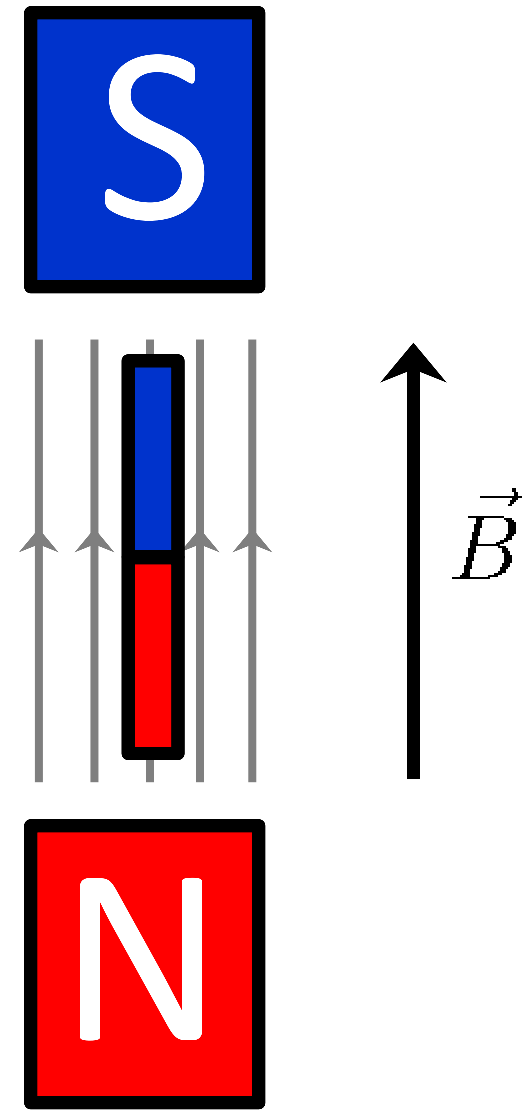
$$
\begin{aligned}
E &= -\vec{\mu}\cdot\vec{B} \\
&= -\mu B\cos\theta
\end{aligned}
$$



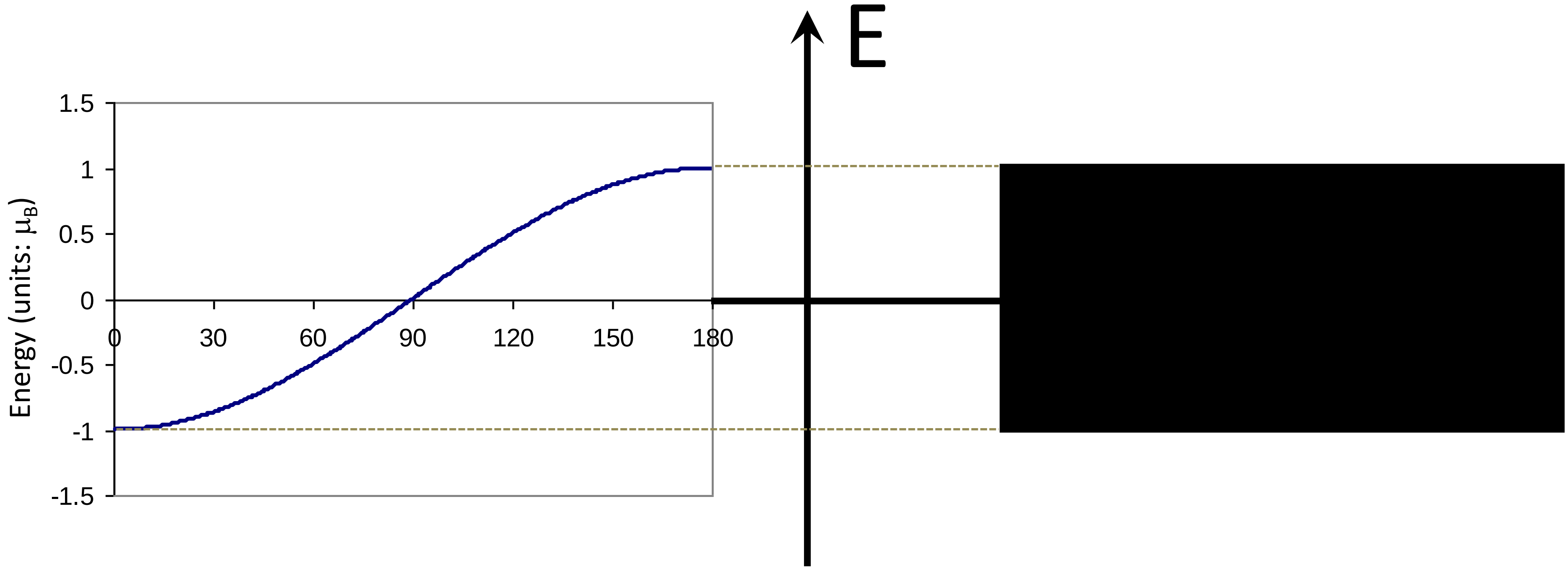


$$E = -\vec{\mu} \cdot \vec{B}$$
$$= -\mu B \cos\theta$$





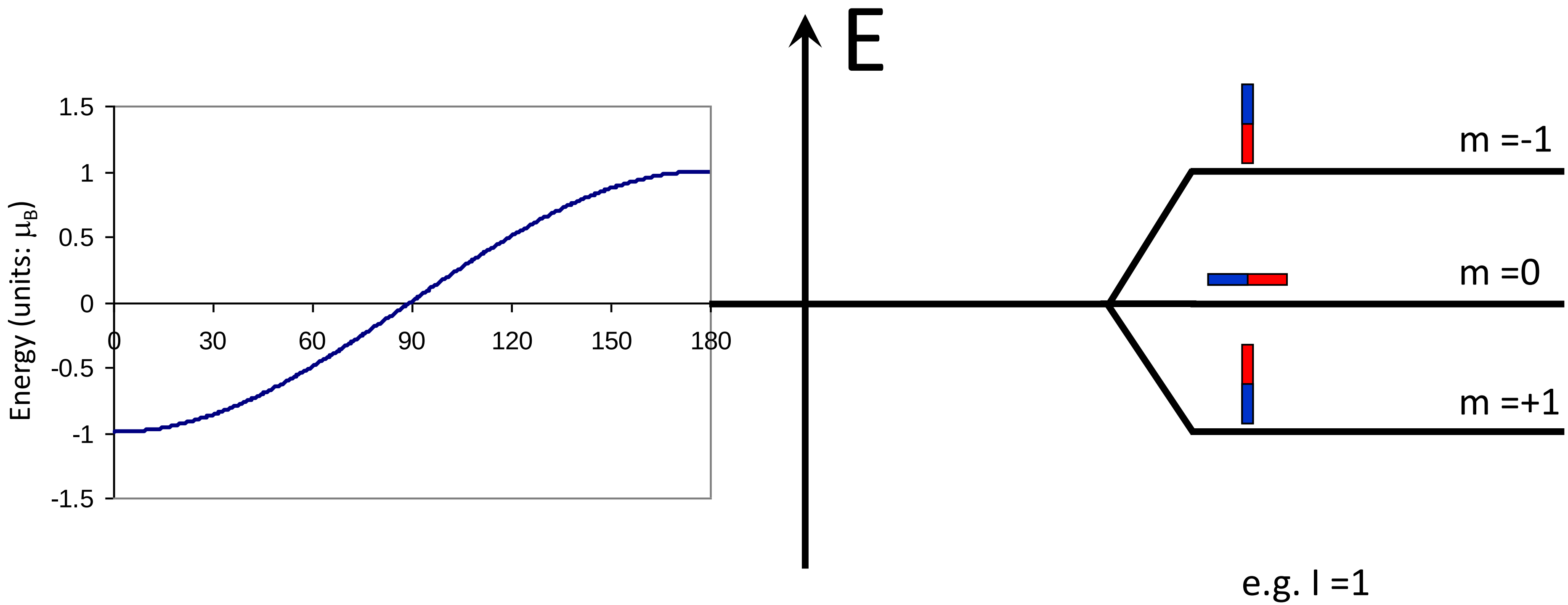
$$
\begin{aligned}
E &= -\vec{\mu} \cdot \vec{B} \\
&= -\mu B \cos\theta
\end{aligned}
$$



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

Classical

Quantum
(=quantization)

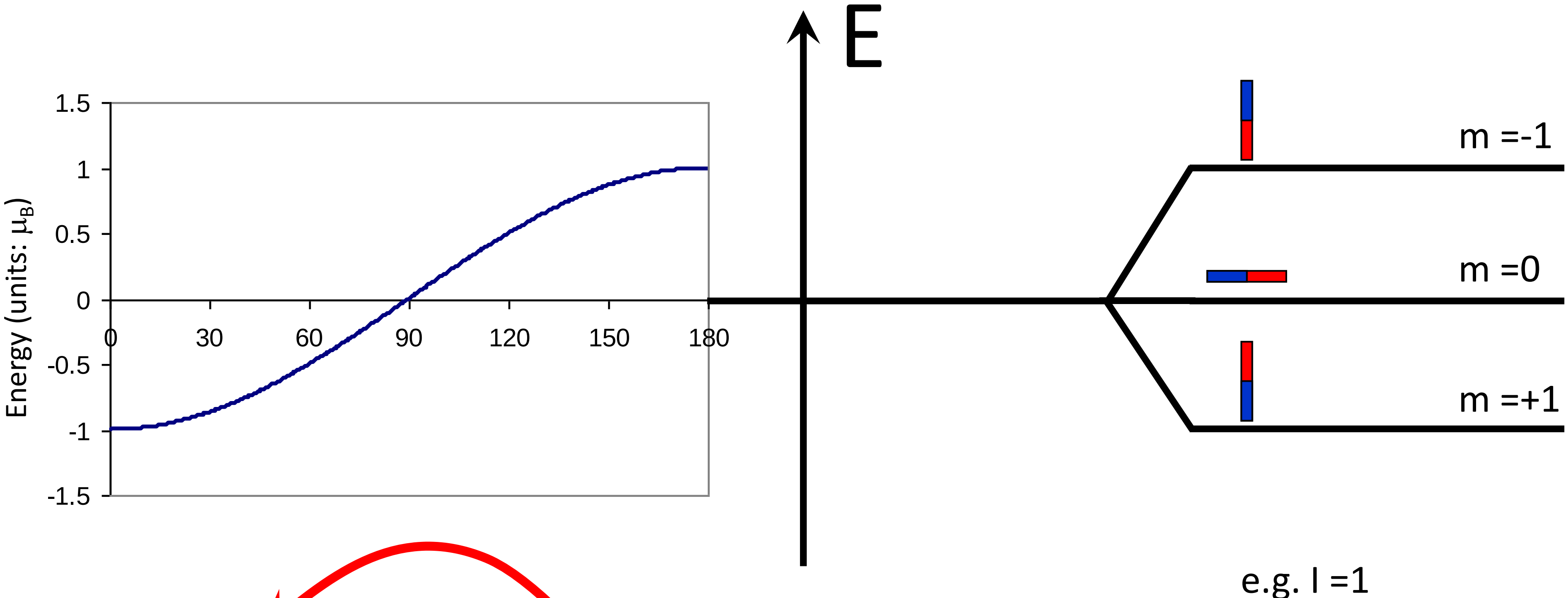


$$
\begin{aligned}
E &= -\vec{\mu}\cdot\vec{B} \\
&= -\mu B\cos\theta
\end{aligned}
$$

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

Classical

Quantum (=quantization)

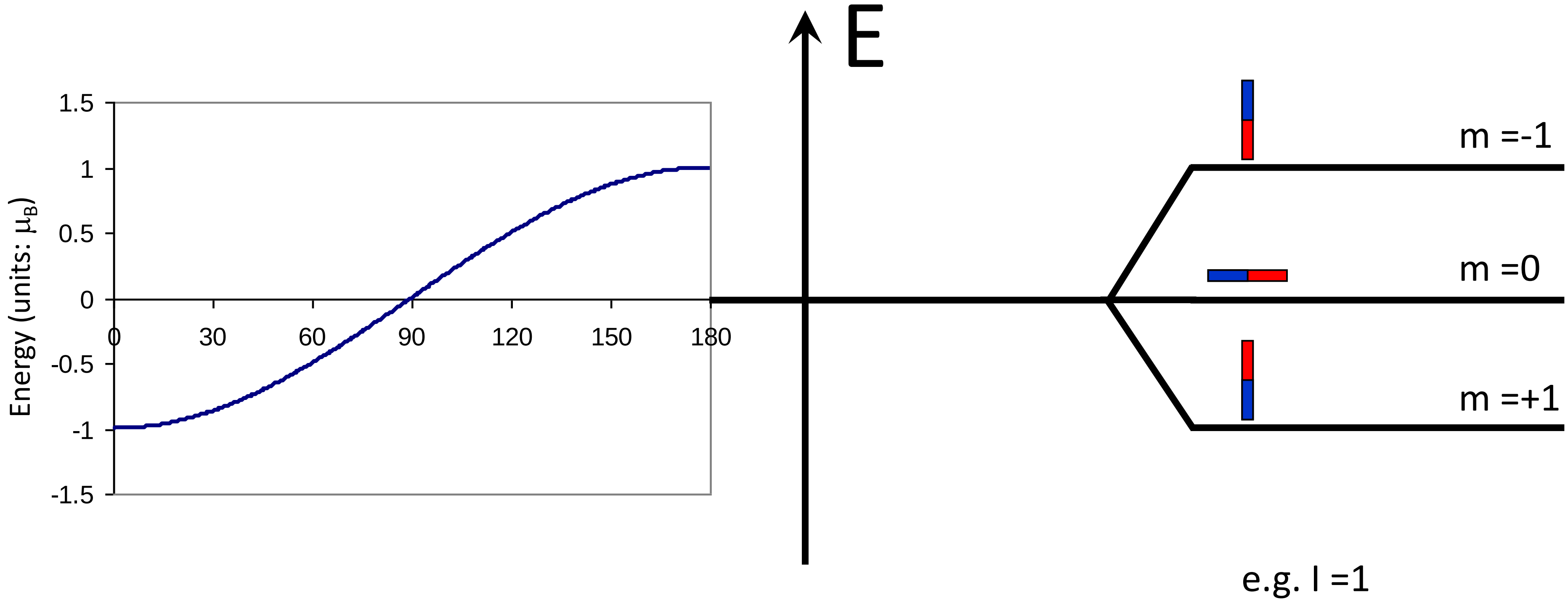


$$E = -\vec{\mu}\cdot\vec{B} = -\mu B\cos\theta$$

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

Classical

Quantum
(=quantization)

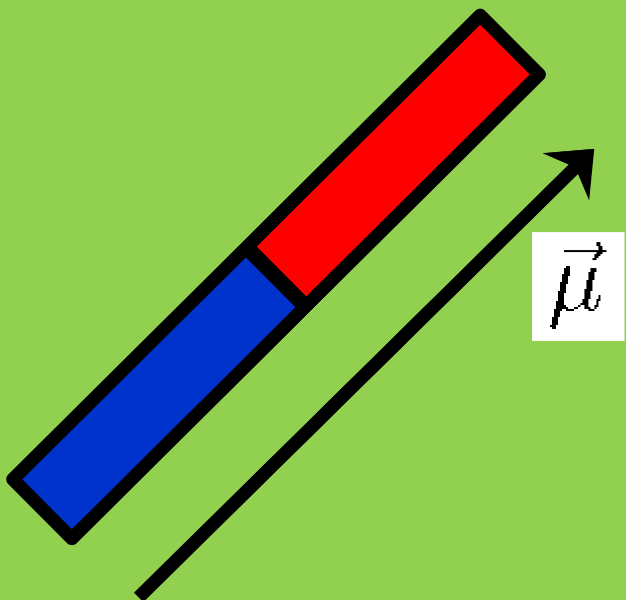


Hamiltonian :

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

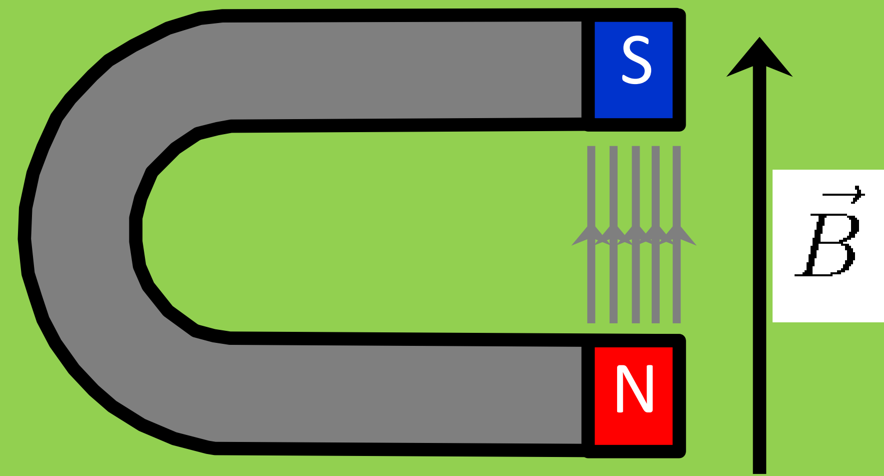
nuclear property

(vector)



electron property

(vector)



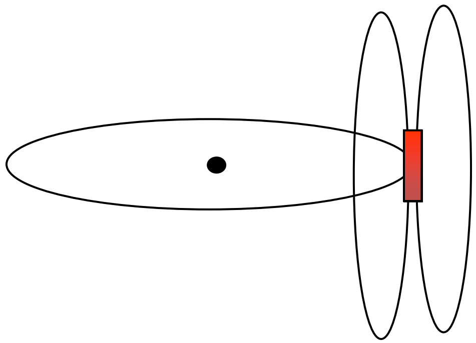
interaction energy (dot product) :

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

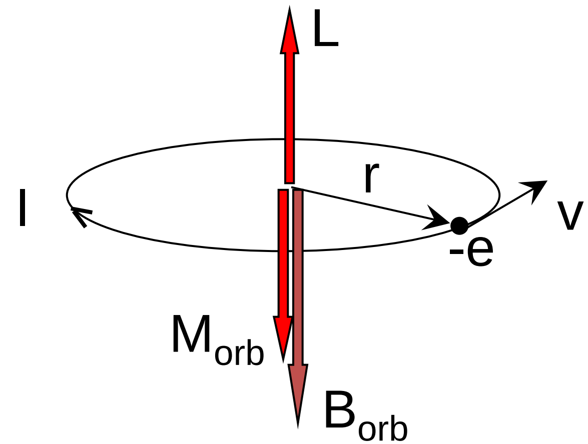
Source of magnetic fields at the nuclear site in an atom/solid

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

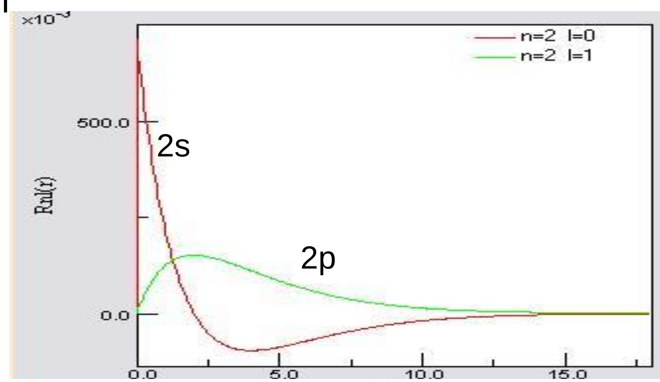
- B_{dip} = electron as bar magnet



- B_{orb} = electron as current loop

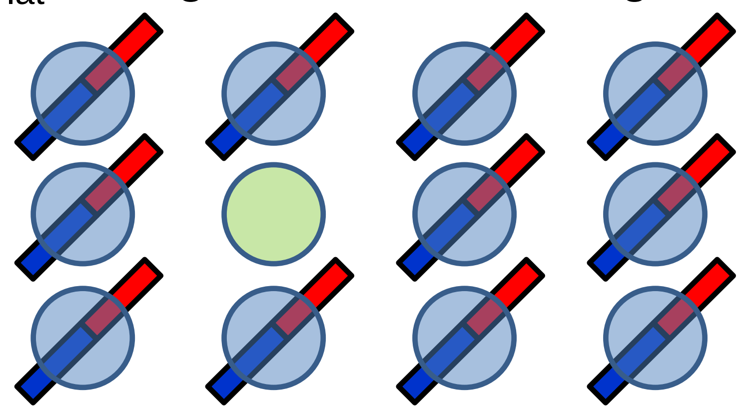


- B_{Fermi} = electron in nucleus



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

- B_{lat} = neighbours as bar magnets



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)

How to do it in WIEN2k ?

Magnetic hyperfine field

step-by-step tutorial video :

https://youtu.be/L4t5ZAJAsoY

In regular scf file:

:HFFxxx (Fermi conta

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 --------------------
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------------------- bottom of file ------------------------
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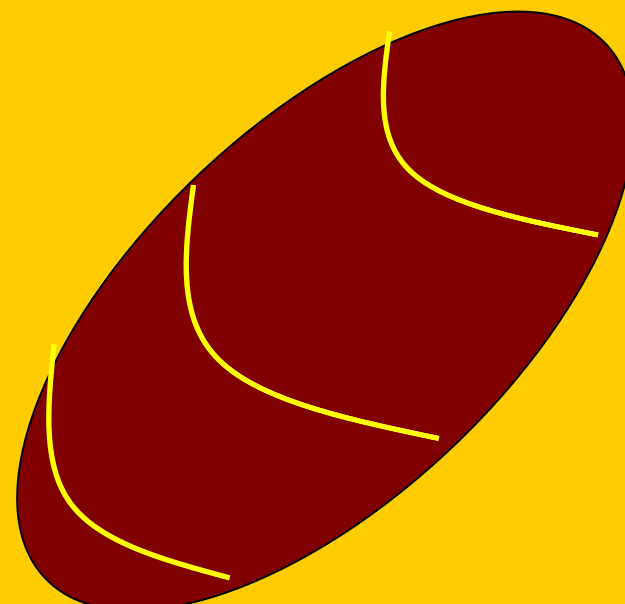
After post-processing with DIPAN :

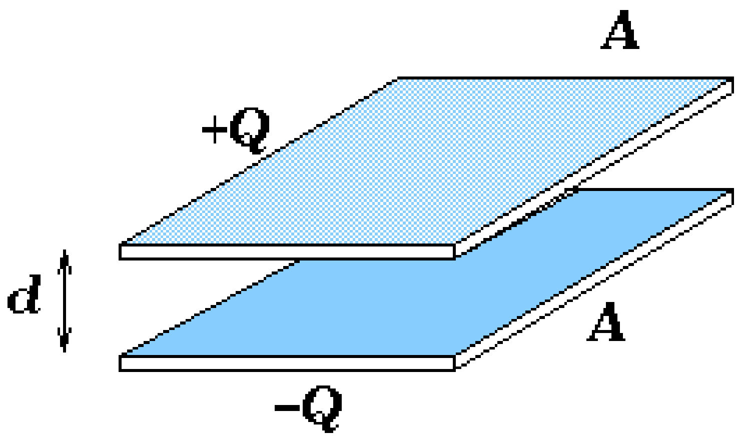
- lattice contribution

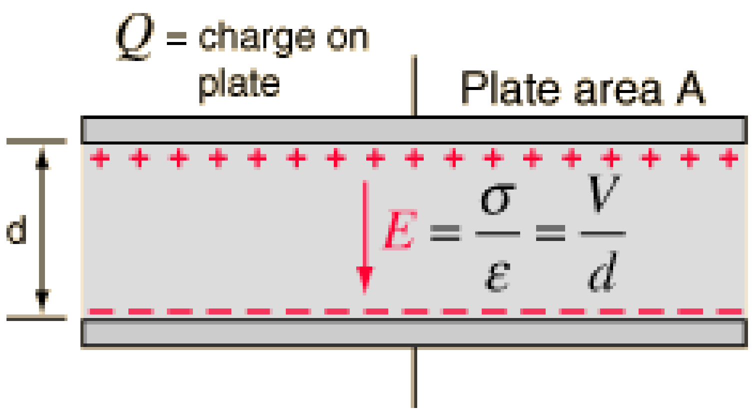
in case.outputdipan

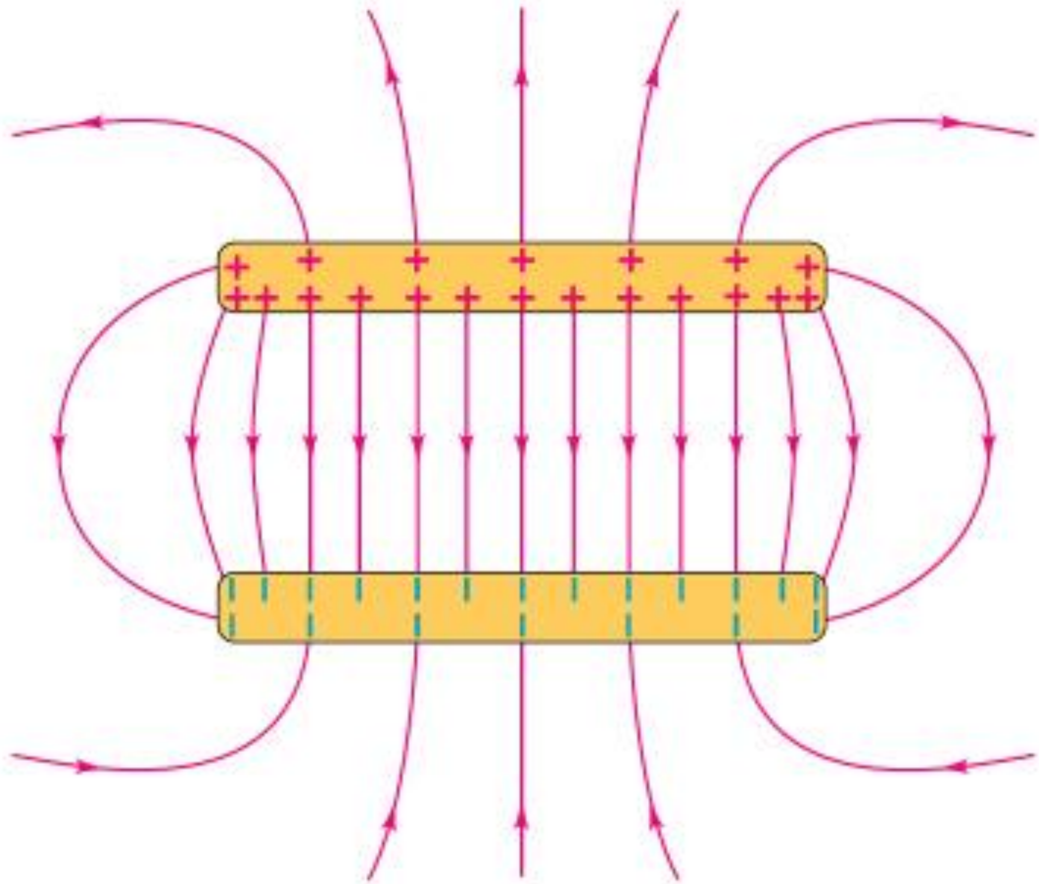
more info:
UG 7.8 (lapwdm)
UG 8.3 (dipan)

- magnetic hyperfine interaction
- electric quadrupole interaction
- isomer shift




A
+Q
d
A
−Q


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

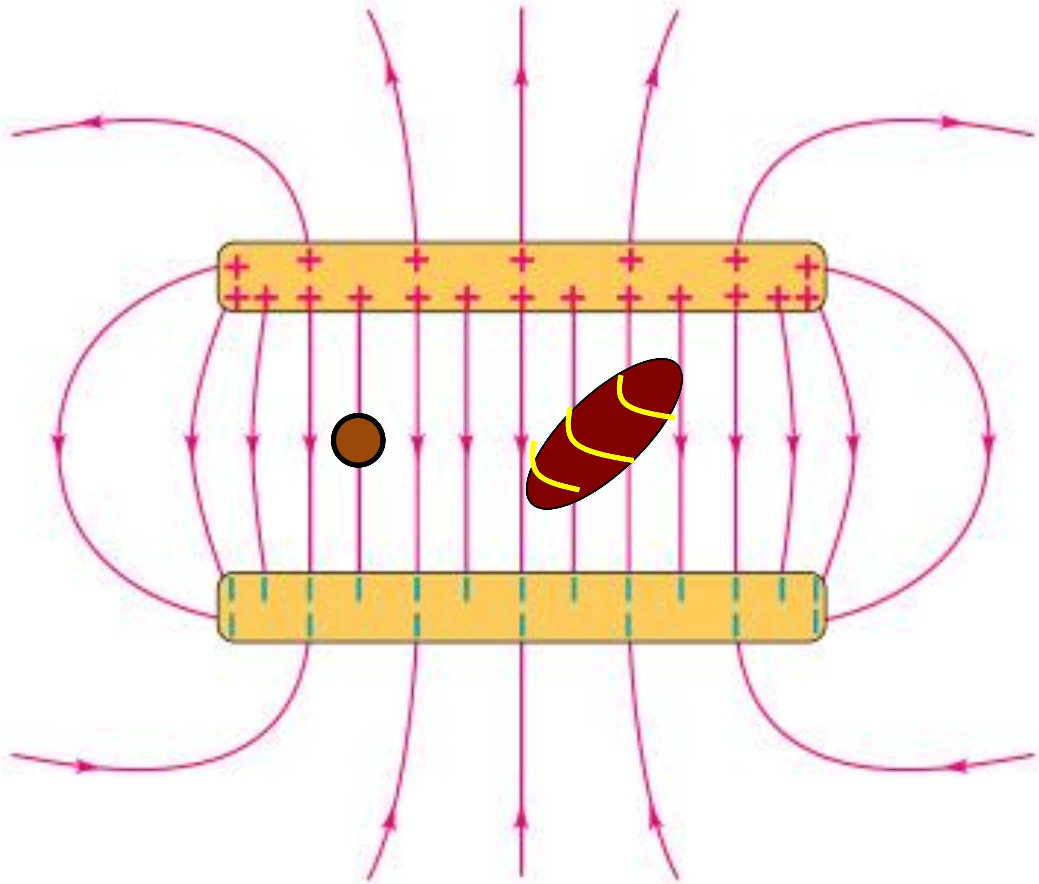


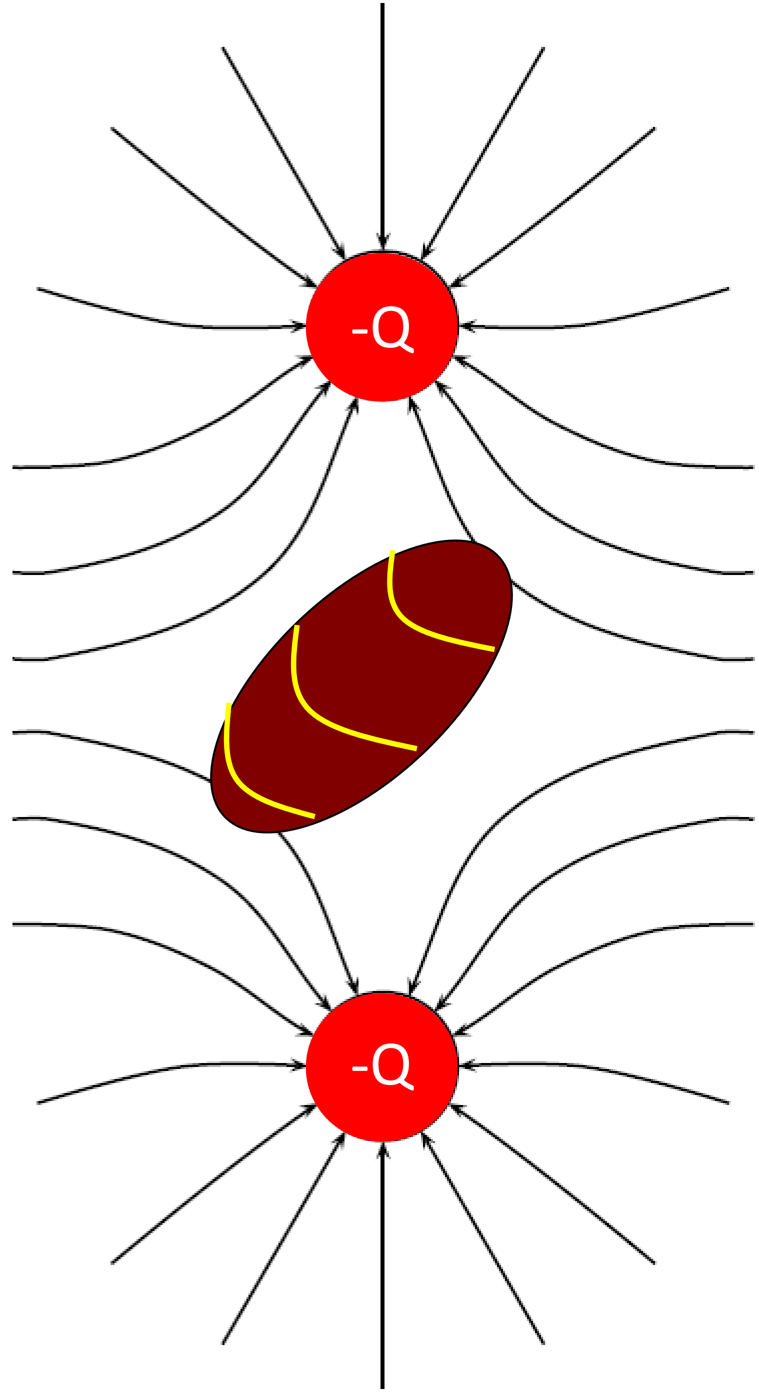
- Force on a point charge:

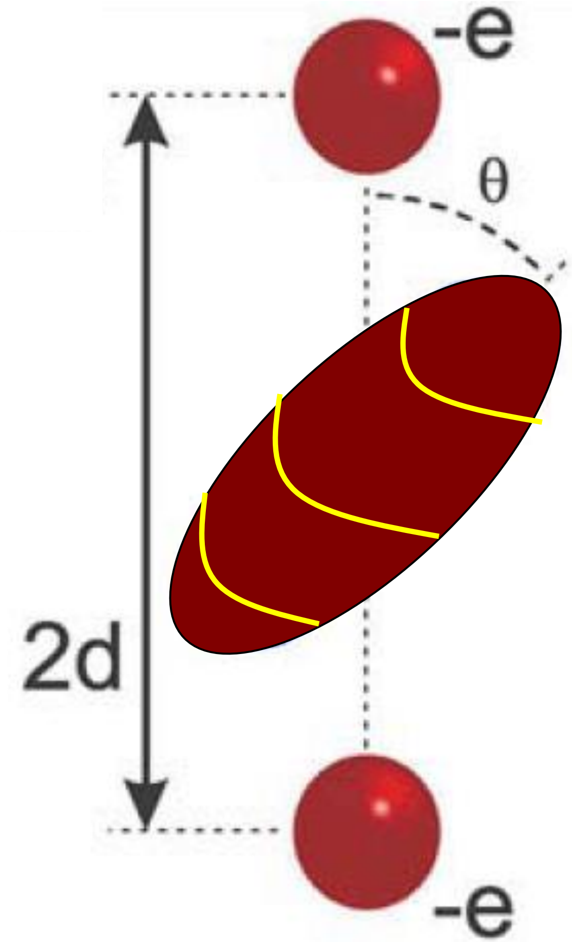
$$\vec{F} = Q\vec{E}$$

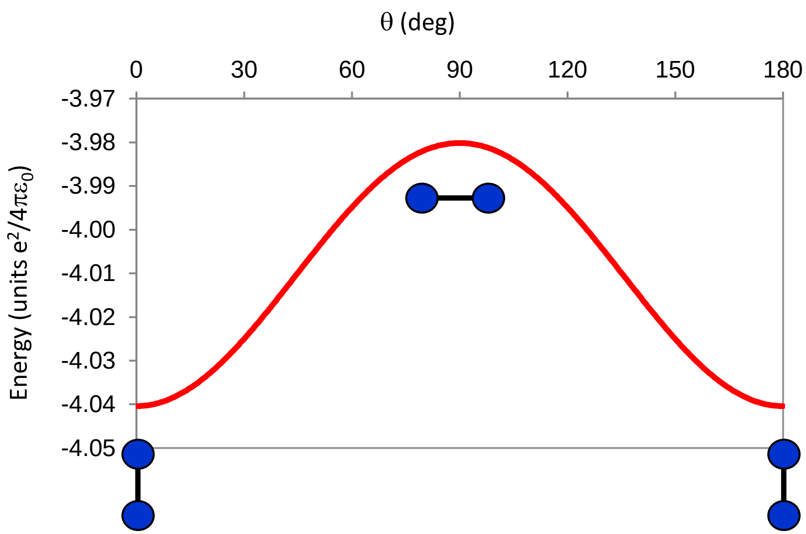
- Force on a general charge:

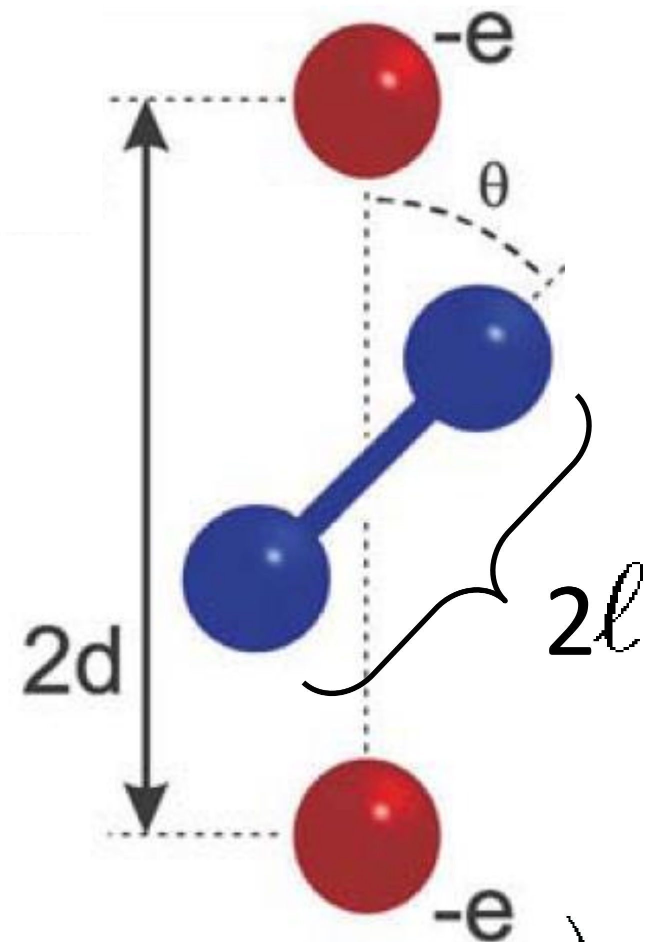
$$\vec{F} = \int \vec{E}\, dQ$$
$$= Q\vec{E}$$




-Q
-Q

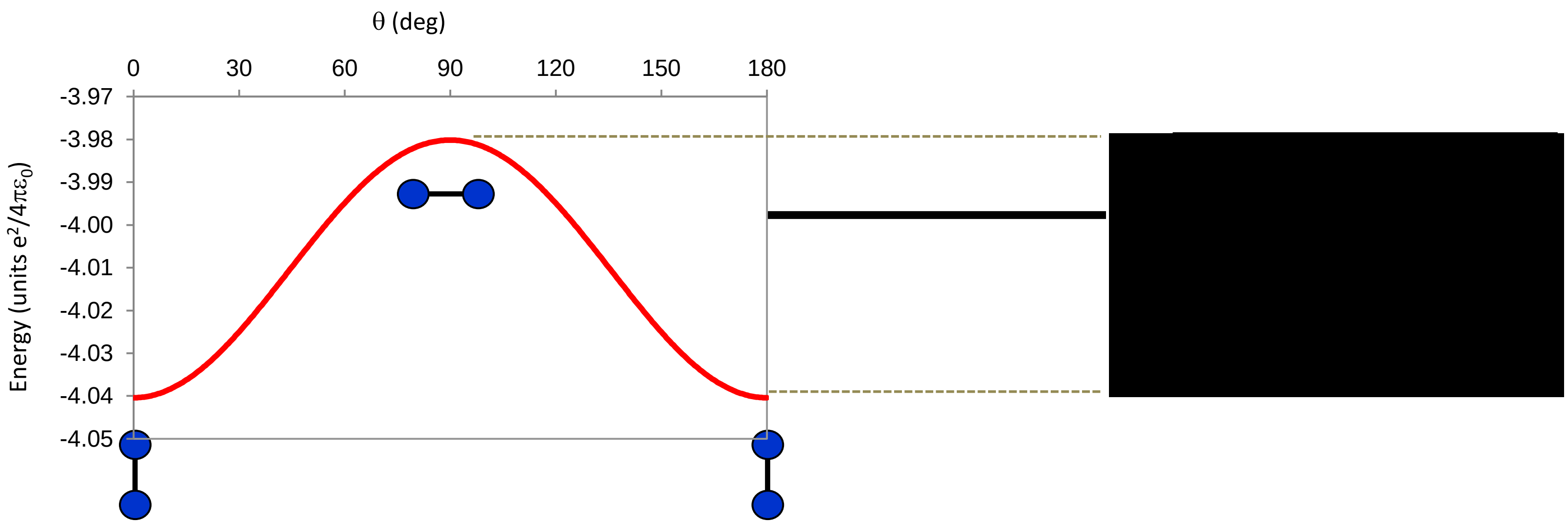

-e
θ
2d
-e

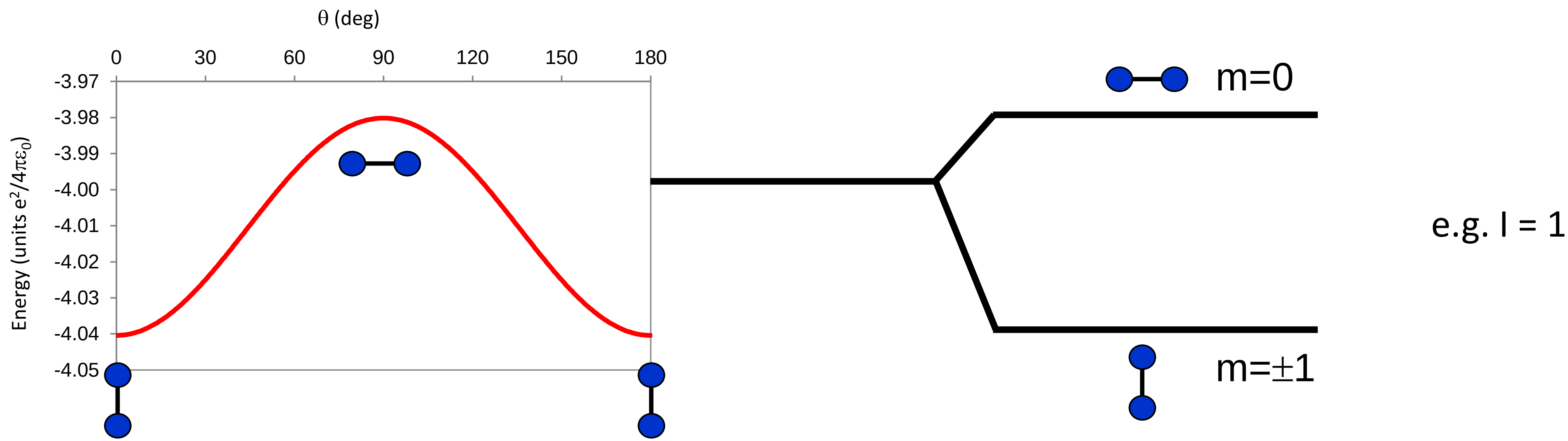




$$C = \mathrm{e}^2/(4\pi\varepsilon_0)$$

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

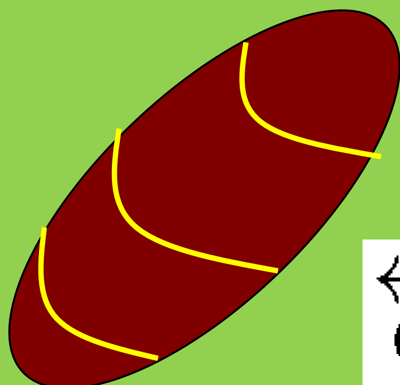

θ (deg)
0
30
60
90
120
150
180
-3.97
-3.98
-3.99
-4.00
-4.01
-4.02
-4.03
-4.04
-4.05
Energy (units $e^2/4\pi\varepsilon_0$)



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

nuclear property

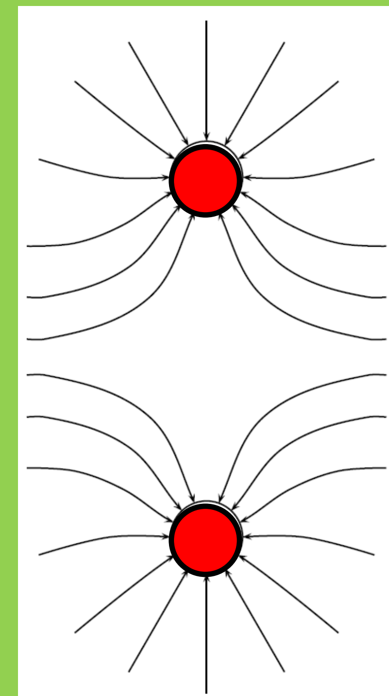
(tensor – rank 2)



$\overleftrightarrow{Q}$

electron property

(tensor – rank 2)



$\overleftrightarrow{V}$

interaction energy (dot product) :

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

How to do it in WIEN2k ?

Electric-field gradient

In regular scf file:

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

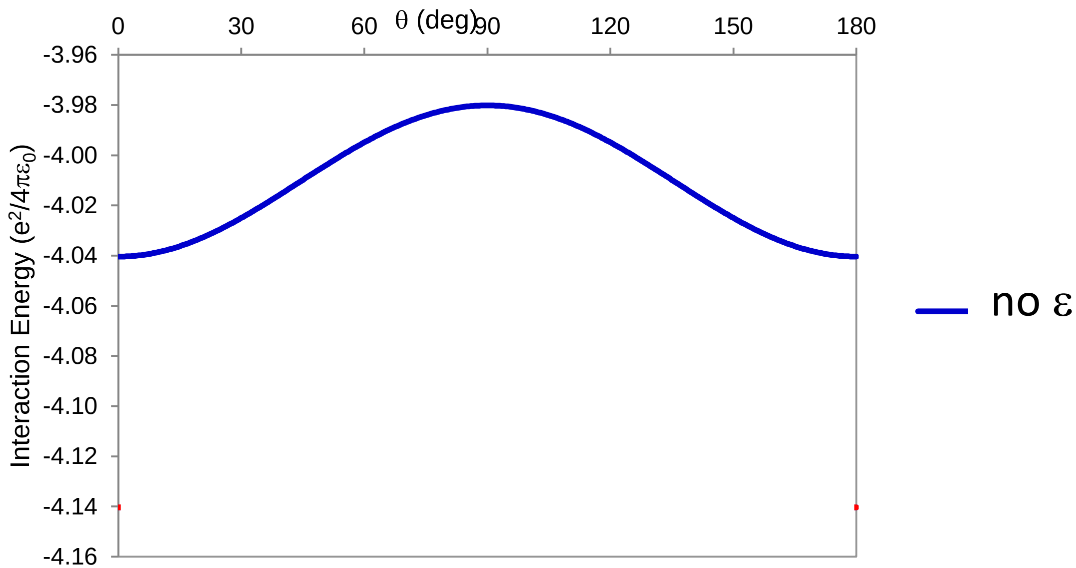
} 5 degrees of freedom

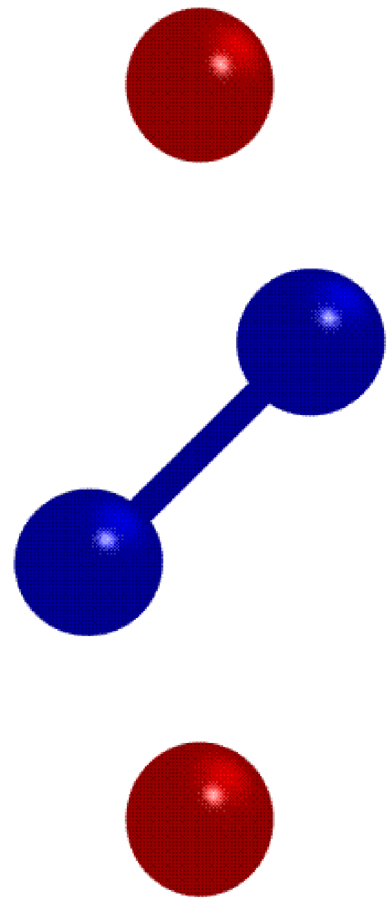
Full analysis printed in case.output2
if EFG keyword in case.in2 is put (UG 7.6)
(split into many different contributions)

more info:

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

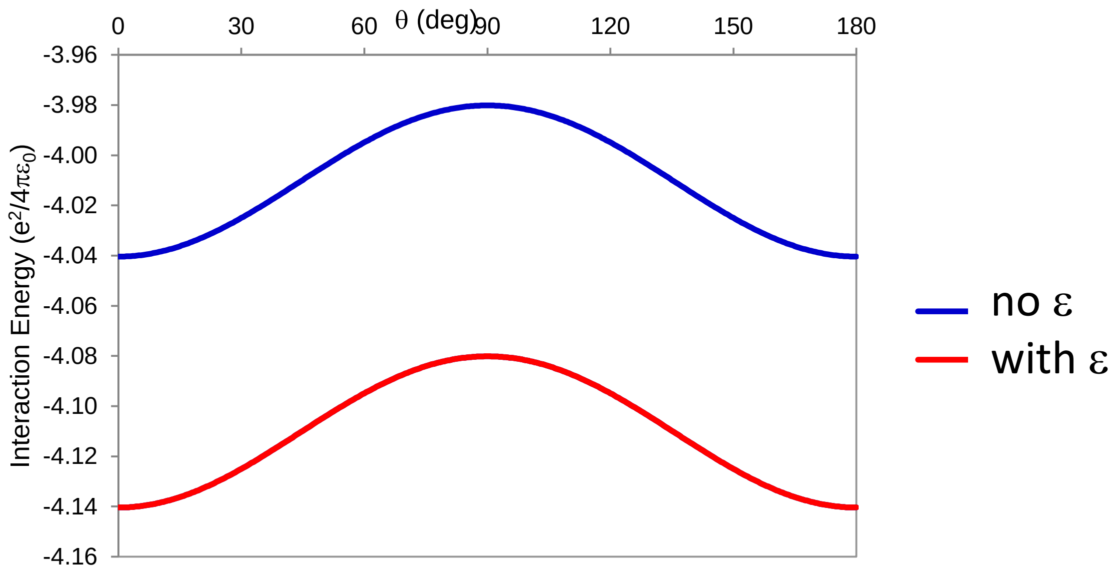
- magnetic hyperfine interaction
- electric quadrupole interaction
- isomer shift

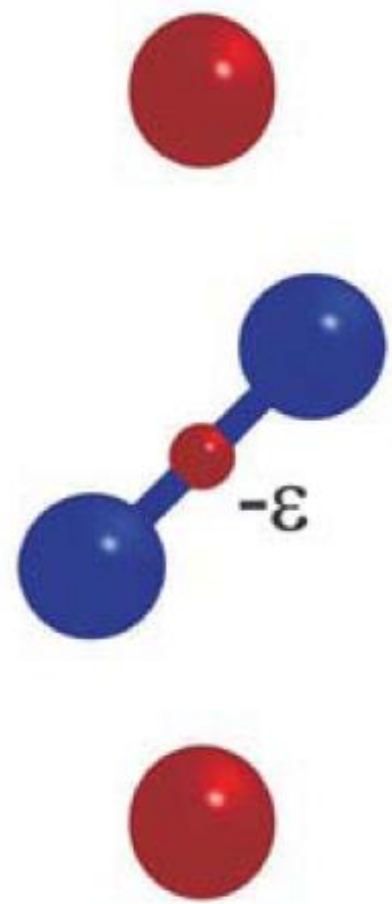




$$E_A(\theta) = E_0(\theta)$$

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

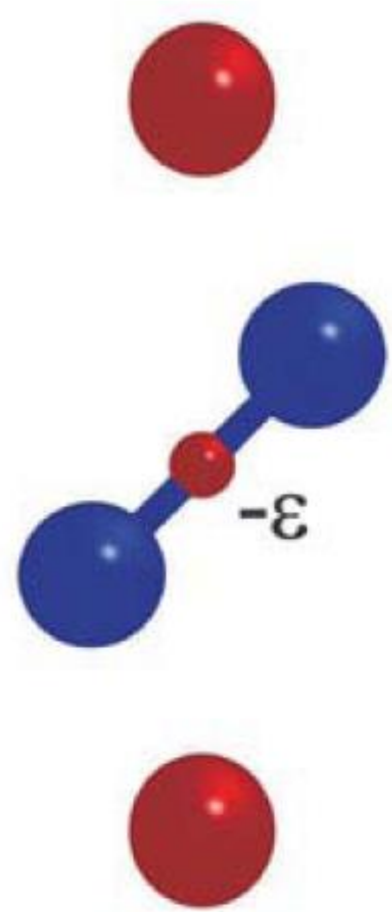




$$E_A(\theta) = E_0(\theta) + \underbrace{\frac{-2\varepsilon C}{e\ell}}_{E_{\mathrm{corA}}}$$

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

$$-\frac{2C}{e}\frac{\epsilon}{\ell} = -\frac{2C}{e}\frac{\epsilon}{\ell^3}\ell^2$$

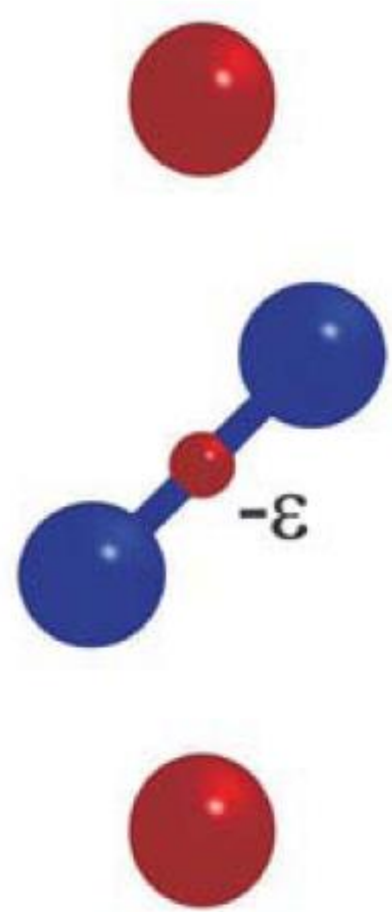


$$E_{\mathrm{A}}(\theta) = E_0(\theta) + \underbrace{\frac{-2\varepsilon C}{e\ell}}_{E_{\mathrm{corA}}}$$

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

$$\rho(0) \quad \langle R^2 \rangle$$

$$-\frac{2C}{e}\frac{\epsilon}{\ell} = -\frac{2C}{e}\frac{\epsilon}{\ell^3}\ell^2$$

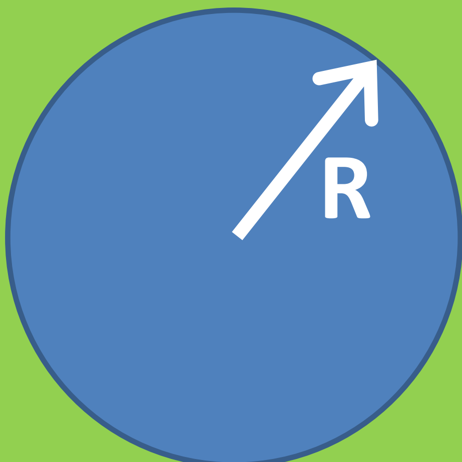


$$E_{\mathrm{A}}(\theta) = E_0(\theta) + \underbrace{\frac{-2\varepsilon C}{e\ell}}_{E_{\mathrm{corA}}}$$

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

nuclear property

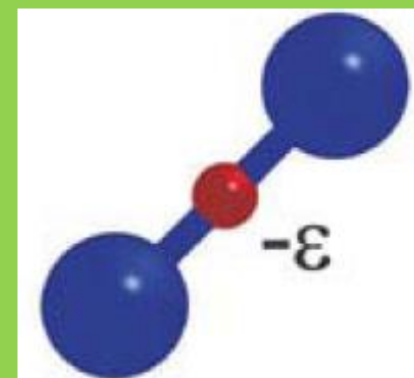
(scalar)



$$\langle R^2 \rangle$$

electron property

(scalar)



$$\rho(0)$$

interaction energy (dot product) :

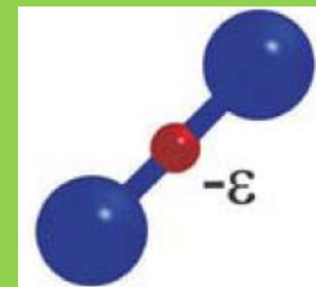
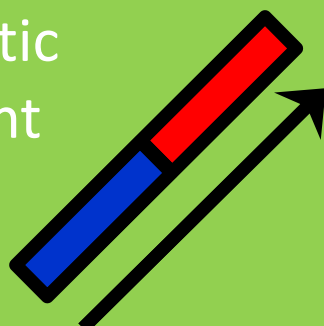
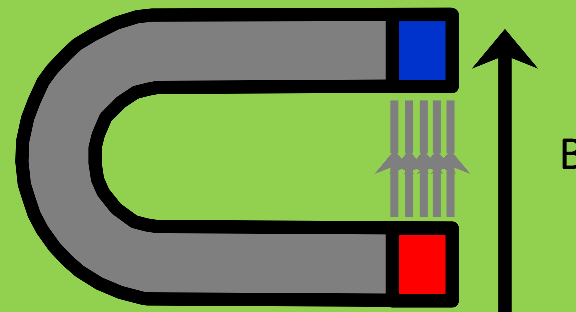
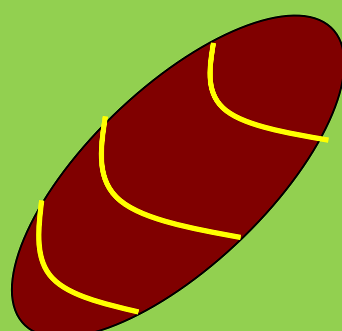
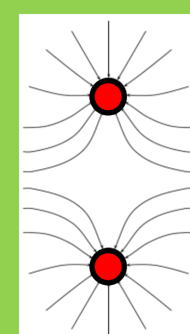
$$E \propto \langle R^2 \rangle \cdot \rho(0)$$

How to do it in WIEN2k ?

Isomer shift calculations

In regular scf file:

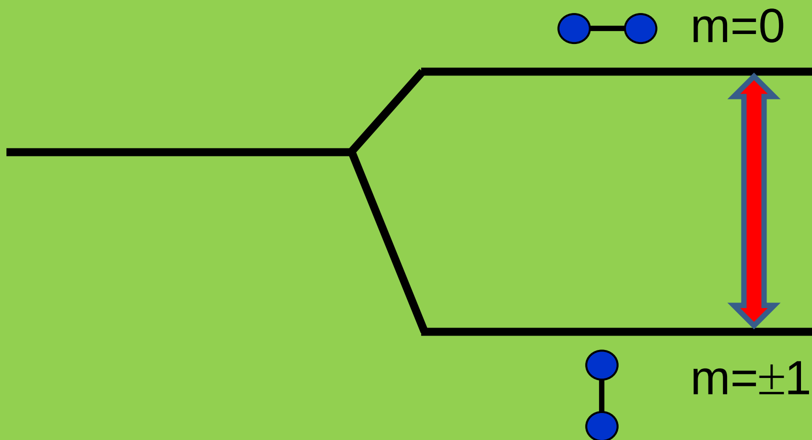
`:RTOxxx` = electron density near the nucleus of atom xxx
(i.e. at the first radial mesh point, typically 0.0005 au)

rank	nuclear property	• (dot product)	electron property
0	volume 		
1	magnetic moment 		
2	shape 		

How to measure hyperfine interactions ?

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

rank	nuclear property • electron property (dot product)



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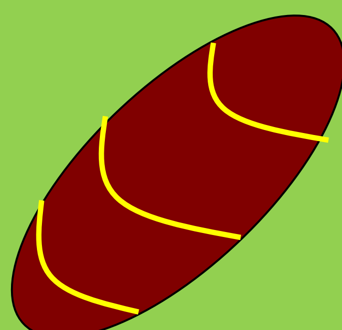
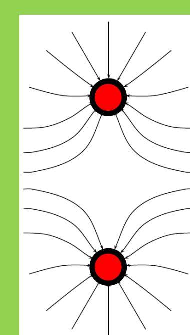
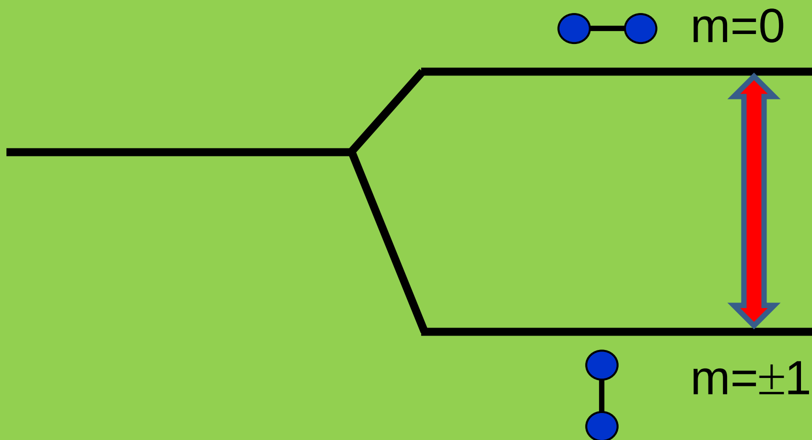
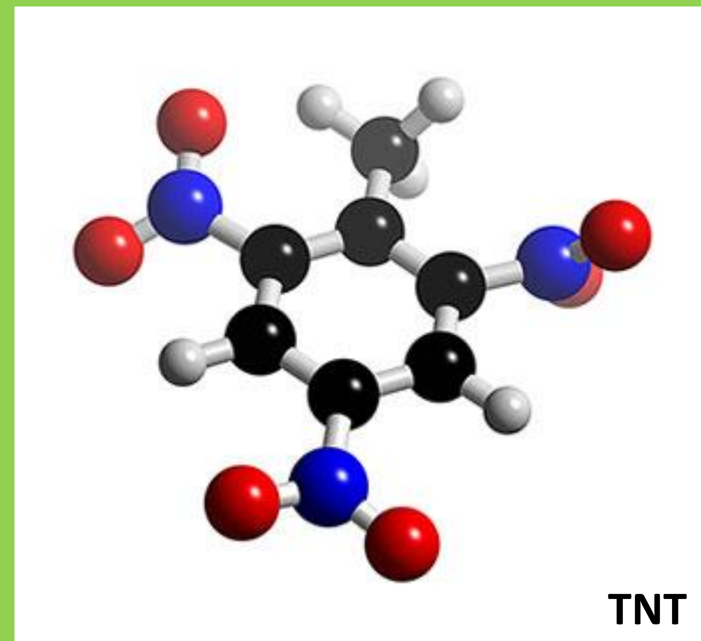




rank | nuclear property • electron property

(dot product)





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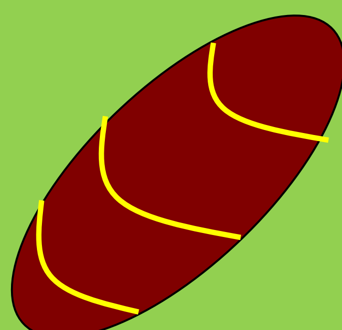

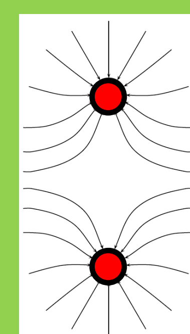

hyperfine interactions
(and how to do it in WIEN2k)

- want to read more ?

Katrin Rose and SC, Phys. Chem. Chem. Phys. 14 (2012) 11308-11317
http://dx.doi.org/10.1039/c2cp40740j

my talks on YouTube
http://goo.gl/P2b1Hs

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