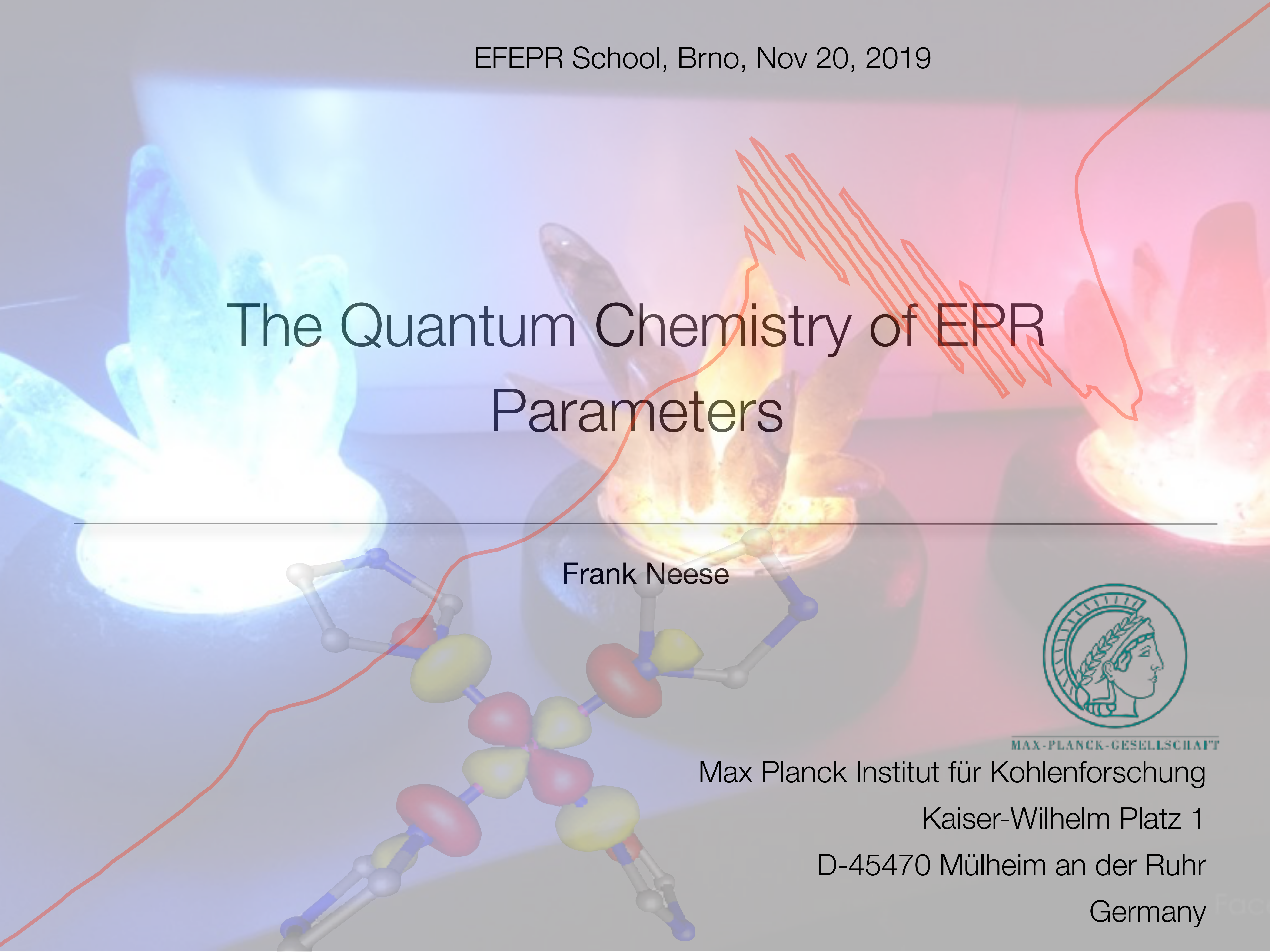
EFEPR School, Brno, Nov 20, 2019



The Quantum Chemistry of EPR Parameters

Frank Neese

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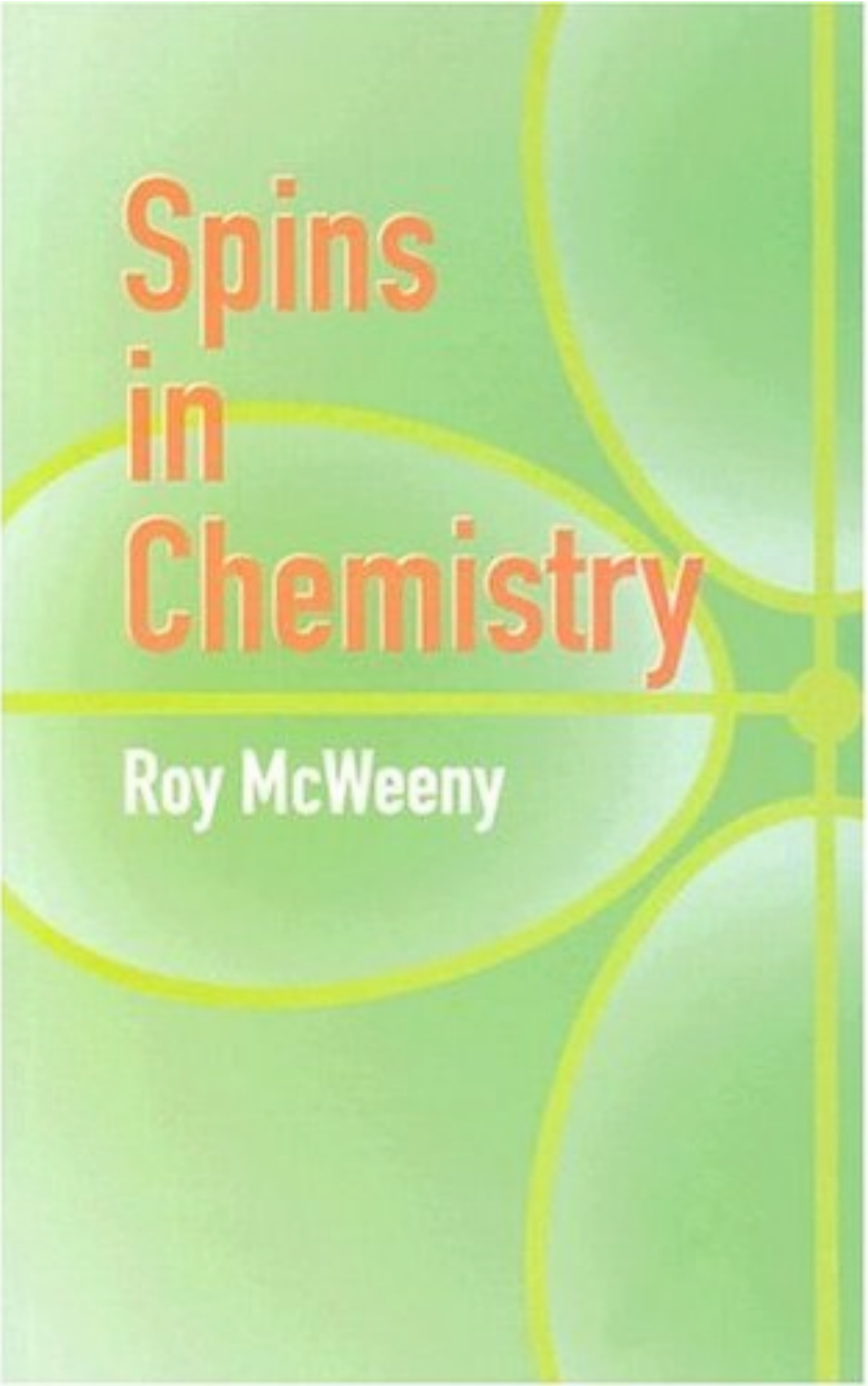
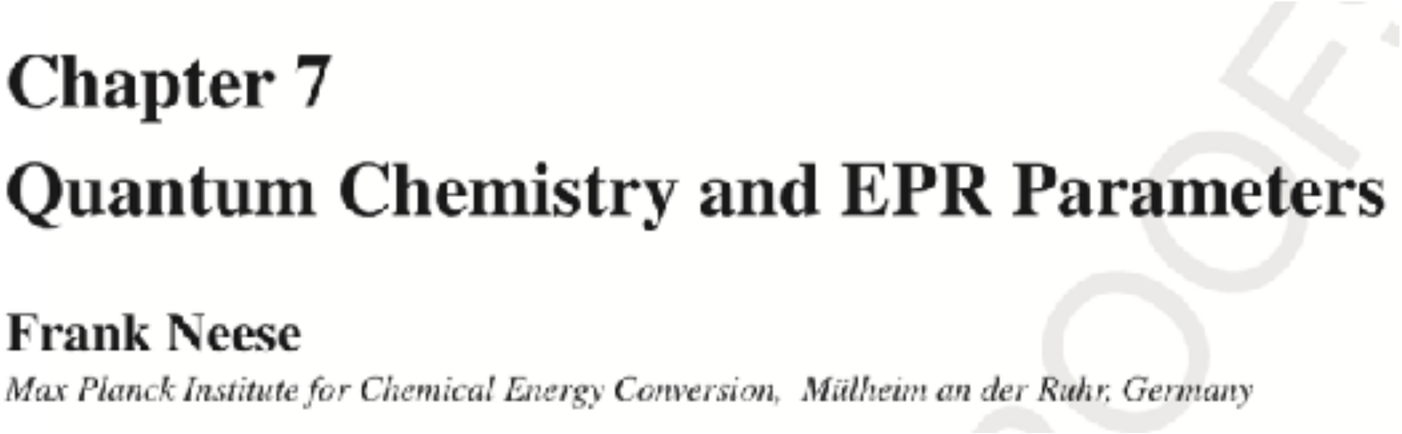
Germany

a recommendation ...




Chapter 7

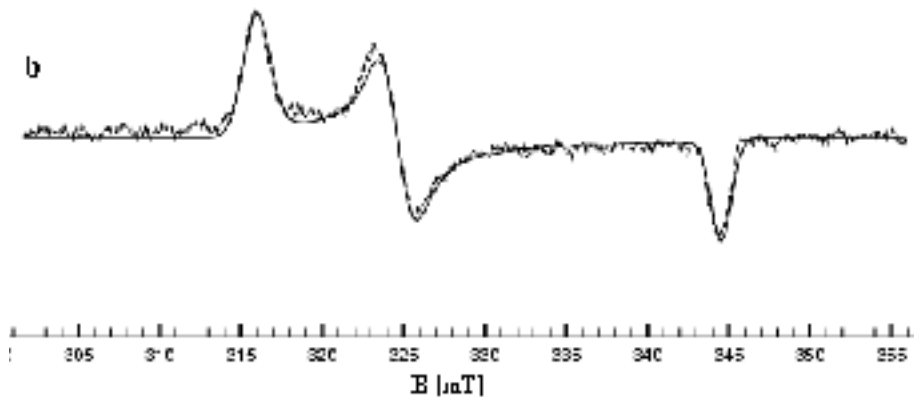
Quantum Chemistry and EPR Parameters

Frank Neese

Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

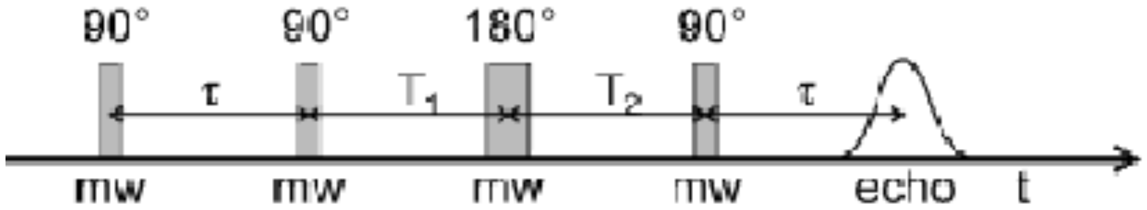
Neese, F. *Emagres* **2017**, *6*, 1.

„Magnetic Resonance Business“

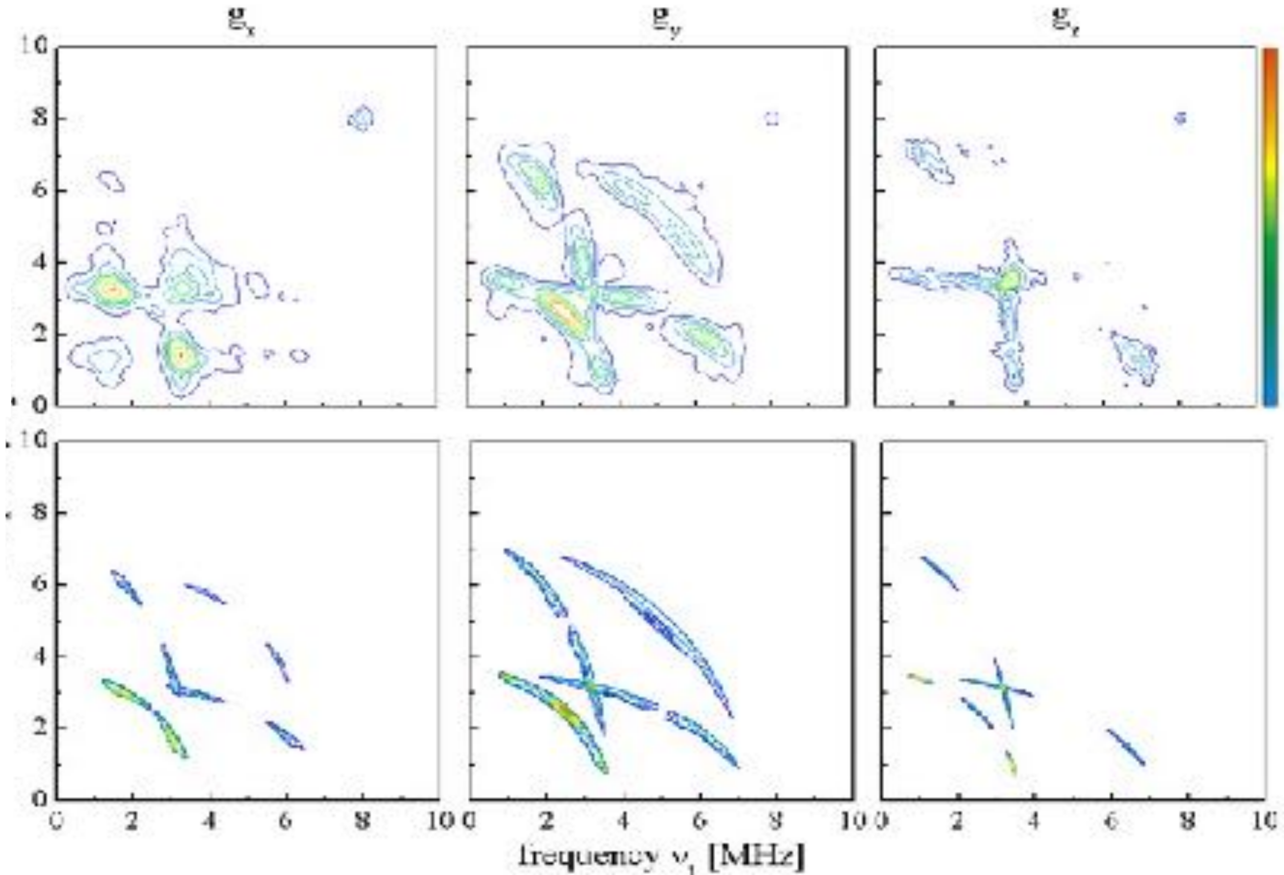


Spectrum

Design an experiment



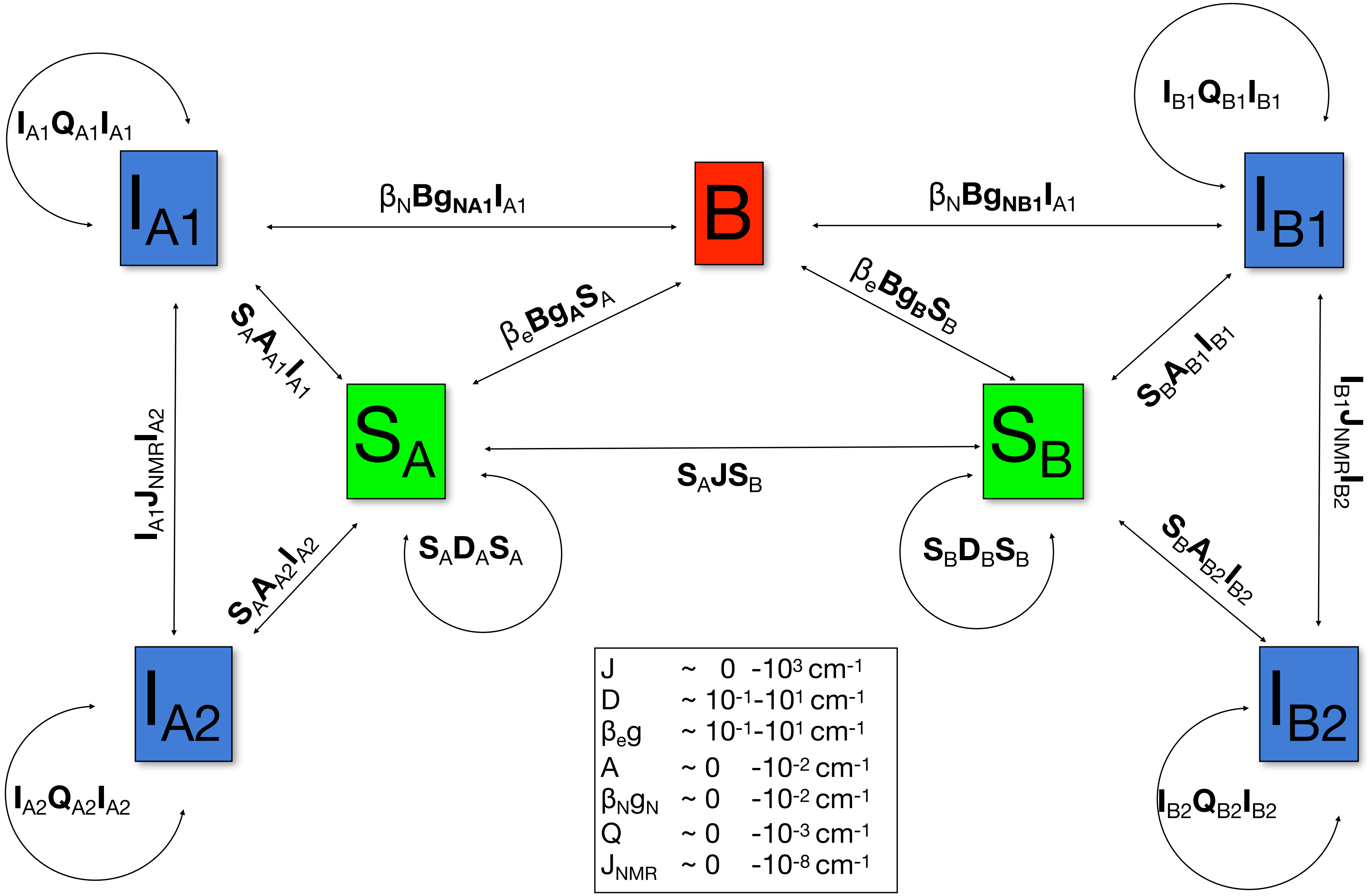
Obtain High Resolution Data



Simulate the Data

And now ?

Magnetic Interactions



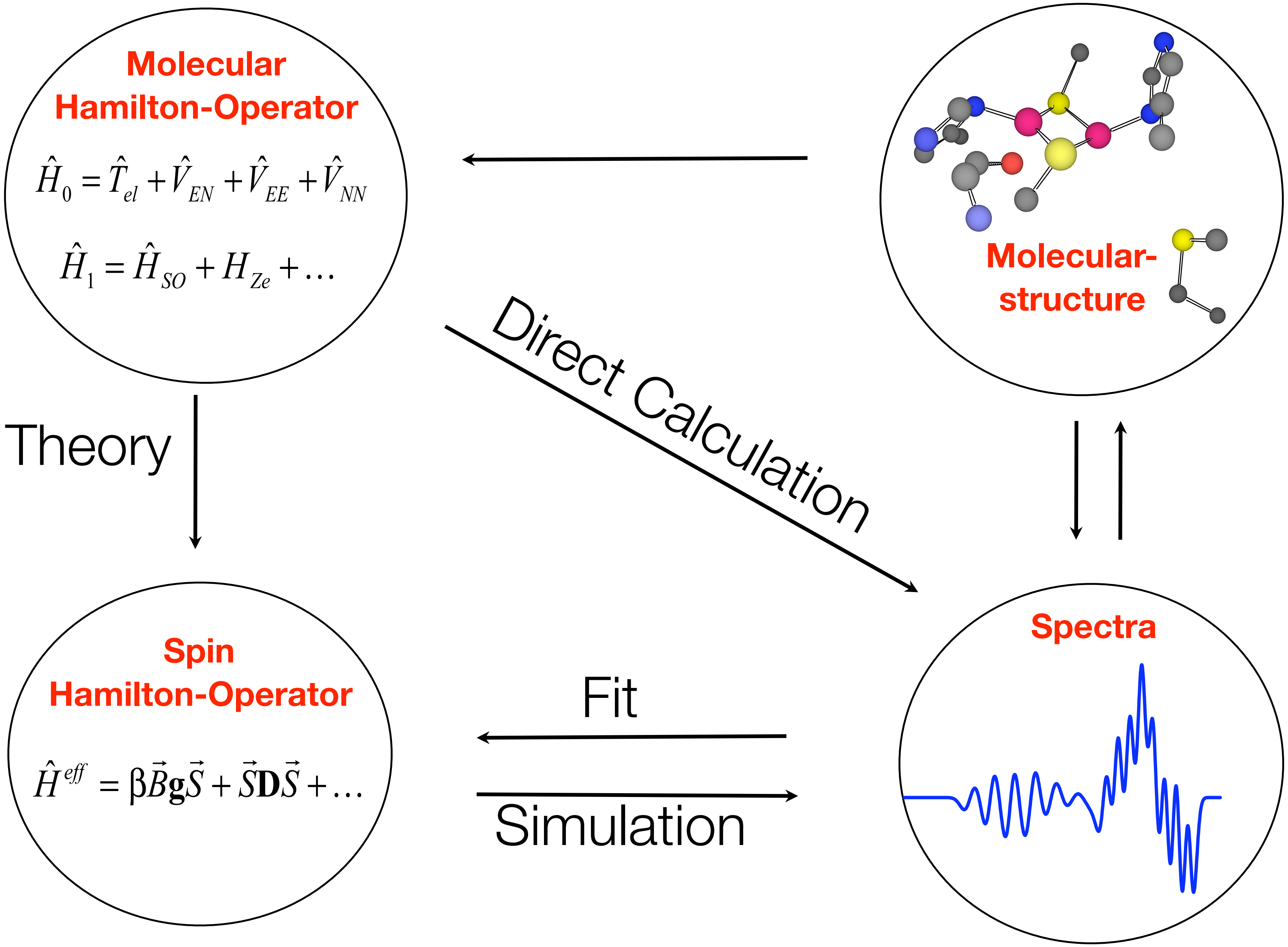
J	~ 0 -10^3 cm^{-1}
D	~ 10^{-1}-10^1 cm^{-1}
$\beta_e g$	~ 10^{-1}-10^1 cm^{-1}
A	~ 0 -10^{-2} cm^{-1}
$\beta_N g_N$	~ 0 -10^{-2} cm^{-1}
Q	~ 0 -10^{-3} cm^{-1}
J_{NMR}	~ 0 -10^{-8} cm^{-1}

The Spin Hamiltonian: Summary

$$
\begin{aligned}
\hat{H}_{Spin} = {} & \vec{S}\mathbf{D}\vec{S} \quad \left(= D\left(S_z^2 - \tfrac{1}{3}S(S+1)\right) + \tfrac{E}{D}\left(S_x^2 - S_y^2\right)\right) && \textbf{Zero-Field Splitting} \\
& + \beta\vec{B}\mathbf{g}\vec{S} && \textbf{Zeeman Term (g-Tensor)} \\
& + \sum_{A} \vec{S}\mathbf{A}^{(A)}\vec{I}^{(A)} && \textbf{Hyperfine Interaction} \\
& + \sum_{A} \vec{I}^{(A)}\mathbf{Q}^{(A)}\vec{I}^{(A)} && \textbf{Quadrupole Interaction} \\
& - \beta_N \sum_{A} \vec{B}\mathbf{g}_N^{(A)}\vec{I}^{(A)} && \textbf{Nuclear Zeeman} \\
& + \sum_{A<B} \vec{I}^{(A)}\mathbf{J}^{(A,B)}\vec{I}^{(B)} && \textbf{Spin-Spin Coupling}
\end{aligned}
$$

$\vec{S}$	Fictitous Electron Spin	β	Bohr‘s Magneton
$\vec{I}^{(A)}$	Nuclear Spin	β_N	Nuclear Magneton

Theoretical Magnetic Spectroscopy



Molecular Hamilton-Operator

$$\hat{H}_0 = \hat{T}_{el} + \hat{V}_{EN} + \hat{V}_{EE} + \hat{V}_{NN}$$

$$\hat{H}_1 = \hat{H}_{SO} + H_{Ze} + \ldots$$

Molecular-structure

Direct Calculation

Theory

Spin Hamilton-Operator

$$\hat{H}^{eff} = \beta \vec{B}\mathbf{g}\vec{S} + \vec{S}\mathbf{D}\vec{S} + \ldots$$

Fit

Simulation

Spectra

Neese, F. Quantum Chemistry and EPR Parameters *eMagRes* **2017**, *6*, 1.
(and many other reviews since 2001)

Why *Theoretical* Spectroscopy?

- ★ Spectra may be very complicated. Theory helps to ***assign peaks*** and greatly facilitates the data ***reduction process***.

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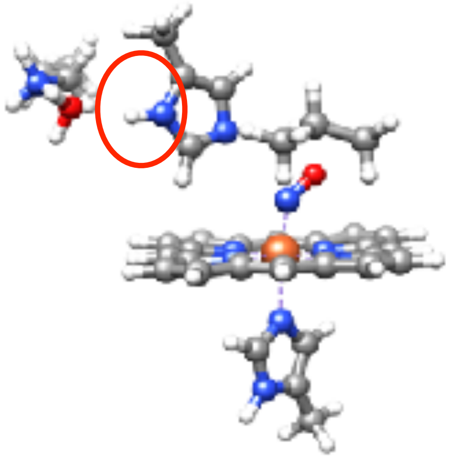

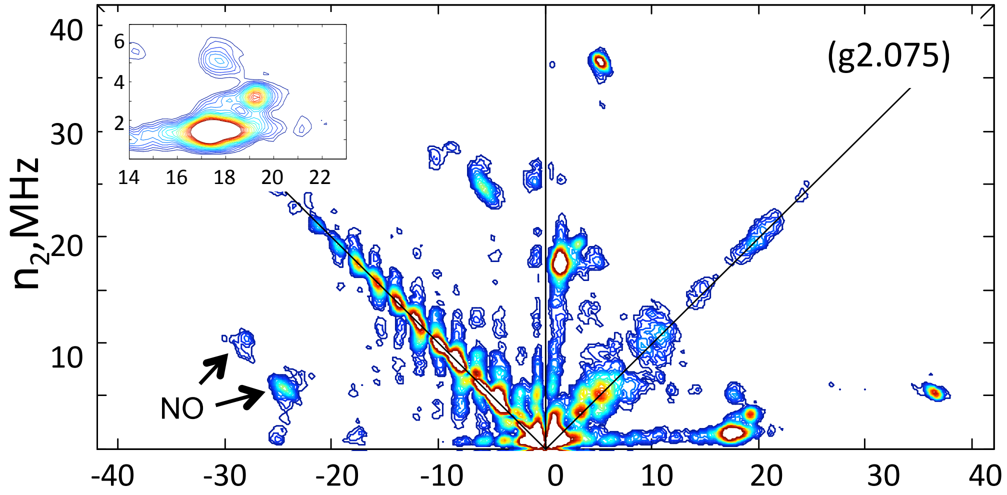

Daniella Goldfarb

> [...] Please see that attached [...]. It shows the experimental HYSCORES and the simulated ones. One is the one that we fitted and one is with the parameters of 14N(His) model 2a , full (table 5). **The agreement is rather good, even better than our simulated ones. This is amazing!** It also shows how difficult it is to find by manual simulations a unique set of parameters, when there are so many

Why *Theoretical* Spectroscopy?

- ★ Spectra may be very complicated. Theory helps to ***assign peaks*** and greatly facilitates the data ***reduction process***.
- ★ Theory greatly helps in ***interpreting*** the information content of the spectra. This is critical for ***identifying unstable and short lived species***

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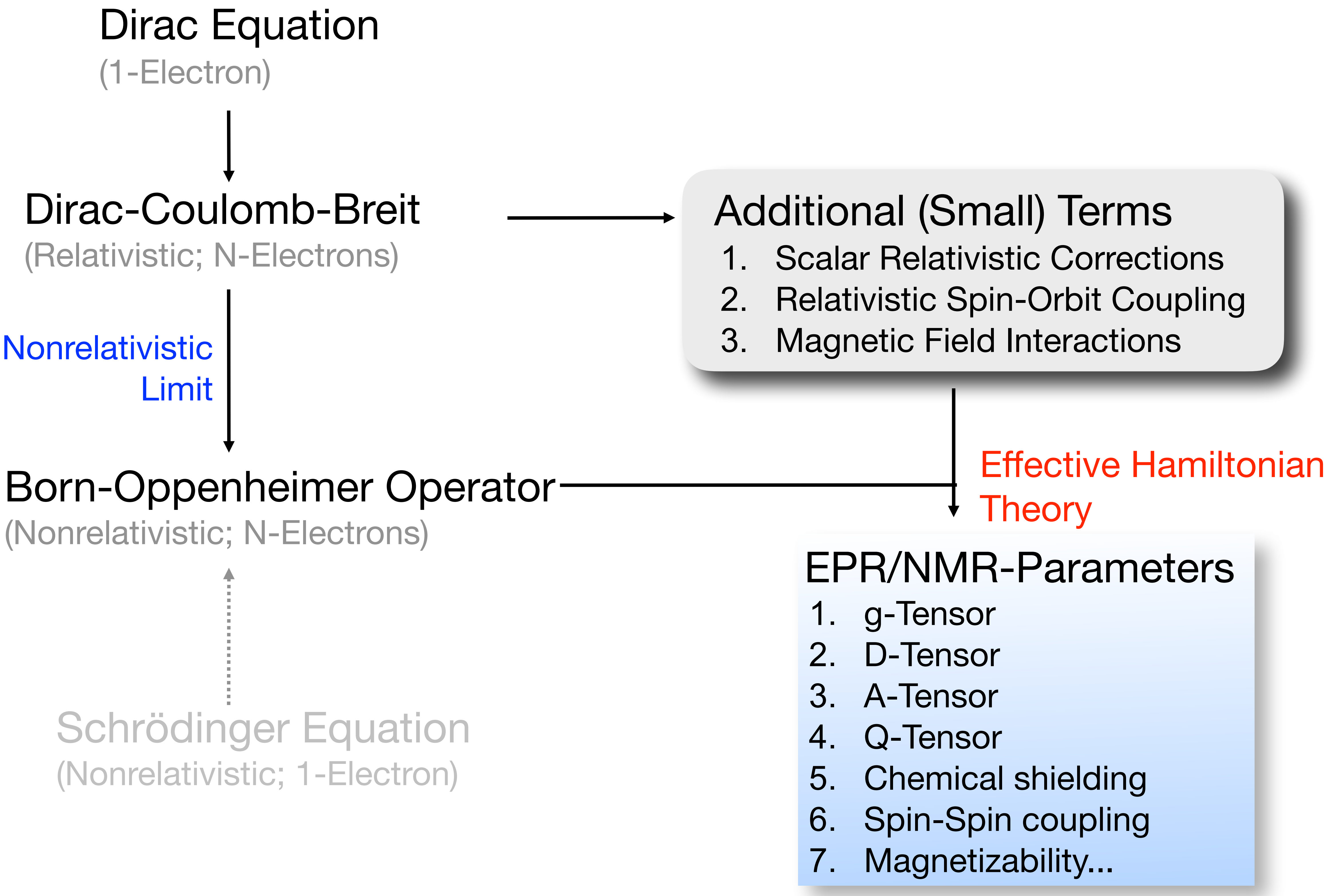
★ Spectra being electronic structure fingerprints can be used to ***validate*** the calculated electronic structures

★ It‘s not only challenging - it‘s

Effective Hamiltonian Theory

Where do the Extra Terms come From?



Dirac Equation
(1-Electron)

Dirac-Coulomb-Breit
(Relativistic; N-Electrons)

Nonrelativistic Limit

Born-Oppenheimer Operator
(Nonrelativistic; N-Electrons)

Schrödinger Equation
(Nonrelativistic; 1-Electron)

Additional (Small) Terms

1. Scalar Relativistic Corrections
2. Relativistic Spin-Orbit Coupling
3. Magnetic Field Interactions

Effective Hamiltonian Theory

EPR/NMR-Parameters

1. g-Tensor
2. D-Tensor
3. A-Tensor
4. Q-Tensor
5. Chemical shielding
6. Spin-Spin coupling
7. Magnetizability...

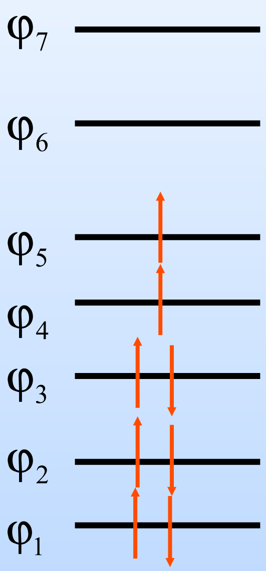
Perturbation Theory of SH Parameters

Divide the Complete Set of Many Electron States into Two Sets

1. „**Model Space**“: $|a;S_0M\rangle$ $M=S_0,S_0-1,\ldots,-S_0$
   The 2S+1 components of the orbitally nondegenerate ground state
2. „**Outer Space**“: $|b;S_bM\rangle$
   All other states of any multiplicity and symmetry

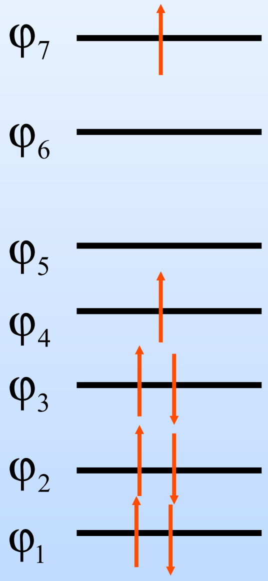
Example:

Ground State $^3\Gamma$:



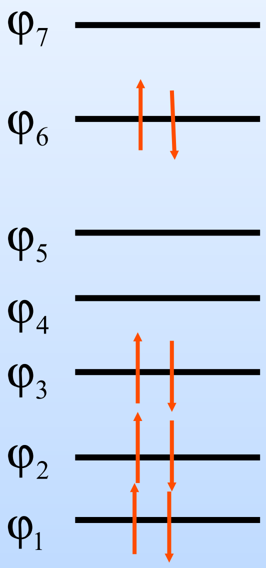
$|^3\Gamma;1,1\rangle, |^3\Gamma;1,-1\rangle, |^3\Gamma;1,0\rangle$

Exc. State $^3\Gamma'$:



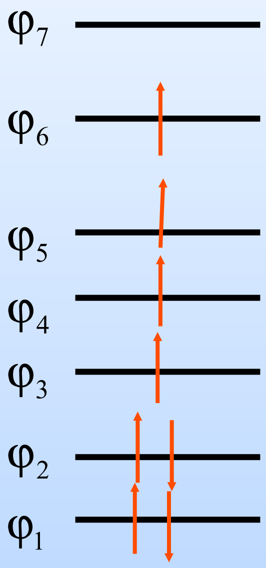
$|^3\Gamma';1,1\rangle, |^3\Gamma';1,-1\rangle, |^3\Gamma';1,0\rangle$

Exc. State $^1\Gamma''$:



$|^1\Gamma'';0,0\rangle$

Exc. State $^5\Gamma'''$:



$|^5\Gamma''';2,M\rangle$

The Effective Hamiltonian

- Partitioning:

$$\begin{pmatrix} \mathbf{H}^{AA} & \mathbf{H}^{AB} \\ \mathbf{H}^{BA} & \mathbf{H}^{BB} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{A} \\ \mathbf{C}^{B} \end{pmatrix} = E \begin{pmatrix} \mathbf{C}^{A} \\ \mathbf{C}^{B} \end{pmatrix}$$

- Few lines of math:

$$\boxed{\begin{aligned} (\mathbf{H}^{eff})_{IJ} &= \delta_{IJ} E_I^{(0)} + \left\langle \Psi_I^{(0)} \,\middle|\, H^{(1)} \,\middle|\, \Psi_j^{(0)} \right\rangle \\ &\quad - \sum_{K \in 'b'} \frac{\left\langle \Psi_I^{(0)} \,\middle|\, H^{(1)} \,\middle|\, \Psi_K^{(0)} \right\rangle \left\langle \Psi_K^{(0)} \,\middle|\, H^{(1)} \,\middle|\, \Psi_J^{(0)} \right\rangle}{E_K^{(0)} - E_a} \end{aligned}}$$

- This looks like second order perturbation theory but is more general since the crucial coupling of the ‚a‘ space functions via the perturbing operator H_1 is taken into account.

Derivation of the g-Tensor

- Let:

$$\begin{aligned} H^{(1)} &= H_{LS} + H_{SOC} \\ &= \mu_B \mathbf{B} \sum_i (\hat{\mathbf{l}}_i + g_e \hat{\mathbf{s}}_i) + \sum_i \mathbf{h}_i^{SOC} \hat{\mathbf{s}}_i \end{aligned}$$

- 1st order: $\left\langle aSM \mid H^{(1)} \mid aSM' \right\rangle = 0$

- 2nd order (linear in B and S):

$$\begin{aligned} (\mathbf{H}^{eff})_{MM'} = &-\mu_B \mathbf{B} \sum_{bS'M''} \Delta_b^{-1} \left\langle aSM \mid \textstyle\sum_i \mathbf{l}_i + 2\hat{\mathbf{s}}_i \mid bS'M'' \right\rangle \left\langle bS'M'' \mid \textstyle\sum_i \mathbf{h}^{SOC} \hat{\mathbf{s}}_i \mid aSM' \right\rangle \\ &- \mu_B \mathbf{B} \sum_{bS'M''} \Delta_b^{-1} \left\langle aSM \mid \textstyle\sum_i \mathbf{h}^{SOC} \hat{\mathbf{s}}_i \mid bS'M'' \right\rangle \left\langle bS'M'' \mid \textstyle\sum_i \mathbf{l}_i + 2\hat{\mathbf{s}}_i \mid aSM' \right\rangle \end{aligned}$$

- The LS matrix elements:

$$\left\langle aSM \mid \mathbf{B} \textstyle\sum_i \mathbf{l}_i + 2\hat{\mathbf{s}}_i \mid bS'M' \right\rangle = \delta_{SS'} \left\langle aSM \mid \mathbf{B} \textstyle\sum_i \mathbf{l}_i \mid bS'M' \right\rangle$$

The Spin-Orbit Coupling Matrix Elements

- The SOC matrix elements are more subtle. Here one has to make use of the Wigner-Eckart theorem that tells us that for any operator of the form:

$$\hat{O} = \sum_i f_i \, s_i^{(m)}$$

- where *m* is a ‚spherical tensor component‘ (*m* = 0, ±1):

$$\left\langle \Psi_I^{SM} \middle| \sum_i f_i \, s_i^{(m)} \middle| \Psi_J^{S'M'} \right\rangle = \underbrace{\left(\begin{array}{cc|c} S' & 1 & S \\ M' & m & M \end{array} \right)}_{Clebsch\_Gordon\,Coefficient} \underbrace{\left\langle \Psi_I^{S} \, || \sum_i f_i \, || \, \Psi_J^{S'} \right\rangle}_{\mathrm{Re}\,duced\,Matrix\,Element\,Y_{IJ}^{SS'}}$$

- This fairly esoteric looking equation says that all the M-dependence of the SOC matrix elements is in the **‚Clebsch-Gordon coefficient‘** and that the rest (the hard part!) comes from the **‚reduced matrix element‘**. Hence, we only need the **‚standard components‘** *M* = *S* of each multiplet to calculate the entire (2*S*‘+1)(2*S*+1) block.
- Note also that this equation tells us that a general operator that depends on the individual electron spins couples states of different multiplicity!

Reduced Matrix Elements

★ Without proof: the reduced matrix elements are calculated from the standard states as:

$$\left\langle \Psi_I^S \,||\, \sum_i f_i \,||\, \Psi_J^S \right\rangle = \frac{\sqrt{S\left(S+1\right)}}{S} \left\langle \Psi_I^{SS} \,|\, \sum_i f_i \, s_{0,i} \,|\, \Psi_J^{SS} \right\rangle$$

$$\left\langle \Psi_I^S \,||\, \sum_i f_i \,||\, \Psi_J^{S+1} \right\rangle = \sqrt{\frac{2S+3}{2S+1}} \left\langle \Psi_I^{SS} \,|\, \sum_i f_i \, s_{-1,i} \,|\, \Psi_J^{S+1S+1} \right\rangle$$

$$\left\langle \Psi_I^S \,||\, \sum_i f_i \,||\, \Psi_J^{S+1} \right\rangle = \left\langle \Psi_I^{SS} \,|\, \sum_i f_i \, s_{+1,i} \,|\, \Psi_J^{S-1S-1} \right\rangle$$

★ With the ‚spherical tensor components‘ of the spin operators being given by:

$$s_{0,i} = s_{z,i}$$

$$s_{+1,i} = -\frac{1}{\sqrt{2}}\left(s_{x,i} + i s_{y,i}\right)$$

$$s_{-1,i} = \frac{1}{\sqrt{2}}\left(s_{x,i} - i s_{y,i}\right)$$

FN, EI Solomon *Inorg. Chem.*, **1998**. 37,6568

The Second Order g-Tensor

- Compare

$$\mu_B B_z g_{zz} \left\langle SS \,|\, S_z \,|\, SS \right\rangle = \mu_B B_z g_{zz} S$$

- Now the same for our perturbation sum:

$$\begin{aligned}\left(\mathbf{H}^{eff}\right)_{SS} = &-\mu_B B_z \sum_{bS} \Delta_b^{-1} \left\langle aSS \,|\, \textstyle\sum_i l_{iz} \,|\, bSS \right\rangle \left\langle bSS \,|\, \textstyle\sum_i h_z^{SOC} \hat{s}_{0,i} \,|\, aSS \right\rangle \\ &- \mu_B B_z \sum_{bS'} \Delta_b^{-1} \left\langle aSS \,|\, \textstyle\sum_i h_z^{SOC} \hat{s}_{0,i} \,|\, bSS \right\rangle \left\langle bSS \,|\, \textstyle\sum_i l_{iz} \,|\, aSS \right\rangle\end{aligned}$$

compare to find the expression for g!

- Thus:

$$\boxed{\begin{aligned}g_{KL} = &-\frac{1}{S} \sum_{bS} \Delta_b^{-1} \left\langle aSS \,|\, \textstyle\sum_i l_{iK} \,|\, bSS \right\rangle \left\langle bSS \,|\, \textstyle\sum_i h_L^{SOC} \hat{s}_{0,i} \,|\, aSS \right\rangle \\ &- \frac{1}{S} \sum_{bS'} \Delta_b^{-1} \left\langle aSS \,|\, \textstyle\sum_i h_K^{SOC} \hat{s}_{0,i} \,|\, bSS \right\rangle \left\langle bSS \,|\, \textstyle\sum_i l_{iL} \,|\, aSS \right\rangle\end{aligned}}$$

- ★ **Note**: Only excited states of the same spin as the ground state
- ★ **Note**: Only standard components M=S

From EPR g-Tensors to to NMR Chemcial Shifts

Electrons

Nuclei

$$\hat{\mathrm{H}}_{\mathrm{el-Ze}} = \mu_{\mathrm{B}}\mathbf{B}\sum_{\mathrm{i}}\hat{\mathrm{l}}_{\mathrm{i}} + \mathrm{g}_{\mathrm{e}}\hat{\mathrm{s}}_{\mathrm{i}}$$

Electron Zeeman

$$\hat{\mathrm{H}}_{\mathrm{Nuc-Ze}} = \mu_{\mathrm{N}}\mathbf{B}\sum_{\mathrm{A}}\hat{\mathrm{I}}_{\mathrm{A}}$$

Nuclear Zeeman

$$\hat{\mathrm{H}}_{\mathrm{SOC}} = \sum_{\mathrm{i}}\hat{\mathbf{h}}_{\mathrm{i}}^{\mathrm{SOC}}\hat{\mathrm{s}}_{\mathrm{i}} = \frac{\alpha^{2}}{2}\sum_{\mathrm{i,A}}\mathrm{Z}_{\mathrm{A}}^{\mathrm{eff}}\frac{\hat{\mathrm{l}}_{\mathrm{i}}^{(\mathrm{A})}\hat{\mathrm{s}}_{\mathrm{i}}}{\mathrm{r}_{\mathrm{iA}}^{3}}$$

Spin-orbit coupling

$$\hat{\mathrm{H}}_{\mathrm{NOC}} = \frac{\alpha}{2}\mu_{\mathrm{N}}\sum_{\mathrm{i,A}}\mathrm{g}_{\mathrm{N}}^{(\mathrm{A})}\frac{\hat{\mathrm{l}}_{\mathrm{i}}^{(\mathrm{A})}\hat{\mathrm{I}}_{\mathrm{A}}}{\mathrm{r}_{\mathrm{iA}}^{3}}$$

Nucleus-orbit coupling

The g-Tensor(s) vs Chemical Shifts

First-order (diagmagnetic term)

EPR

$$\mathrm{g}_{\mathrm{ZZ}}^{(\mathrm{D,SB})} = \frac{1}{\mathrm{S}} \langle \Psi_0^{SS} \mid \sum_{\mathrm{A}} \sum_{\mathrm{i}} \left(\frac{\alpha^2 \mathrm{Z}_{\mathrm{A}}^{\mathrm{eff}}}{2} \right) \mathrm{r}_{\mathrm{iA}}^{-3} (\mathbf{r}_{\mathrm{i}} \mathbf{r}_{\mathrm{iA}} - \mathrm{z}_{\mathrm{i}} \mathrm{z}_{\mathrm{iA}}) \hat{\mathrm{s}}_{\mathrm{zi}} \mid \Psi_0^{SS} \rangle$$

(property of the entire system)

NMR

$$\mathrm{g}_{\mathrm{ZZ}}^{(\mathrm{D,SB;A})} = \left\langle \Psi_0^{\mathrm{SS}} \mid \sum_{\mathrm{i}} \mathrm{r}_{\mathrm{iA}}^{-3} (\mathbf{r}_{\mathrm{i}} \mathbf{r}_{\mathrm{iA}} - \mathrm{z}_{\mathrm{i}}^{\mathrm{T}} \mathrm{z}_{\mathrm{iA}}) \mid \Psi_0^{\mathrm{SS}} \right\rangle$$

(property of nucleus A)

Second-order (paramagnetic term)

EPR

$$\mathrm{g}_{\mathrm{ZZ}}^{(\mathrm{LB,LS})} = \frac{1}{\mathrm{S}} \sum_{\substack{\mathrm{I}>0 \\ (\mathrm{S}''=\mathrm{S})}} \Delta_{\mathrm{I}}^{-1} \left(\left\langle \Psi_0^{\mathrm{SS}} \middle| \sum_{\mathrm{i}} \hat{\mathrm{l}}_{\mathrm{zi}} \middle| \Psi_{\mathrm{I}}^{\mathrm{S''S''}} \right\rangle \left\langle \Psi_{\mathrm{I}}^{\mathrm{S''S''}} \middle| \sum_{\mathrm{i}} \mathrm{h}_{\mathrm{z}}^{\mathrm{SOC}} \hat{\mathrm{s}}_{0\mathrm{i}} \middle| \Psi_0^{\mathrm{SS}} \right\rangle + \mathrm{cc} \right)$$

(property of the entire system)

NMR

$$\mathrm{g}_{\mathrm{ZZ}}^{(\mathrm{LB,LS;A})} = \frac{1}{\mathrm{S}} \sum_{\substack{\mathrm{I}>0 \\ (\mathrm{S}''=\mathrm{S})}} \Delta_{\mathrm{I}}^{-1} \left(\left\langle \Psi_0^{\mathrm{SS}} \middle| \sum_{\mathrm{i}} \hat{\mathrm{l}}_{\mathrm{zi}} \middle| \Psi_{\mathrm{I}}^{\mathrm{S''S''}} \right\rangle \left\langle \Psi_{\mathrm{I}}^{\mathrm{S''S''}} \middle| \sum_{\mathrm{i}} \mathrm{r}_{\mathrm{iA}}^{-3} \hat{\mathrm{l}}_{\mathrm{zi}}^{(\mathrm{A})} \middle| \Psi_0^{\mathrm{SS}} \right\rangle + \mathrm{cc} \right)$$

(property of nucleus A)

In practice nobody uses a „nuclear g-tensors“, but the NMR culture consists of thinking about the chemical shift as a modification of the external field

$$\hat{\mathrm{H}}_{\mathrm{Spin}} = \mu_{\mathrm{N}} \mathbf{B} \sum_{\mathrm{A}} \mathbf{g}_{\mathrm{N}}^{(\mathrm{A})} \hat{\mathrm{I}}_{\mathrm{A}} = -\mu_{\mathrm{N}} \mathbf{B} \sum_{\mathrm{A}} \mathrm{g}_{\mathrm{N}}^{(\mathrm{A})} \left(1 - \sigma^{(\mathrm{A})} \right) \hat{\mathrm{I}}_{\mathrm{A}}$$

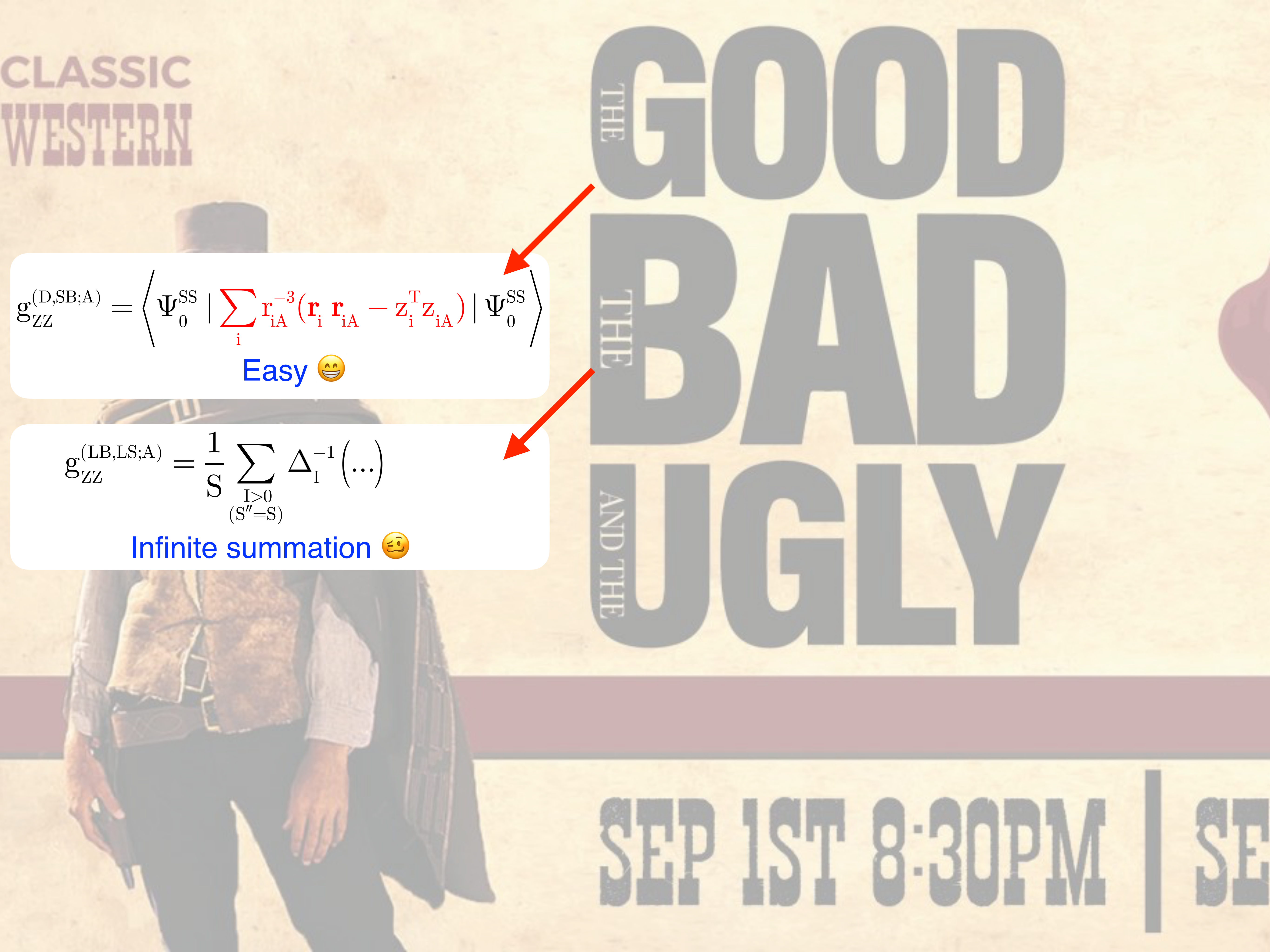
CLASSIC
WESTERN

THE GOOD THE BAD AND THE UGLY

SEP 1ST 8:30PM | SE

$$\mathrm{g}_{\mathrm{ZZ}}^{(\mathrm{D,SB;A})} = \left\langle \Psi_0^{\mathrm{SS}} \mid \sum_{\mathrm{i}} \mathrm{r}_{\mathrm{iA}}^{-3} \left(\mathbf{r}_{\mathrm{i}}\, \mathbf{r}_{\mathrm{iA}} - \mathrm{z}_{\mathrm{i}}^{\mathrm{T}} \mathrm{z}_{\mathrm{iA}} \right) \mid \Psi_0^{\mathrm{SS}} \right\rangle$$

Easy 😁

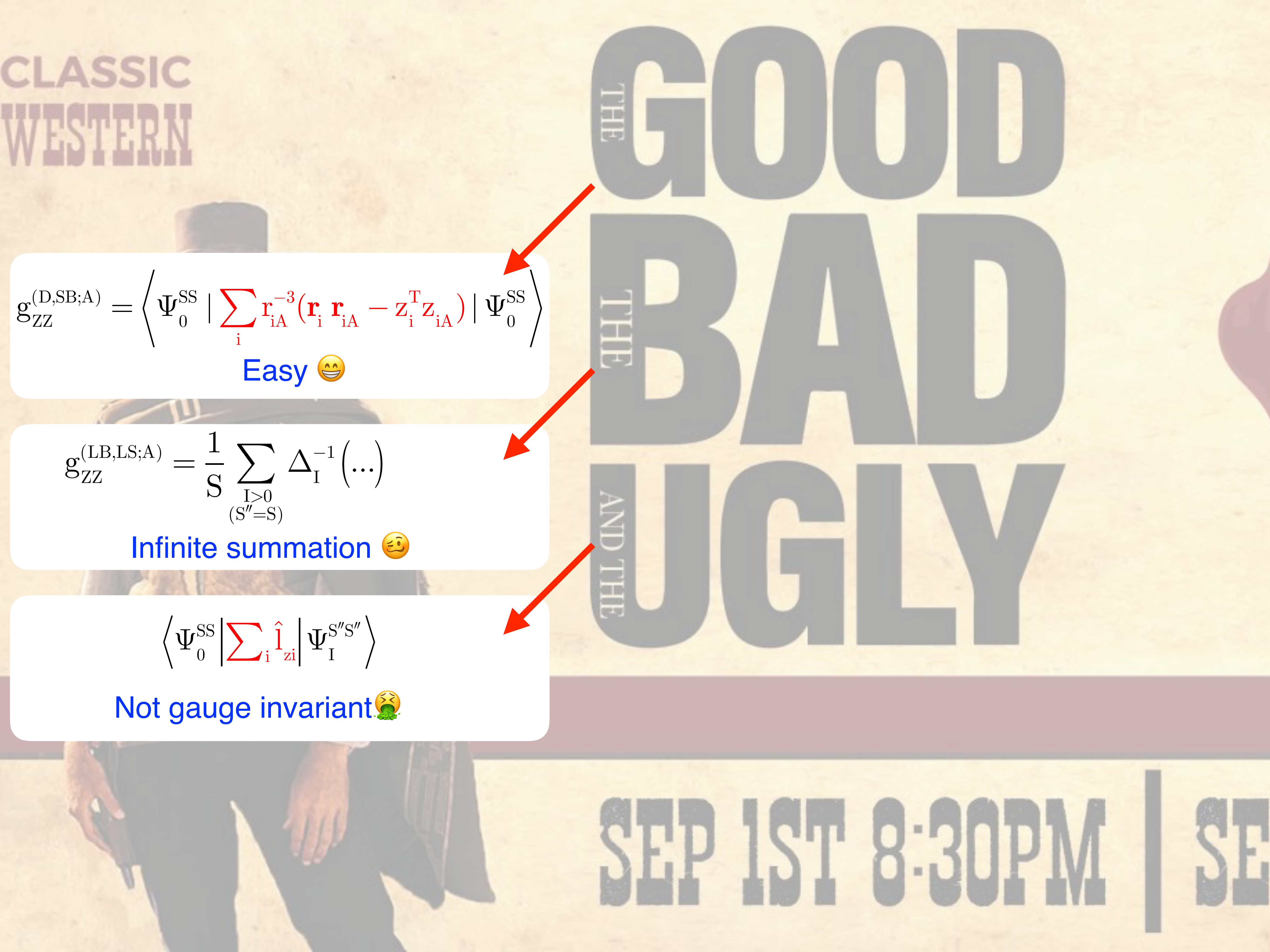


$$g_{ZZ}^{(D,SB;A)} = \left\langle \Psi_0^{SS} \mid \sum_i r_{iA}^{-3} \left(\mathbf{r}_i \, \mathbf{r}_{iA} - z_i^{T} z_{iA} \right) \mid \Psi_0^{SS} \right\rangle$$

Easy 😁

$$g_{ZZ}^{(LB,LS;A)} = \frac{1}{S} \sum_{\substack{I>0 \\ (S''=S)}} \Delta_I^{-1} \left(\ldots \right)$$

Infinite summation 🥴



$$g_{ZZ}^{(D,SB;A)} = \left\langle \Psi_0^{SS} \,|\, \sum_i r_{iA}^{-3} (\mathbf{r}_i \cdot \mathbf{r}_{iA} - z_i^T \cdot z_{iA}) \,|\, \Psi_0^{SS} \right\rangle$$

Easy 😁

$$g_{ZZ}^{(LB,LS;A)} = \frac{1}{S} \sum_{\substack{I>0 \\ (S''=S)}} \Delta_I^{-1} \left(\dots \right)$$

Infinite summation 🥴

$$\left\langle \Psi_0^{SS} \middle| \sum_i \hat{l}_{zi} \middle| \Psi_I^{S''S''} \right\rangle$$

Not gauge invariant🤮

Dealing with the Ugly: GIAO’s

A lack of Gauge invariance is not acceptable. Cure:

Gauge including Atomic Orbitals:

Normal basis function: $\varphi_\mu^{(A)}(\mathbf{r}) = S_{lm}^{(\mu)}(\theta,\phi)\sum_k d_k^{(\mu)} \exp\left(-\alpha_k^{(\mu)} r_A^2\right)$

GIAO: $\tilde{\varphi}_\mu^{(A)}(\mathbf{r},\mathbf{B}) = e^{\frac{i}{2c}(\mathbf{B}\times\mathbf{R}_A)\mathbf{r}}\varphi_\mu^{(A)}(\mathbf{r})$

Consequence:

$$\frac{\partial(\mu\nu\,|\,\kappa\tau)}{\partial\mathbf{B}} = 0 \quad ⇨ \quad \frac{\partial(\tilde{\mu}\tilde{\nu}\,|\,\tilde{\kappa}\tilde{\tau})}{\partial\mathbf{B}} = \frac{i}{2}\left(\mu^C\nu^D \,\middle|\, \frac{Q_{CD}\mathbf{r}_1 + Q_{EF}\mathbf{r}_2}{r_{12}} \,\middle|\, \kappa^E\tau^F\right)$$

etc. …about a dozen different types of new integrals

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GIAO:

Consequence:

$$\frac{\partial(\mu\nu \mid \kappa\tau)}{\partial \mathbf{B}} = 0$$

$$\frac{+ Q_{EF}\mathbf{r}_{2}}{r_{12}} \mid \kappa^{E}\tau^{F})$$

etc. …abo

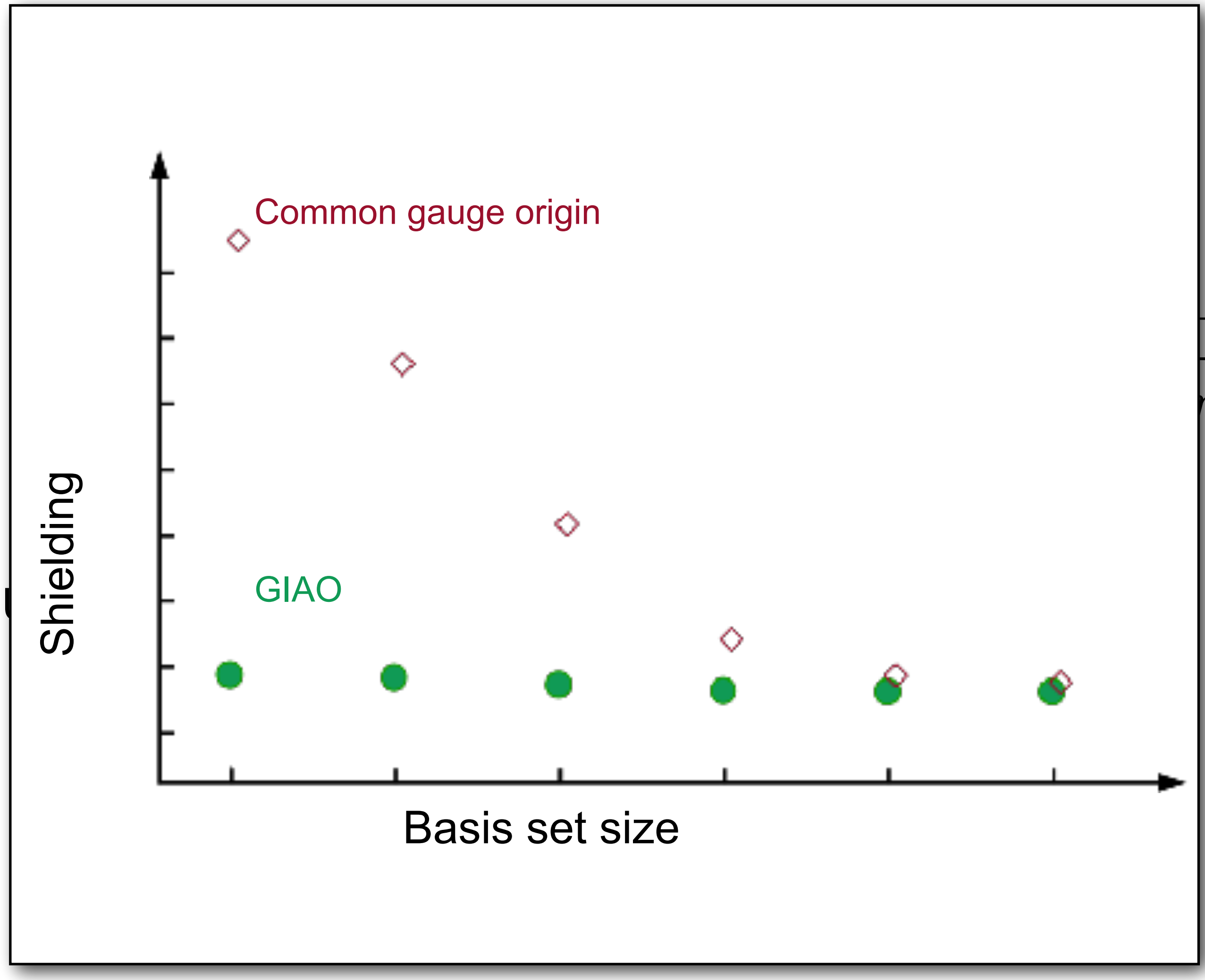
Dealing with the Ugly: GIAO's

A lack of Gauge invariance is not acceptable. Cure:

Gauge including Atomic Orbitals:

Normal basis function: $\varphi_{\mu}^{(A)}(\mathbf{r}) = S_{lm}^{(\mu)}(\theta,\phi)\sum_{k} d_{k}^{(\mu)} \exp\left(-\alpha_{k}^{(\mu)} r_{A}^{2}\right)$

GIAO:



Consequence:

$$\frac{\partial(\mu\nu \mid \kappa\tau)}{\partial \mathbf{B}} = 0$$

$$\frac{+ Q_{EF}\mathbf{r}_2}{r_{12}} \mid \kappa^{E}\tau^{F})$$

etc. …abou

First Order g-Tensor Contributions

- ★ For completeness, we notice that there are also a few relativistic operators that are bilinear in spin and field and hence give rise to **first order contributions**. They read:

$$
\begin{aligned}
g_{KL}^{(first-order)} = {} & \underbrace{\delta_{KL} g_e}_{Spin-Zeeman} \\
& \underbrace{+\,\delta_{KL} \frac{\alpha^2}{S} \left\langle aSS \,\middle|\, \sum\nolimits_i \vec{\nabla}_i^2 s_{zi} \,\middle|\, aSS \right\rangle}_{Reduced-Mass} \\
& \underbrace{+\,\frac{\alpha^2}{2S} \left\langle aSS \,\middle|\, \sum\nolimits_{iA} \frac{Z_A^{eff}}{r_{iA}^3} \left\{ (\mathbf{r}_{iA}\mathbf{r}_{i}) - (\mathbf{r}_{iA})_K (\mathbf{r}_{i})_L \right\} s_{zi} \,\middle|\, aSS \right\rangle}_{Diamagnetic\,Spin-Orbit\ (Gauge\ correction)}
\end{aligned}
$$

- ★ Except for the trivial **g_e=2.002319...** the first order terms are typically much smaller than the second order term.
- ★ α≈1/137 is the **fine structure constant** and Z^{eff} is an *effective nuclear charge* that is semiempirical and has been introduced to avoid expensive (and small) two-electron gauge terms.

The Zero-Field Splitting

- The ZFS is quite hard to do and it wasn‘t clear for a long time whether it could be cast in ‚standard form‘ **SDS**.
- The ZFS arises from ***twice* the SOC** (to second order) and the **direct electron-electron spin-spin interaction** (to first order). The (complicated) derivation yields:

$$D_{kl}^{(SS)} = \frac{1}{2}\frac{\alpha^2}{S\left(2S-1\right)}\left\langle \Psi_0^{SS} \left| \sum_i \sum_{j\neq i} r_{ij}^{-5} \left\{ r_{ij}^2 \delta_{kl} - 3(\mathbf{r}_{ij})_k (\mathbf{r}_{ij})_l \right\} \left\{ 2s_{zi}s_{zj} - s_{xi}s_{xj} - s_{yi}s_{yj} \right\} \right| \Psi_0^{SS} \right\rangle$$

$$D_{kl}^{SO-(0)} = -\frac{1}{S^2} \sum_b \Delta_{bS'}^{-1} \left\langle \Psi_0^{SS} \left| \sum_i h_k^{SOC} s_{i,z} \right| \Psi_b^{SS} \right\rangle \left\langle \Psi_b^{SS} \left| \sum_i h_l^{SOC} s_{i,z} \right| \Psi_0^{SS} \right\rangle$$

$$D_{kl}^{SO-(-1)} = -\frac{1}{S\left(2S-1\right)} \sum_{\substack{b \\ (S'=S-1)}} \Delta_{bS'}^{-1} \left\langle \Psi_0^{SS} \left| \sum_i h_k^{SOC}(i)\hat{s}_{i,+1} \right| \Psi_b^{S-1,S-1} \right\rangle \left\langle \Psi_b^{S-1,S-1} \left| \sum_i h_l^{SOC}(i)\hat{s}_{i,-1} \right| \Psi_0^{SS} \right\rangle$$

$$D_{kl}^{SO-(+1)} = -\frac{1}{(S+1)(2S+1)} \sum_{\substack{b \\ (S'=S+1)}} \Delta_{bS'}^{-1} \left\langle \Psi_0^{SS} \left| \sum_i h_k^{SOC}(i)\hat{s}_{i,-1} \right| \Psi_b^{S+1,S+1} \right\rangle \left\langle \Psi_b^{S+1,S+1} \left| \sum_i h_l^{SOC}(i)\hat{s}_{i,-1} \right| \Psi_0^{SS} \right\rangle$$

- The SOC part of the ZFS contains contributions from excited states that have the same spin as the ground state or differ by +/- 1 unit of spin angular momentum. This together with the ‚singular‘ two electron SS part makes the ZFS a very hard property to calculate

FN, EI Solomon *Inorg. Chem.*, **1998**. 37,6568

The Hyperfine Coupling

- The Hyperfine Coupling is relatively straightforward. The most important terms are of first order and arise from the magnetic dipole interaction between nuclei and electrons:

$$A_{KL}^{(iso)} = \delta_{KL} \frac{4\pi}{3S} \beta\beta_N g_e g_N \left\langle aSS \mid \sum_i \delta(\mathbf{r}_i - \mathbf{R}_A) s_{zi} \mid aSS \right\rangle$$

$$A_{KL}^{(dip)} = \delta_{KL} \frac{1}{2S} \beta\beta_N g_e g_N \left\langle aSS \mid \sum_i r_{iA}^{-5} \left\{ 3(\mathbf{r}_{iA})_K (\mathbf{r}_{iA})_L - \delta_{KL} r_{iA}^2 \right\} s_{zi} \mid aSS \right\rangle$$

- And a second order correction due to spin-orbit coupling and nucleus-orbit couplings:

$$\begin{aligned} A_{KL} = &-\frac{\alpha^2}{S} \beta_N g_N \sum_{bS} \Delta_b^{-1} \left\langle aSS \mid \sum\nolimits_i l_{iK}^{(A)} r_{iA}^{-3} \mid bSS \right\rangle \left\langle bSS \mid \sum\nolimits_i h_L^{SOC} \hat{s}_{0,i} \mid aSS \right\rangle \\ &-\frac{\alpha^2}{S} \beta_N g_N \sum_{bS'} \Delta_b^{-1} \left\langle aSS \mid \sum\nolimits_i h_K^{SOC} \hat{s}_{0,i} \mid bSS \right\rangle \left\langle bSS \mid \sum\nolimits_i l_{iL}^{(A)} r_{iA}^{-3} \mid aSS \right\rangle \end{aligned}$$

- It can become large for transition metal nuclei but is small for light molecules. $l^{(A)}$ is the angular momentum relative to nucleus ‚A‘.

Making it Practical: Linear Response Approach

Linear Response Approach

Search for approximate solutions of: $\hat{H}\Psi = E\Psi$

Explicitly:

$$E\Psi(\mathbf{x}_1 \ldots, \mathbf{x}_N) = \left(\underbrace{T_e + V_{eN} + V_{NN} + V_{ee}}_{H_{BO}} + \underbrace{\lambda V_{magnetic} + \mu V_{electric} + \kappa V_{relativistic}}_{small\ \ corrections} \right) \Psi(\mathbf{x}_1 \ldots, \mathbf{x}_N)$$

FN (**2001**) *J. Chem. Phys.*, 115, 11080

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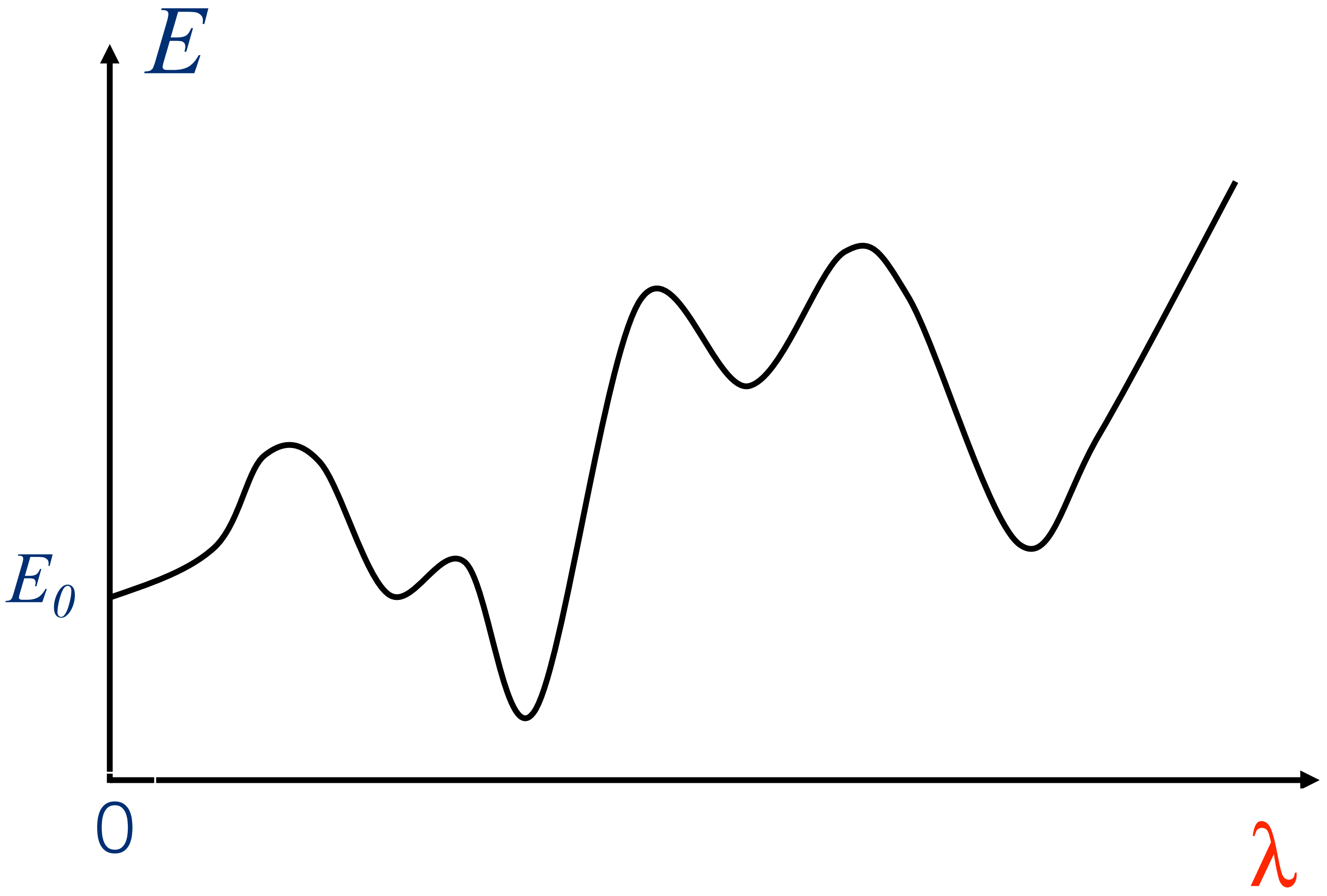

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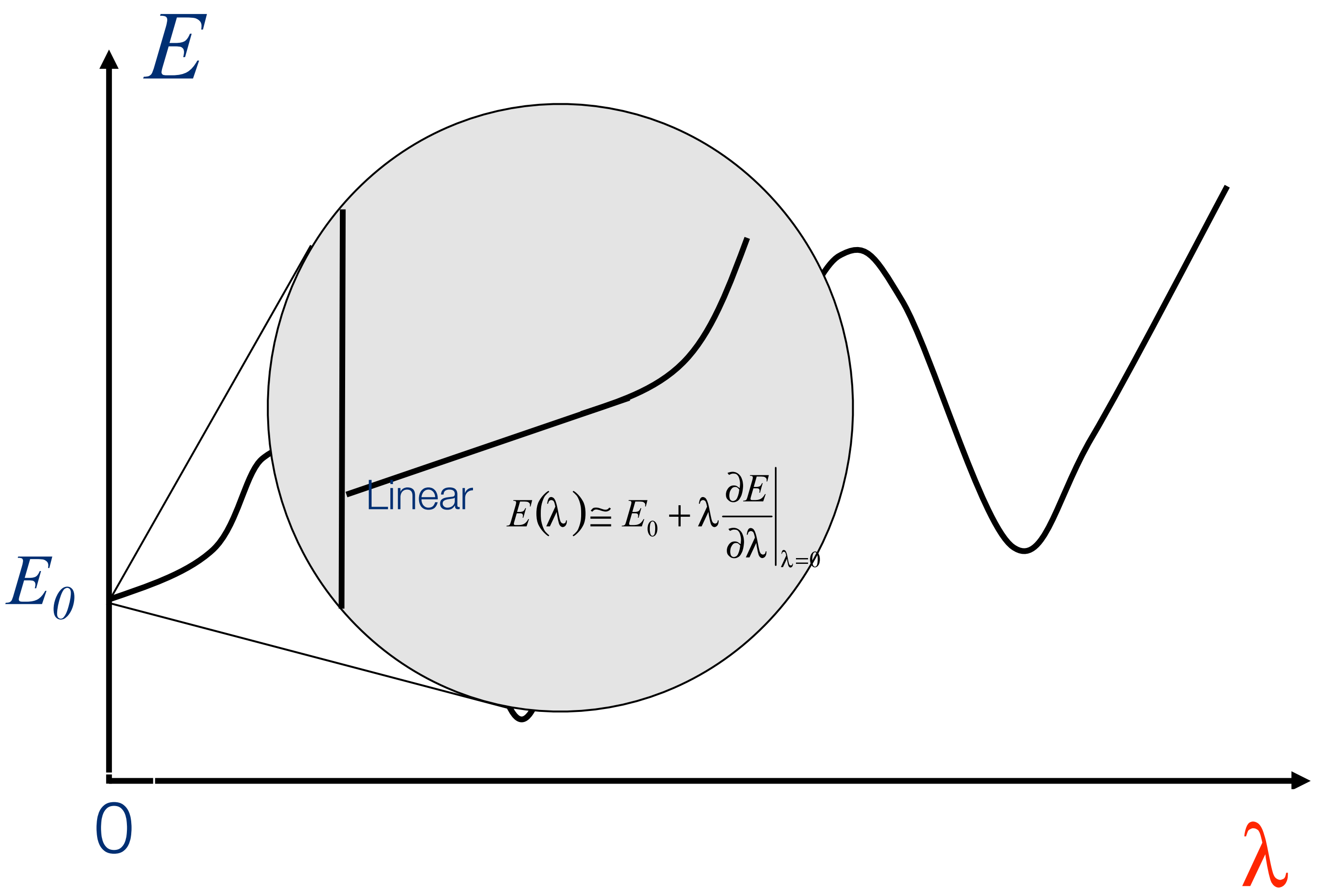

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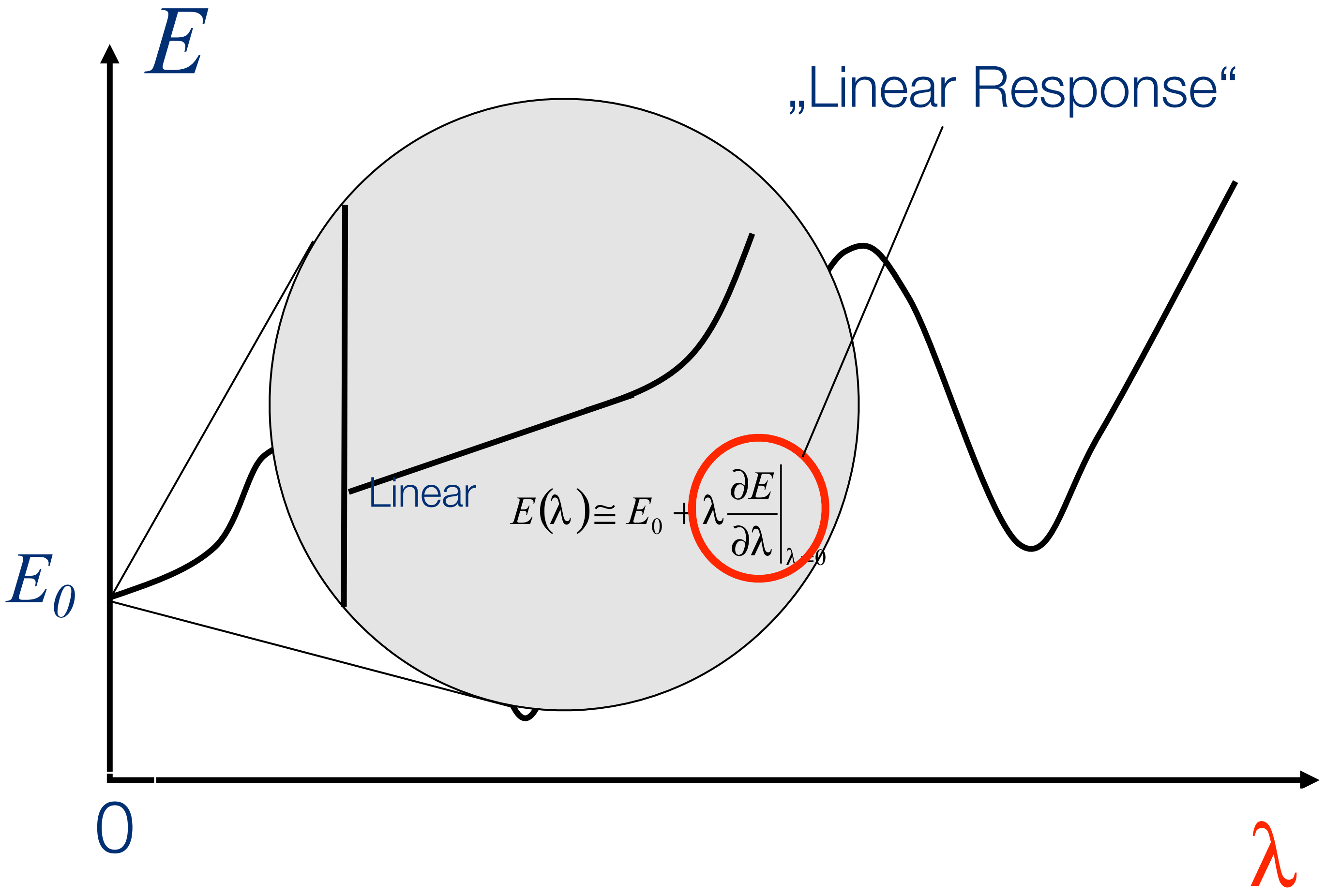

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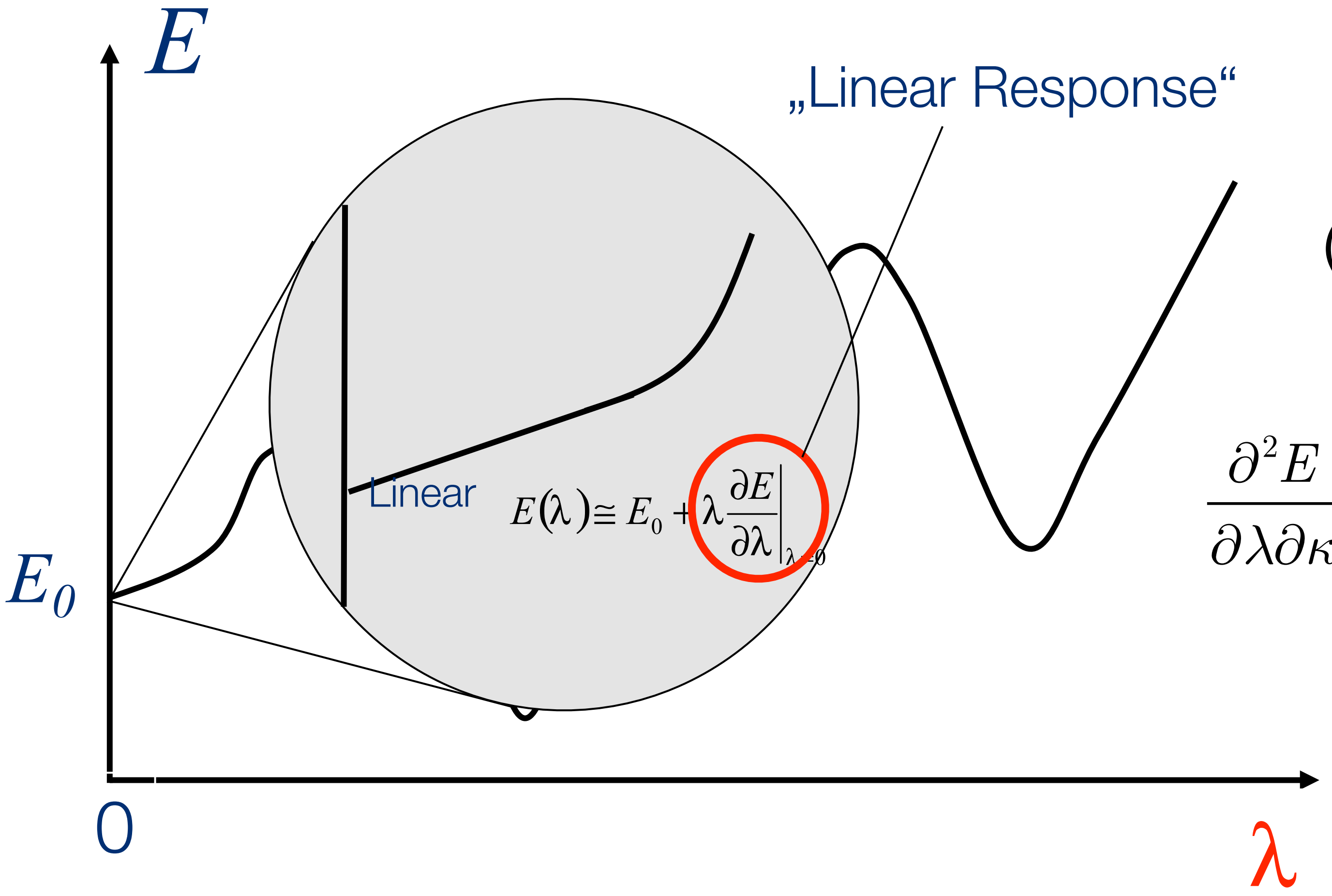


(Almost) all molecular properties

$$\left.\frac{\partial^2 E}{\partial\lambda\partial\kappa}\right|_{\lambda=\kappa=0} = \sum_{\mu\nu} \frac{\partial P^{\pm}_{\mu\nu}}{\partial\kappa}\left\langle \varphi_\mu \left| \frac{\partial h}{\partial\lambda} \right| \varphi_\nu \right\rangle + P^{\pm}_{\mu\nu}\left\langle \varphi_\mu \left| \frac{\partial^2 h}{\partial\lambda\partial\kappa}\right| \varphi_\nu \right\rangle$$

FN (**2001**) *J. Chem. Phys.*, 115, 11080

Exact Equivalence of SOS and LRT

- Assume that we know the exact eigenspectrum of the BO Hamiltonian as our basis. Then the **Hellmann-Feynman theorem** tells us that

$$E_0^{(0)} = \left\langle 0 \mid H_{BO} \mid 0 \right\rangle$$

Ground state energy

$$E(\lambda) = E_0^{(0)} + \lambda \left.\frac{\partial E_0}{\partial \lambda}\right|_{\lambda=0} + \dots$$

Taylor expansion of the perturbed energy

$$\left.\frac{\partial E_0}{\partial \lambda}\right|_{\lambda=0} = \left\langle 0 \mid H^{(\lambda)} \mid 0 \right\rangle = \sum_{pq} D_{pq} \underbrace{h_{pq}^{(\lambda)}}_{=\frac{\partial h_{\mu\nu}}{\partial \lambda}}$$

First Derivative

$$D_{pq} = \left\langle 0 \mid p^{+} q \mid 0 \right\rangle$$

One particle density

- This result is exactly equivalent with the first order perturbation theory. Can we do the same thing for the second derivative?

$$\left.\frac{\partial^2 E_0}{\partial \lambda \partial \mu}\right|_{\lambda=\mu=0} = \sum_{pq} \frac{\partial D_{pq}}{\partial \mu} h_{pq} + \sum_{pq} D_{pq} \frac{\partial^2 h_{pq}}{\partial \lambda \partial \mu} \qquad \left(\frac{\partial D_{pq}}{\partial \mu} = \left\langle \frac{\partial \Psi}{\partial \mu} \mid p^{+} q \mid \Psi \right\rangle + cc \right)$$

Second Derivative and Sum Over States

- ★ First-order perturbation theory tells us that:

$$\left|\frac{\partial\Psi_0}{\partial\mu}\right\rangle = -\sum_n \frac{\langle 0 \,|\, H^{(\mu)} \,|\, n\rangle}{E_n - E_0}\left|n\right\rangle$$

- ★ Hence:

$$\frac{\partial D_{pq}}{\partial\mu} = -\sum_n \frac{\langle 0 \,|\, H^{(\mu)} \,|\, n\rangle\langle n \,|\, p^+q \,|\, \Psi_0\rangle}{E_n - E_0} - \sum_n \frac{\langle 0 \,|\, p^+q \,|\, n\rangle\langle n \,|\, H^{(\mu)} \,|\, 0\rangle}{E_n - E_0}$$

- ★ So:

$$\left.\frac{\partial^2 E_0}{\partial\lambda\partial\mu}\right|_{\lambda=\mu=0} = \sum_{pq}\frac{\partial D_{pq}}{\partial\mu}\frac{\partial h_{pq}}{\partial\lambda} + \sum_{pq} D_{pq}\frac{\partial^2 h_{pq}}{\partial\lambda\partial\mu}$$

$$= -2\sum_n \frac{\langle 0 \,|\, H^{(\mu)} \,|\, n\rangle\langle n \,|\, H^{(\lambda)} \,|\, \Psi_0\rangle}{E_n - E_0} + \langle 0 \,|\, H^{(\mu,\lambda)} \,|\, 0\rangle$$

- ★ Thus, *second derivatives are exactly equivalent to the H^{eff} to second order!*

see FN Mol. Phys, ***2007****,* *105, 2507* *FN J. Chem. Phys.,* ***2007****,* *127,* 164112

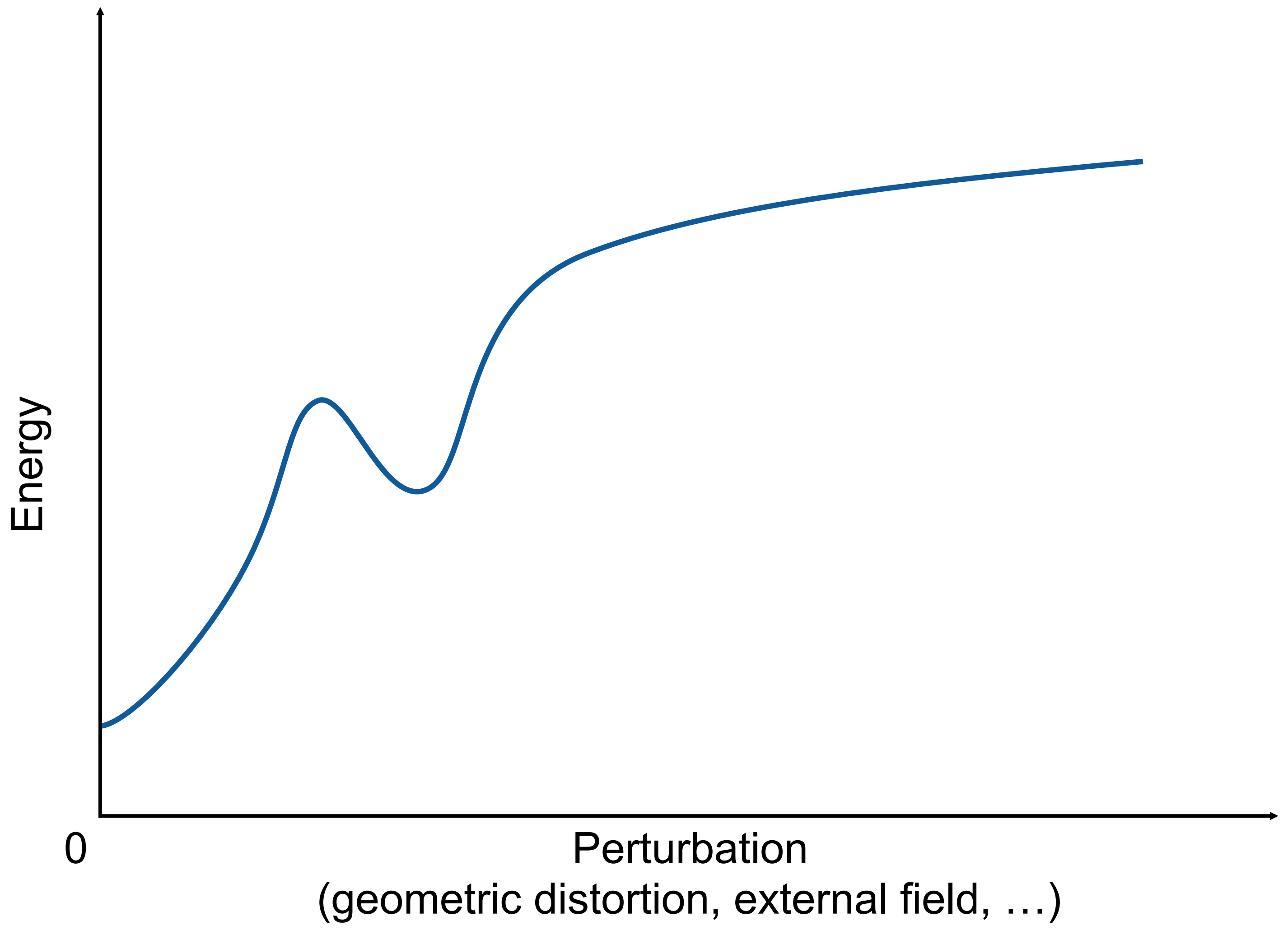
Explicit Expressions from the Response Theory

$$
\begin{aligned}
\hat{H}_{Spin} &= \underbrace{\beta\mathbf{BgS}}_{Zeeman} + \underbrace{\mathbf{SDS}}_{Zero-Field-Splitting} + \sum_{K} \underbrace{\mathbf{SA}^{(K)}\mathbf{I}^{(K)}}_{Hyperfine} - \underbrace{g_N^{(K)}\beta_N\mathbf{BI}^{(K)}}_{Nuclear-Zeeman} + \underbrace{\mathbf{I}^{(K)}\mathbf{Q}^{(K)}\mathbf{I}^{(K)}}_{Quadrupole} \\
&= \beta\mathbf{B}\left\{ -\frac{\alpha^2}{S}\sum_{\mu,\nu} P_{\mu\nu}^{\alpha-\beta}\left\langle \phi_\mu \middle| \hat{T} \middle| \phi_\nu \right\rangle + \frac{1}{2S}\sum_{\mu,\nu} P_{\mu\nu}^{\alpha-\beta}\left\langle \varphi_\mu \middle| \sum_A \xi\left(r_A\right)(\mathbf{r}_A\mathbf{r} - \mathbf{r}_{A,k}\mathbf{r}_l) \middle| \varphi_\nu \right\rangle + \frac{1}{2S}\sum_{\mu\nu}\frac{\partial P_{\mu\nu}^{(\alpha-\beta)}}{\partial B_k}\left\langle \varphi_\mu \middle| \hat{z}_l^{SOMF} \middle| \varphi_\nu \right\rangle \right\}\mathbf{S} \\
&\quad + \mathbf{S}\left\{ -\frac{g_e^2}{16}\frac{\alpha^2}{S\left(2S-1\right)}\sum_{\mu\nu}\sum_{\kappa\tau}\left\{P_{\mu\nu}^{\alpha-\beta}P_{\kappa\tau}^{\alpha-\beta} - P_{\mu\kappa}^{\alpha-\beta}P_{\nu\tau}^{\alpha-\beta}\right\}\left\langle \mu\nu \middle| r_{12}^{-5}\left\{3r_{12,k}r_{12,l} - \delta_{kl}r_{12}^2\right\} \middle| \kappa\tau \right\rangle \right. \\
&\quad \left. - \frac{1}{4S^2}\sum_{\mu\nu}\left\langle \mu \mid h_k^{SOC} \mid \nu \right\rangle \frac{\partial P_{\mu\nu}^{(0)}}{\partial S_l^{(0)}} + \frac{1}{2\left(S+1\right)\left(2S+1\right)}\sum_{\mu\nu}\left\langle \mu \mid h_k^{SOC} \mid \nu \right\rangle \frac{\partial P_{\mu\nu}^{(-1)}}{\partial S_l^{(+1)}} + \frac{1}{2S\left(2S-1\right)}\sum_{\mu\nu}\left\langle \mu \mid h_k^{SOC} \mid \nu \right\rangle \frac{\partial P_{\mu\nu}^{(+1)}}{\partial S_l^{(-1)}} \right\}\mathbf{S} \\
&\quad + \sum_K \mathbf{S}\left\{ \delta_{kl}\frac{8\pi}{3}\frac{P^{(K)}}{2S}\rho^{\alpha-\beta}\left(\mathbf{R}_K\right) + \frac{P^{(K)}}{2S}\sum_{\mu\nu} P_{\mu\nu}^{\alpha-\beta}\left\langle \varphi_\kappa \middle| r_K^{-5}\left(r_K^2\delta_{\mu\nu} - 3r_{K;\mu}r_{A;\nu}\right) \middle| \varphi_\tau \right\rangle - \frac{P_A}{S}\sum_{\mu\nu}\frac{\partial P_{\mu\nu}^{\alpha-\beta}}{\partial \hat{I}_k^{(A)}}\left\langle \varphi_\mu \mid z_l^{SOMF} \mid \varphi_\nu \right\rangle \right\}\mathbf{I}^{(K)} \\
&\quad - g_N^{(K)}\beta_N\mathbf{BI}^{(K)} + \mathbf{I}^{(K)}\left\{ \frac{e^2Q^{(K)}}{4I\left(2I-1\right)}\sum_{\kappa,\tau} P_{\kappa\tau}^{\alpha+\beta}\left\langle \varphi_\kappa \middle| r_K^{-5}\left(r_K^2\delta_{\mu\nu} - 3r_{K;\mu}r_{A;\nu}\right) \middle| \varphi_\tau \right\rangle \right\}\mathbf{I}^{(K)}
\end{aligned}
$$

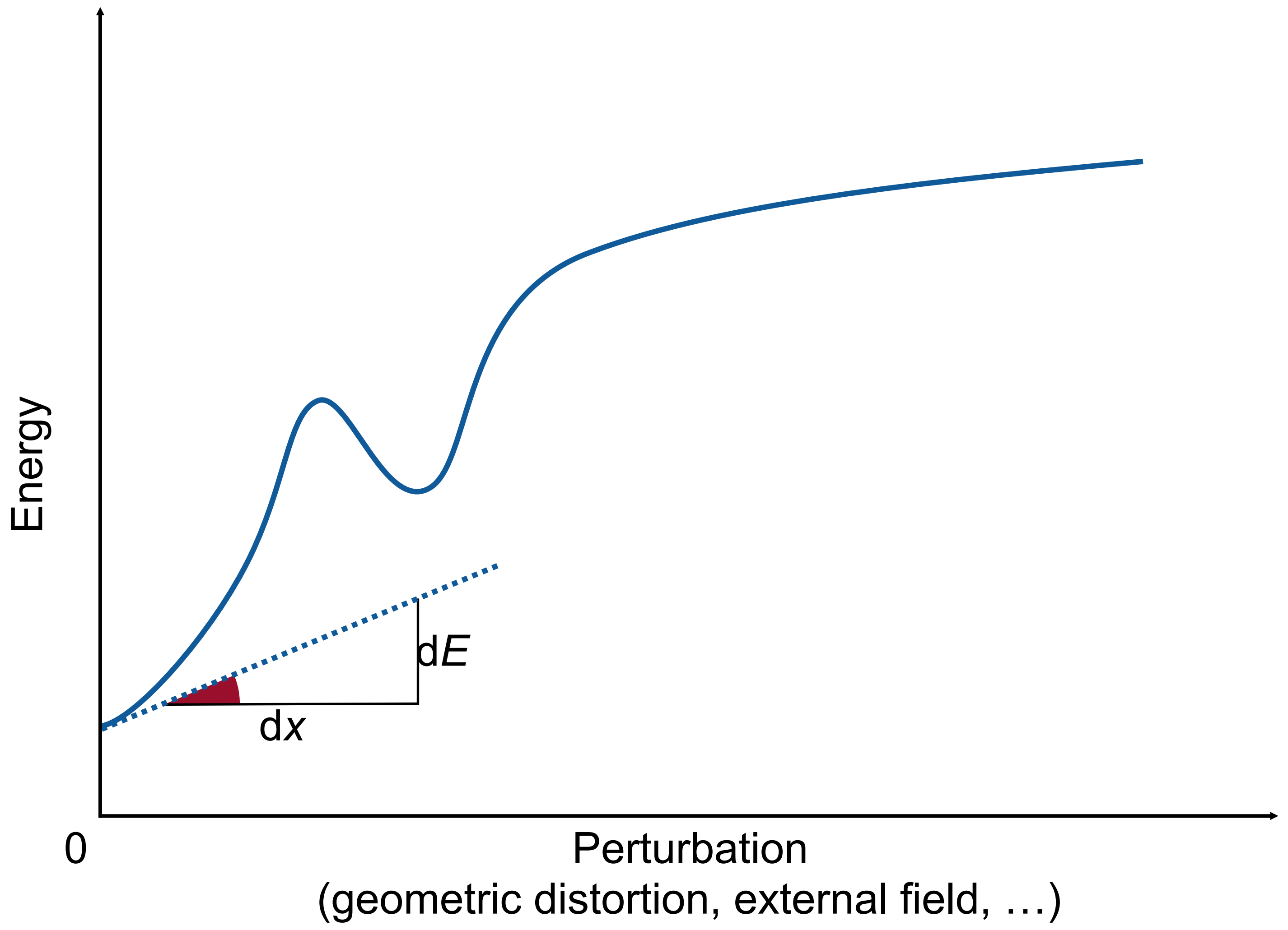
First-order one-electron terms First-order two-electron terms Second-order one-electron terms

Only completely realized in the framework of density functional theory in the ORCA program under the assumption that the exact wavefunction coincides with the Kohn-Sham determinant

Molecular Properties as Derivatives



Molecular Properties as Derivatives



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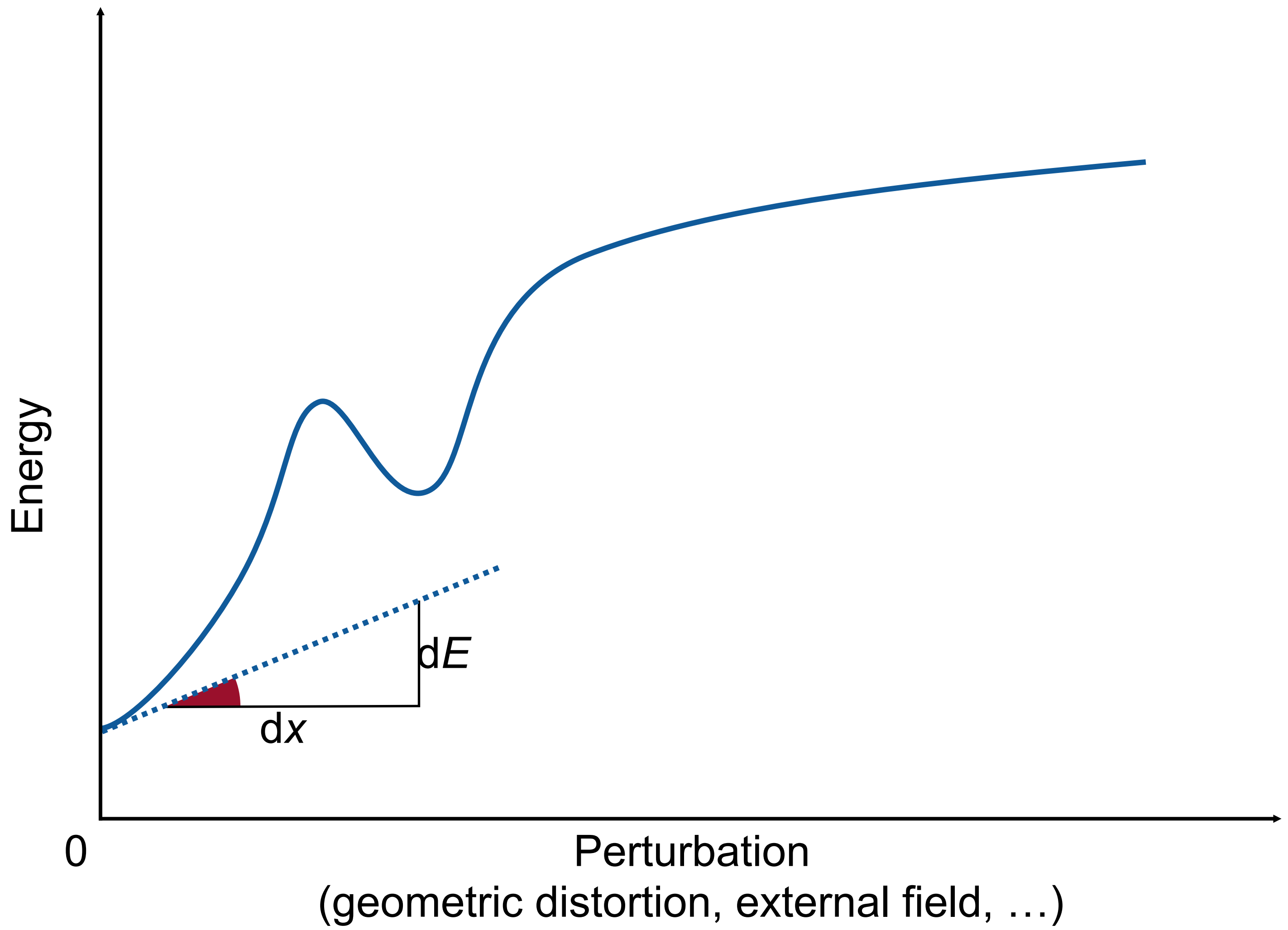
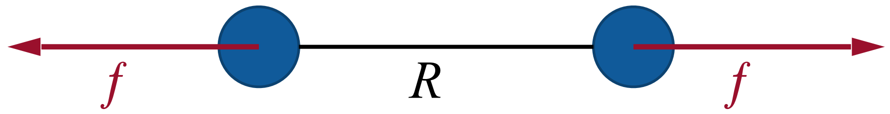
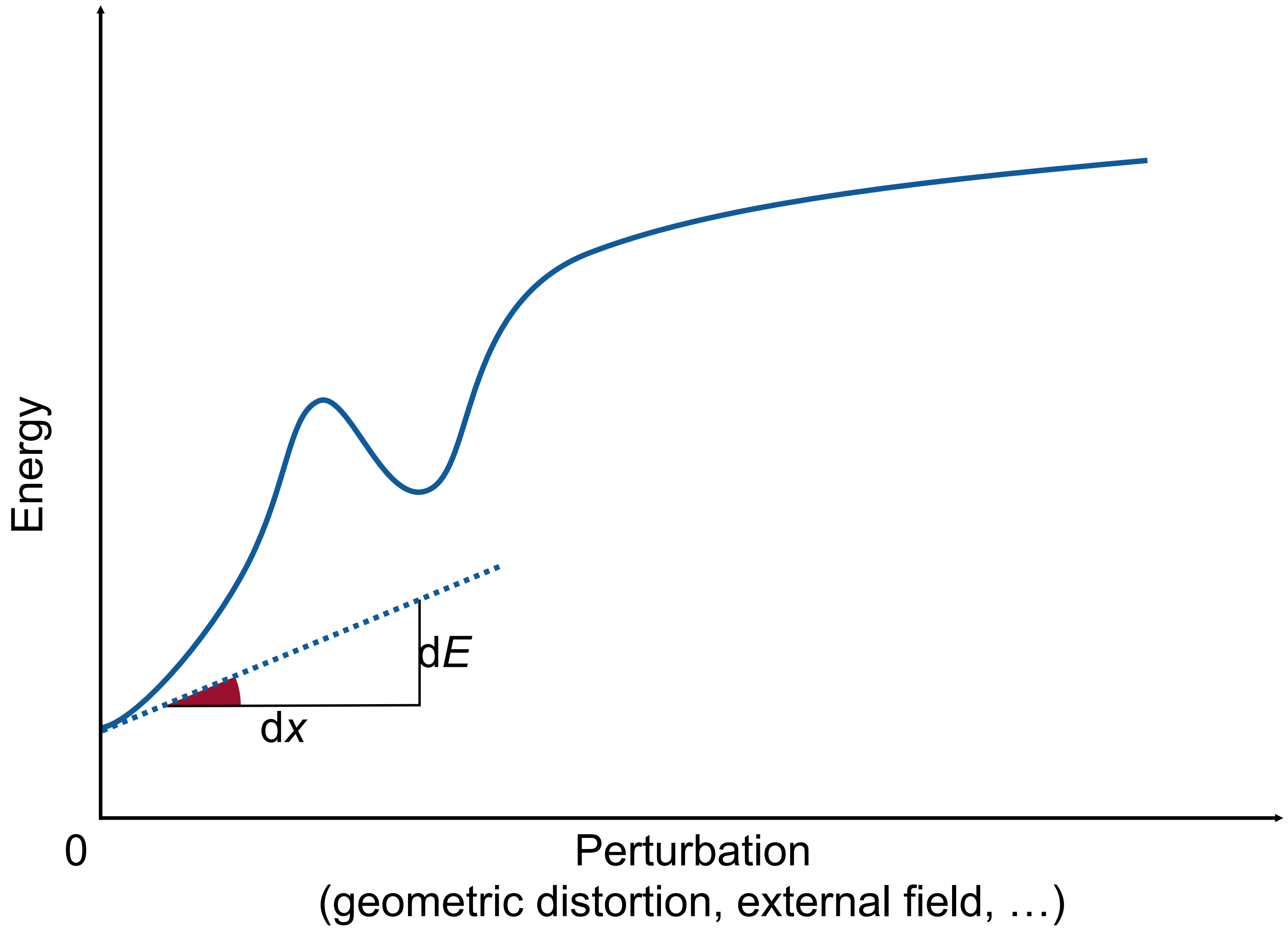
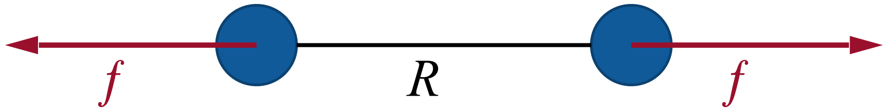




$$f = -\frac{\partial E}{\partial R}$$

Molecular Properties as Derivatives





$$f = -\frac{\partial E}{\partial R}$$

$\frac{\partial E}{\partial \mathbf{E}}$ → Dipole moment

$\frac{\partial^2 E}{\partial \mathbf{E}^2}$ → Polarizability

$\frac{\partial^2 E}{\partial \mathbf{R}^2}$ → Vibrational frequency

$\frac{\partial^2 E}{\partial \mathbf{R} \partial \mathbf{E}}$ → IR intensity

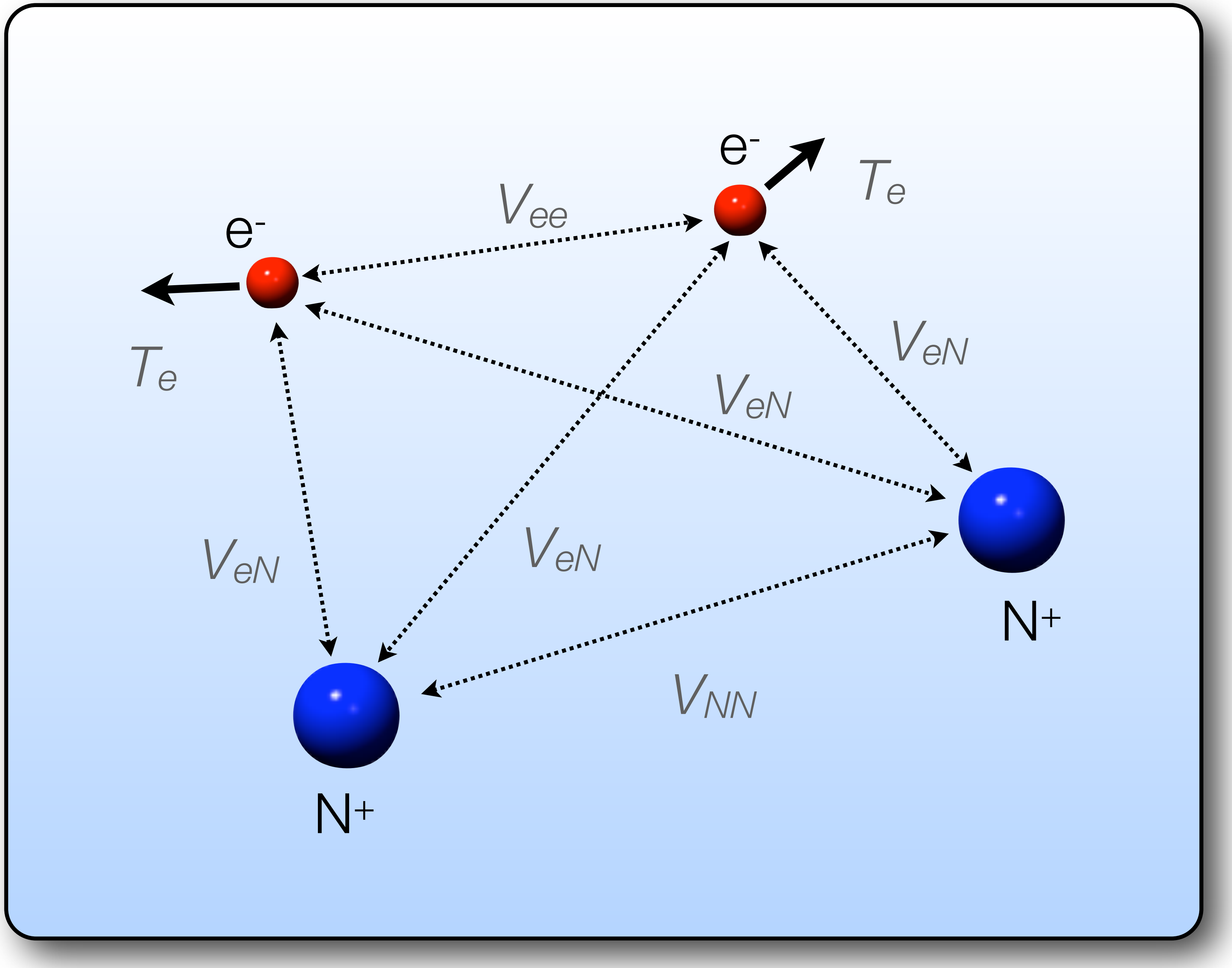
$\frac{\partial^3 E}{\partial \mathbf{R} \partial \mathbf{E}^2}$ → Raman intensity

$\frac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{M}_A}$ → NMR shielding

$\frac{\partial^2 E}{\partial \mathbf{M}_A \partial \mathbf{M}_B}$ → Indirect nuclear spin-spin coupling

Implementation: Electronic Structure Methods

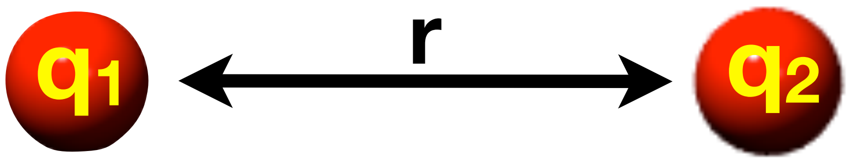
Fundamental Interactions in Molecules



$$E = T_e + T_N + V_{eN} + V_{NN} + V_{ee}$$

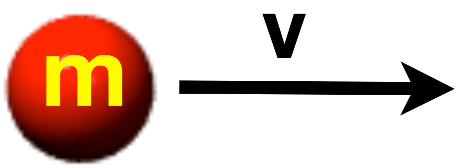
Just 2 Laws:

1. Coulomb's Law



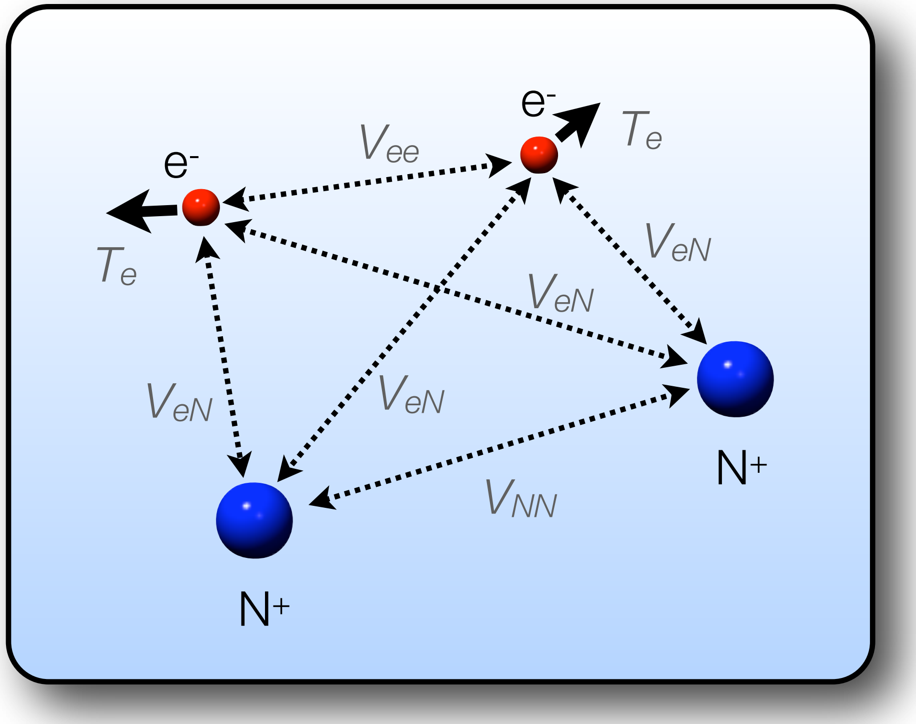
$$E = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

2. Kinetic Energy

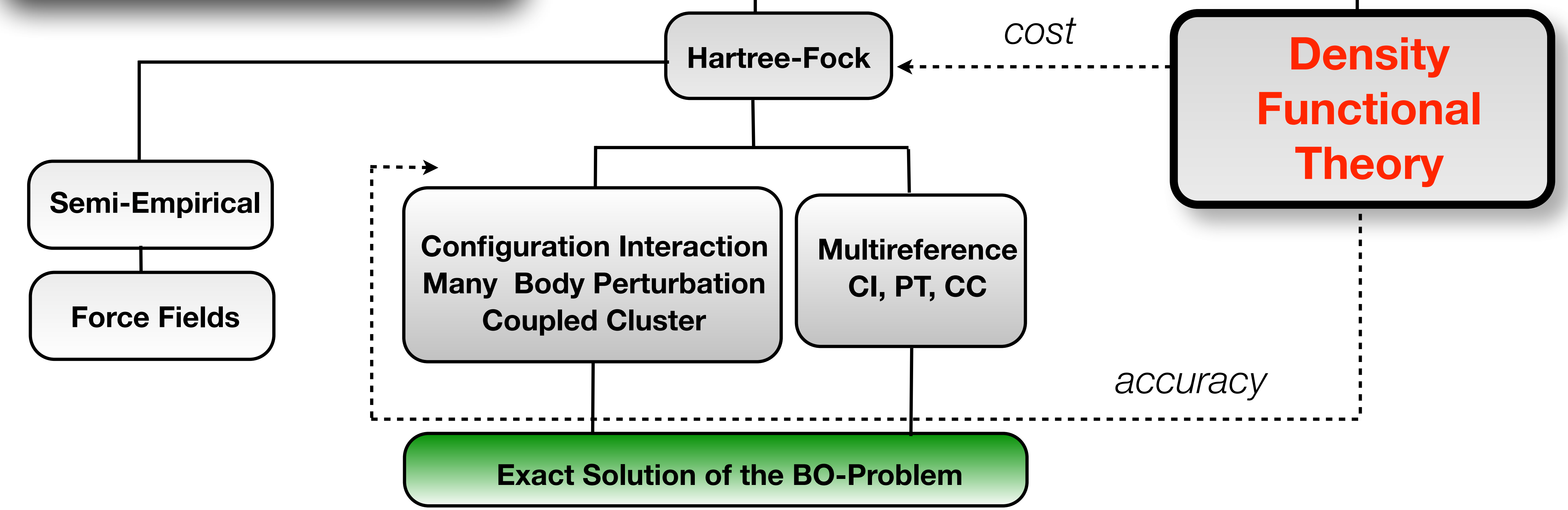


$$E = \frac{1}{2} m v^2 = \frac{p^2}{2m}$$

Approximate Quantum Mechanical Methods



$$\hat{H}(\mathbf{x},\mathbf{R})\Psi(\mathbf{x}_1,\dots,\mathbf{x}_N \mid \mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{x}_1,\dots,\mathbf{x}_N \mid \mathbf{R})$$



Hartree-Fock

cost

Density Functional Theory

Semi-Empirical

Force Fields

Configuration Interaction
Many Body Perturbation
Coupled Cluster

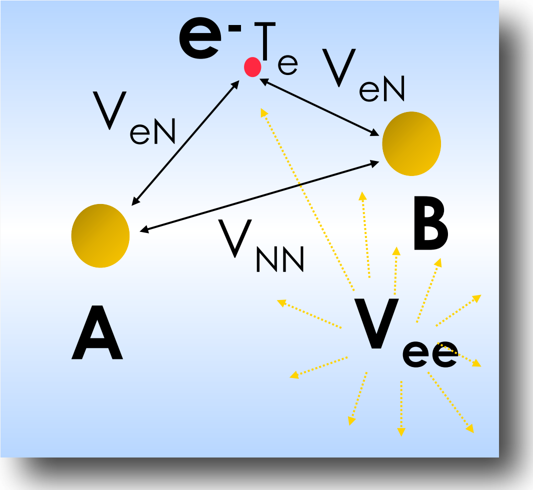
Multireference
CI, PT, CC

accuracy

Exact Solution of the BO-Problem

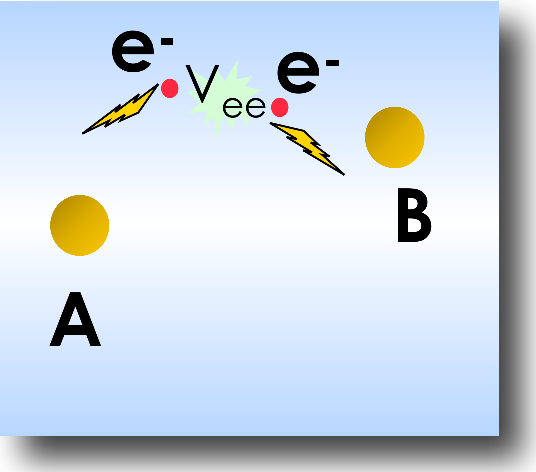
Mean Field Theory to Exact Solutions

Exact Energy =



"Mean Field"
Hartree-Fock

+



Instantaneous electron-electron interaction

Correlation energy= $\frac{1}{2} \sum_{i,j \text{ Electron pairs}} \varepsilon_{ij}(\uparrow\uparrow) + \varepsilon_{ij}(\uparrow\downarrow)$

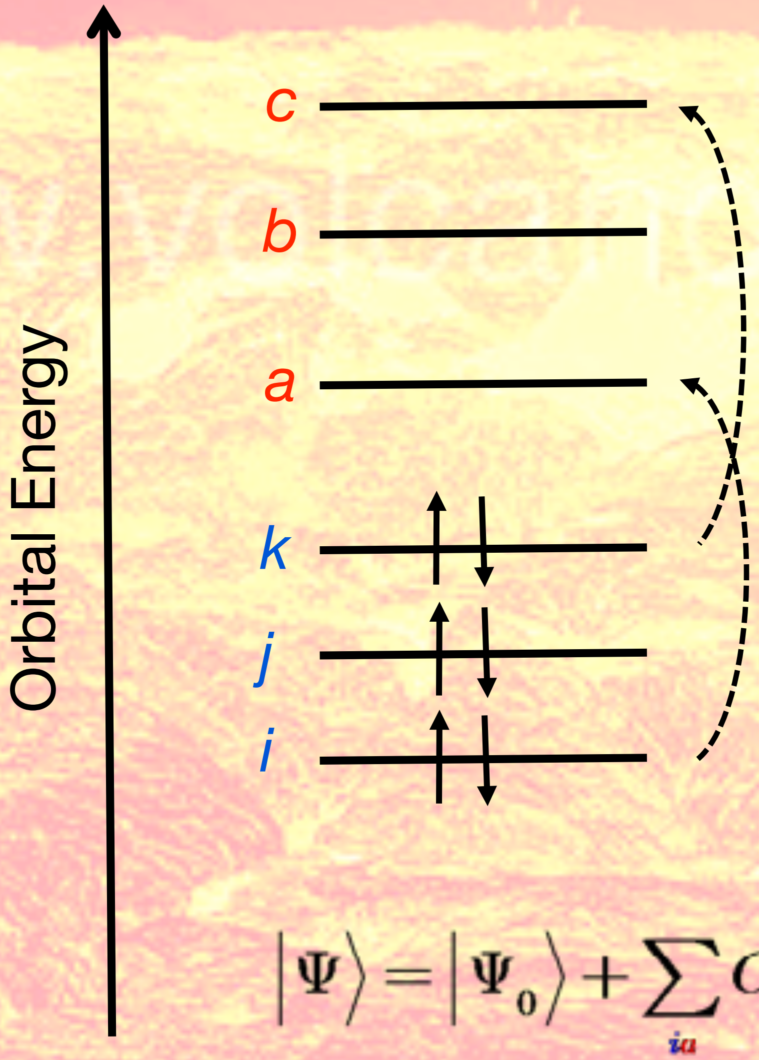
Fermi-Correlation ↑

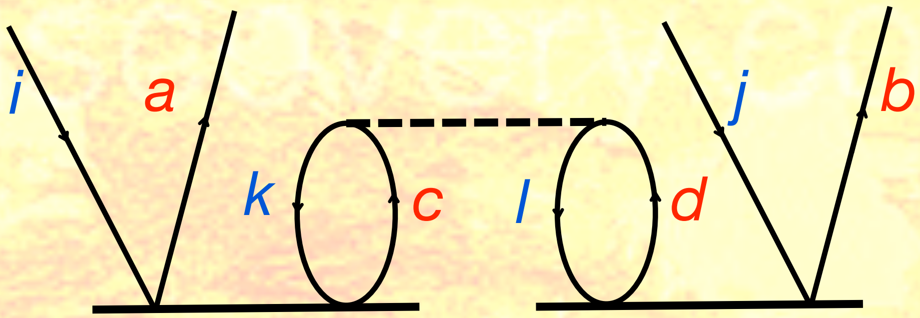
Relatively easy due to "Fermi hole" in the mean-field

Coulomb-correlation ↑

Extremely hard to calculate due to interelectronic cusp at the coalescence point $\boldsymbol{r}_1=\boldsymbol{r}_2$

„Coupled Cluster Theory“





$$\frac{1}{2}P_{ij}P_{ab}\sum_{klcd}\langle kl\|cd\rangle t^{ik}_{ac}t^{lj}_{db}$$

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{ia} C^{i}_{a}|\Psi^{a}_{i}\rangle + \frac{1}{4}\sum_{ijab} C^{ij}_{ab}|\Psi^{ab}_{ij}\rangle + \frac{1}{36}\sum_{ijkabc} C^{ijk}_{abc}|\Psi^{abc}_{ijk}\rangle + \dots$$

Coupled Cluster Theory in a Nutshell

$$\Psi = \exp\left(T\right)\Psi_0$$

Ansatz
(Coester & Kuemmel)

$$\Psi_0 = \left|\phi_1 \ldots \phi_N\right|$$

Reference determinant

$$\phi_i\left(\mathbf{r}\right) = \sum_\mu c_{\mu i}\ \varphi_\mu\left(\mathbf{r}\right)$$

MOs **MO coeffs** **BFs**

Cluster Operator $T = T_1 + T_2 + T_3 + \ldots$

Cluster Amplitudes

$$T_1 = \sum_{ia} t_a^i a_a^+ a_i \qquad T_2 = \tfrac{1}{4}\sum_{ijab} t_{ab}^{ij} a_b^+ a_a^+ a_i\, a_j$$

CC wavefucntion

$$\Psi = \left(1 + (T_1 + T_2 + \ldots) + \tfrac{1}{2}(T_1 + T_2 + \ldots)^2 + \ldots\right)\Psi_0$$

$$= \left(1 + \underbrace{T_1 + T_2}_{\substack{\text{Connceted excitations}\\ \text{like CI, linear}}} + \underbrace{\tfrac{1}{2}T_1^2 + T_1 T_2 + \tfrac{1}{2}T_2^2 + \ldots}_{\substack{\text{disconnected excitations}\\ \text{(statistically uncorrelated)}}}\right)\Psi_0$$

Determination of the energy and the cluster amplitudes

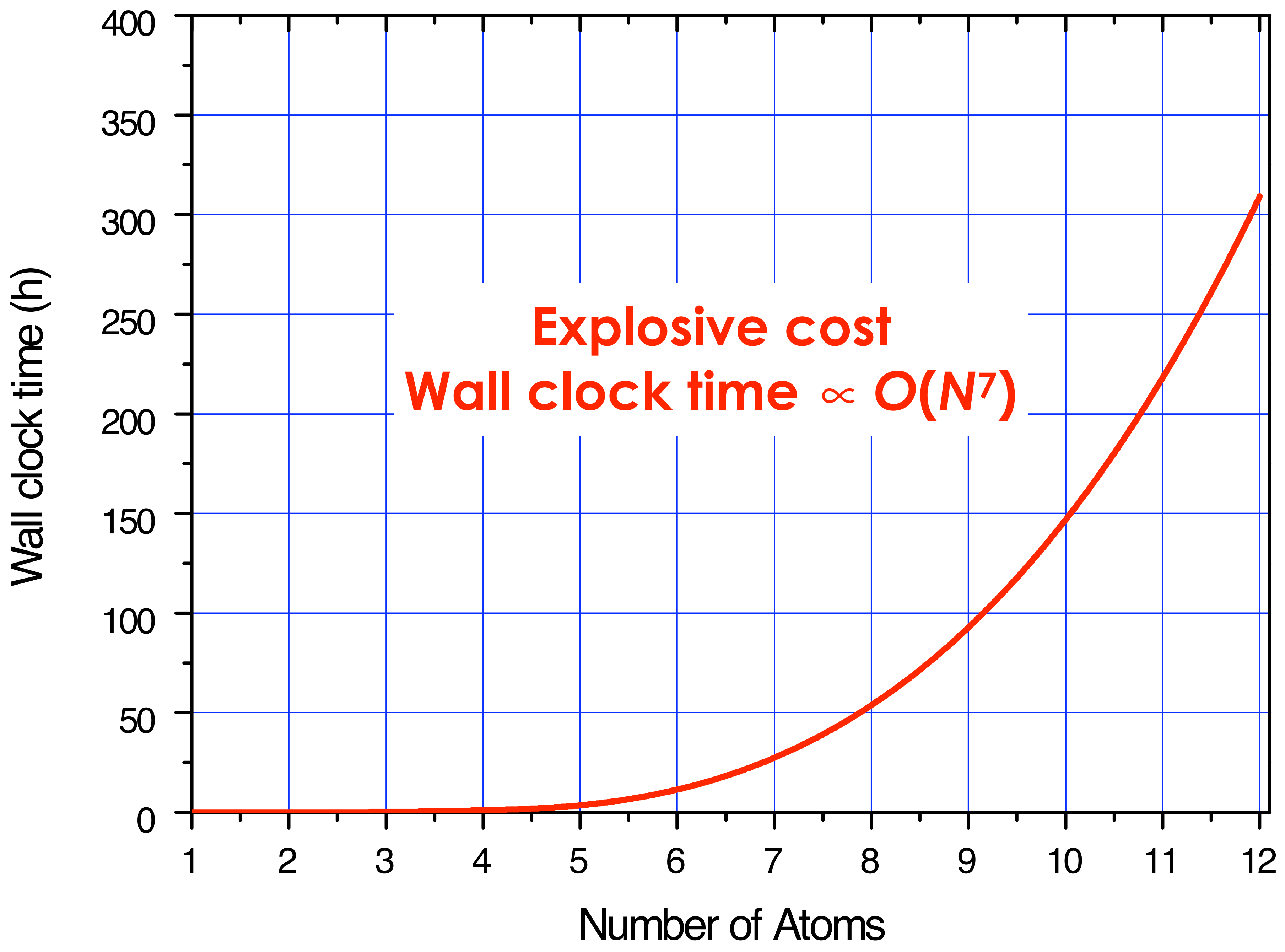
$$E_{CC} = \left\langle \Psi_0 \,|\, e^{-T}\hat{H}e^{T} \,|\, \Psi_0 \right\rangle$$

$$R_K = \left\langle t_K \Psi_0 \,|\, e^{-T}\hat{H}e^{T} \,|\, \Psi_0 \right\rangle = 0$$

Nonlinear equation set,
not hard to solve;
up to 4th power of amplitudes

Gold Standard:
CCSD(T)

Problems with Coupled Cluster Theory

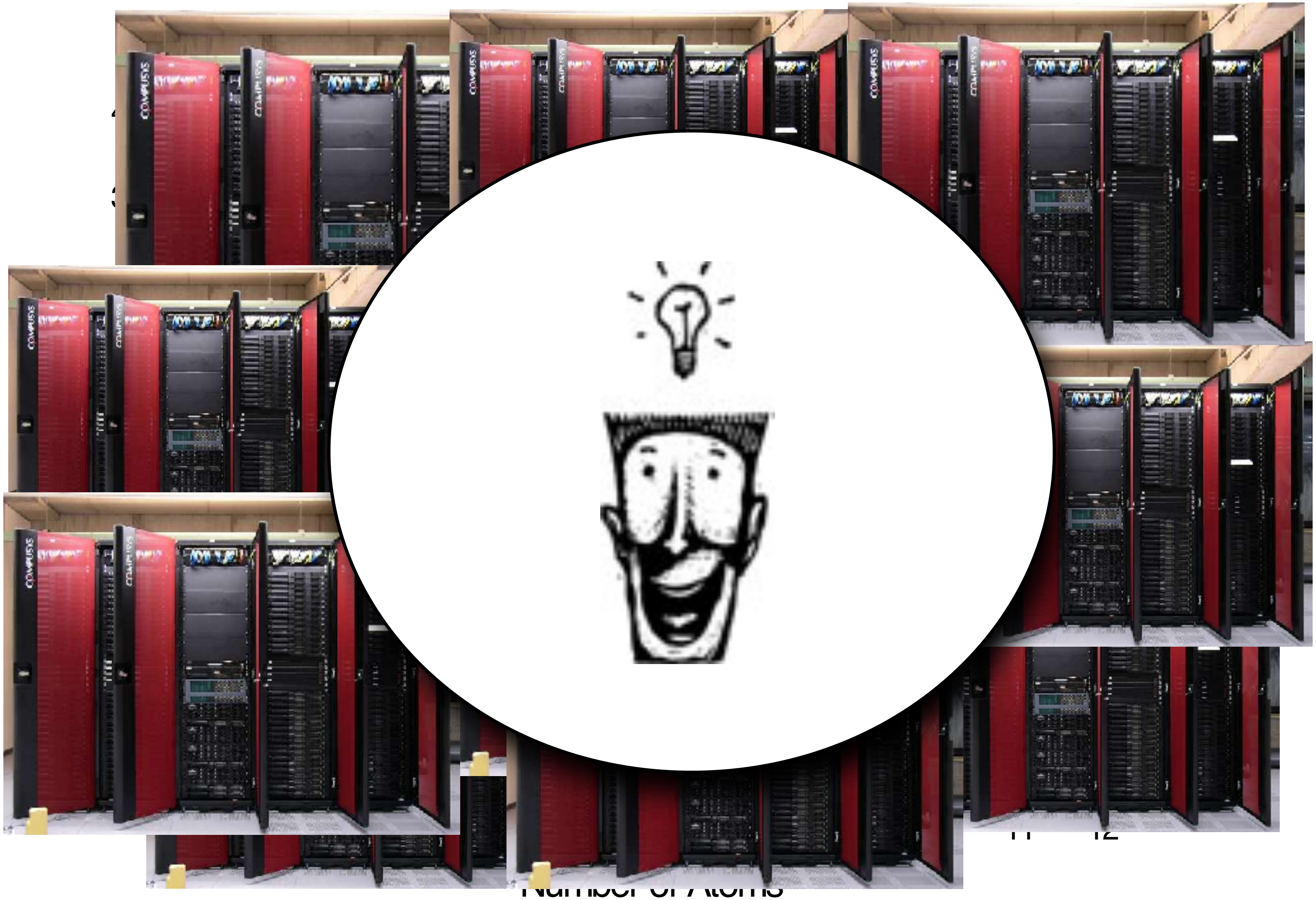


Explosive cost

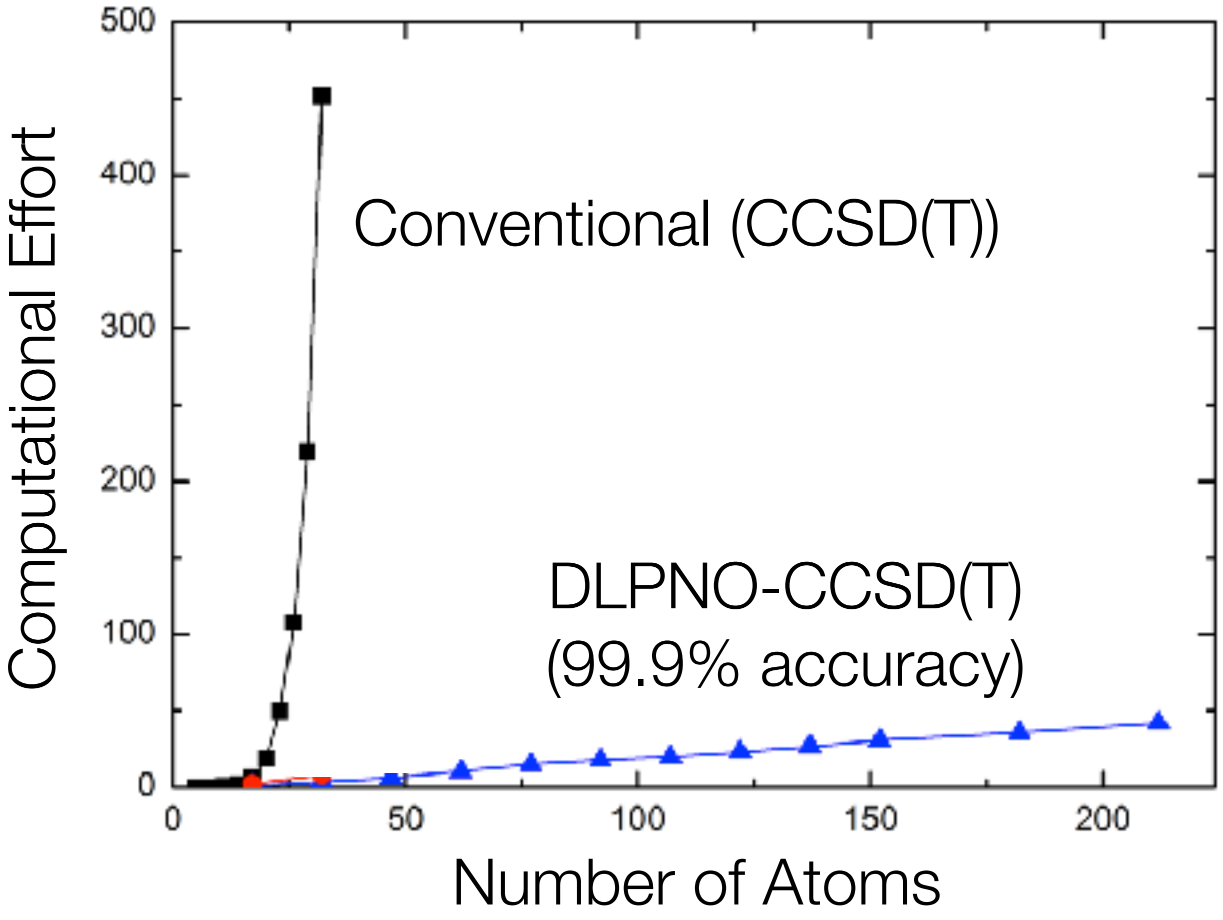
Wall clock time $\propto O(N^7)$

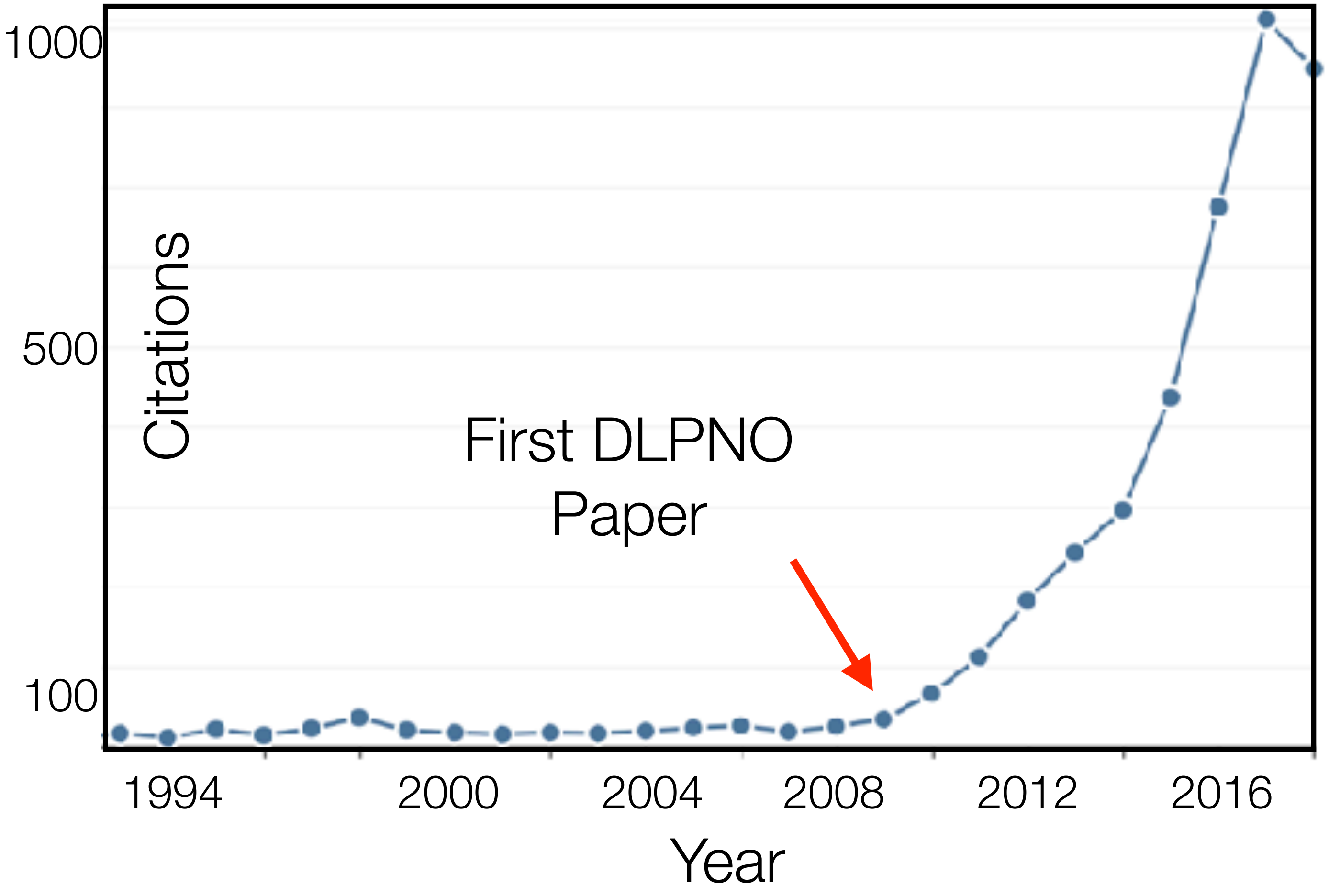
Problems with Coupled Cluster Theory

Problems with Coupled Cluster Theory



Breaking the Curse: Local Correlation

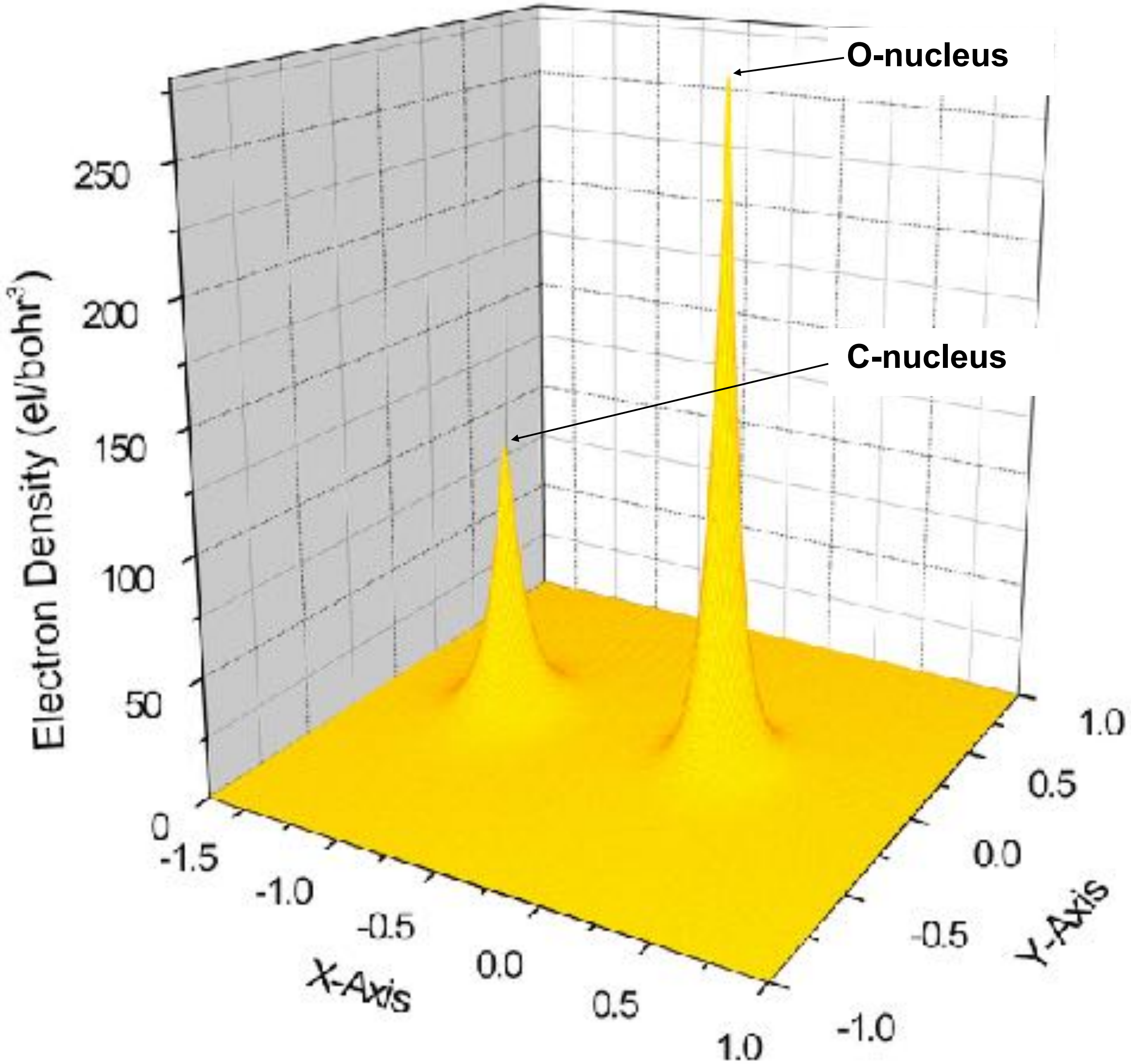




Zitationen: „Pair Natural Orbital“

Neese, F.; Hansen, A.; Liakos, D. G. *JCP* **2009**, *131*.
Riplinger, C.; Neese, F. *JCP* **2013**, *138*.
Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *JCP* **2013**, *139*.
Riplinger, C.; Pinski, P.; Becker, U.; Valeev, E. F.; Neese, F. *JCP* **2016**, *144*
…

Cheating on the Curse: Density Functional Theory



Electron Density of the CO molecule

$$\lim_{r \to 0} \left[\frac{\partial}{\partial r} + 2Z_A \right] \bar{\rho}(r) = 0$$

$$\boxed{\int \rho(\mathbf{r}) d\mathbf{r} = N}$$

↓

We can reconstruct the nuclear positions and charges from the electron density

↓

This means, we can reconstruct the BO Hamiltonian of the molecule from ρ(r) alone

The Hohenberg Kohn-Theorems

If we know the BO Hamiltonian of the molecule we could (in principle) solve the Schrödinger equation. Hence, the exact *N*-particle wavefunction, the exact energy and all expectation values are **functionals** of the electron density!

$$\begin{tikzcd} \text{Knowing } \rho(\mathbf{r}) \arrow[r, "\text{Deduce}"] \arrow[rrr, dotted, bend right, "\text{Somehow possible}"'] & V_{eN}, N \arrow[r, "\text{Deduce}"] & H_{BO} \arrow[r, "\text{Solve!}"] & E, \Psi \end{tikzcd}$$

The "**big dream**" is to go directly from the electron density to the exact energy. From the DFT logics this must be "somehow" possible, but we don't know how!

1)The existance of the "universal" functional E[ρ] is guaranteed by the **first Hohenberg-Kohn** (HK) theorem.

2)The **second HK theorem** establishes a variational principle that states that E[ρ'] (ρ' being a test density) ≥ E[ρ]

Navigating the Density Functional Zoo

$$E^{\text{DFT-D}} = E_{\text{1-el}} + J + E_{\text{XC}} + E_{\text{Disp.}}$$

✓ Hybrid DFT

✓ Double-hybrid DFT[2]

✓ Dispersion-corrected spin-component-scaled double-hybrid DFT[3]

Grimme S. [1] JCC **2004**, *25*, 1463; [2] *JCP* **2006**, *124*, 034108. [3] Kozuch, S. et al. *JPC C* **2010**, *114*, 20801.

Navigating the Density Functional Zoo

- ✓ Density functional theory (dispersion-corrected)[1]

$$E^{\text{DFT-D}} = E_{\text{1-el}} + J + E_{\text{XC}} + E_{\text{Disp.}}$$

- ✓ Hybrid DFT

$$E_{\text{XC}}^{\text{H-DFT}} = aE_{\text{X}}^{\text{HF}} + \left(1-a\right)E_{\text{X}}^{\text{DFT}} + E_{\text{C}}^{\text{DFT}}$$

- ✓ Double-hybrid DFT[2]

$$E_{\text{XC}}^{\text{DH-DFT}} = aE_{\text{X}}^{\text{HF}} + \left(1-a\right)E_{\text{X}}^{\text{DFT}} + bE_{\text{C}}^{\text{DFT}} + cE^{\text{MP2}}$$

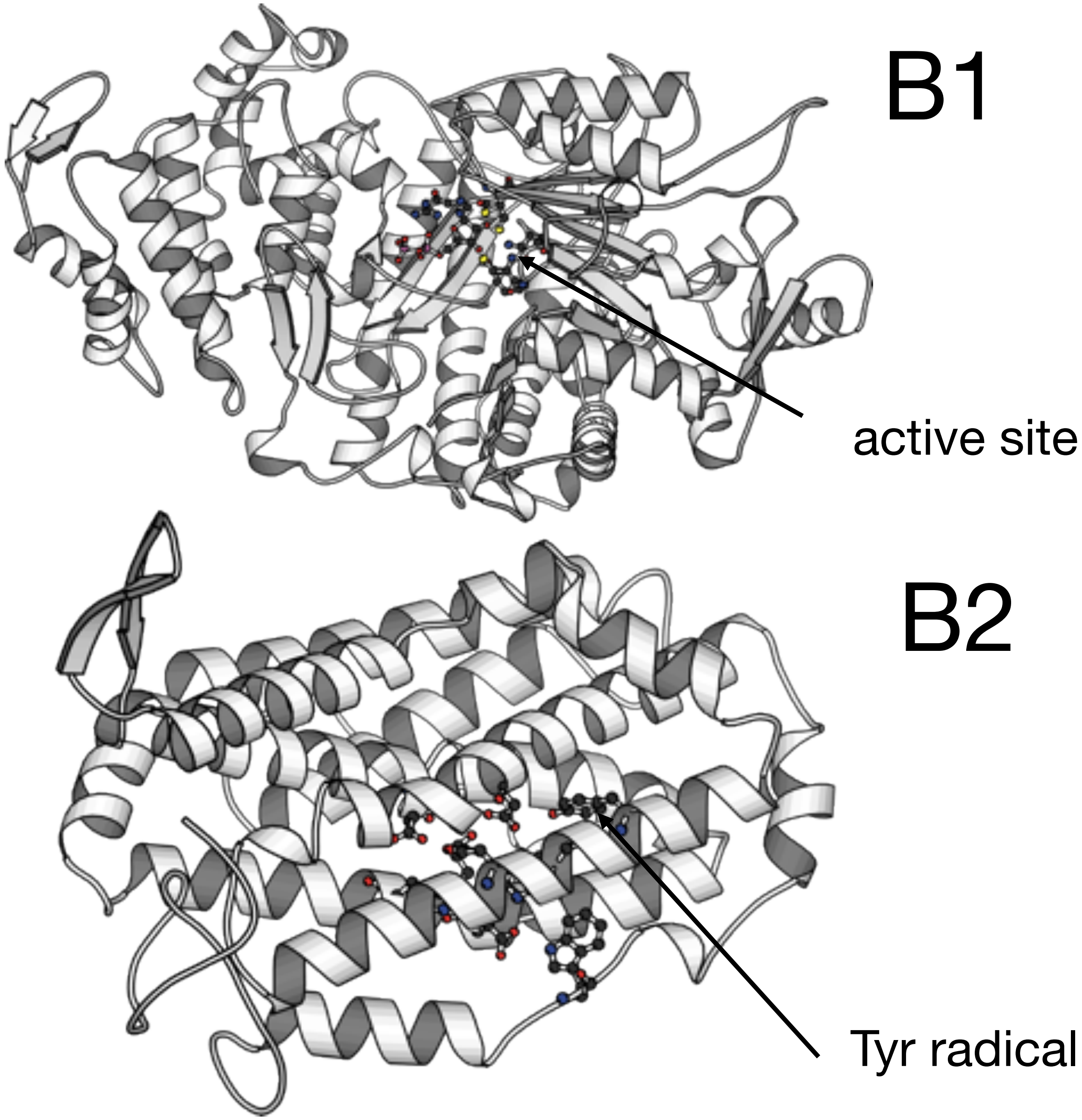
- ✓ Dispersion-corrected spin-component-scaled double-hybrid DFT[3]

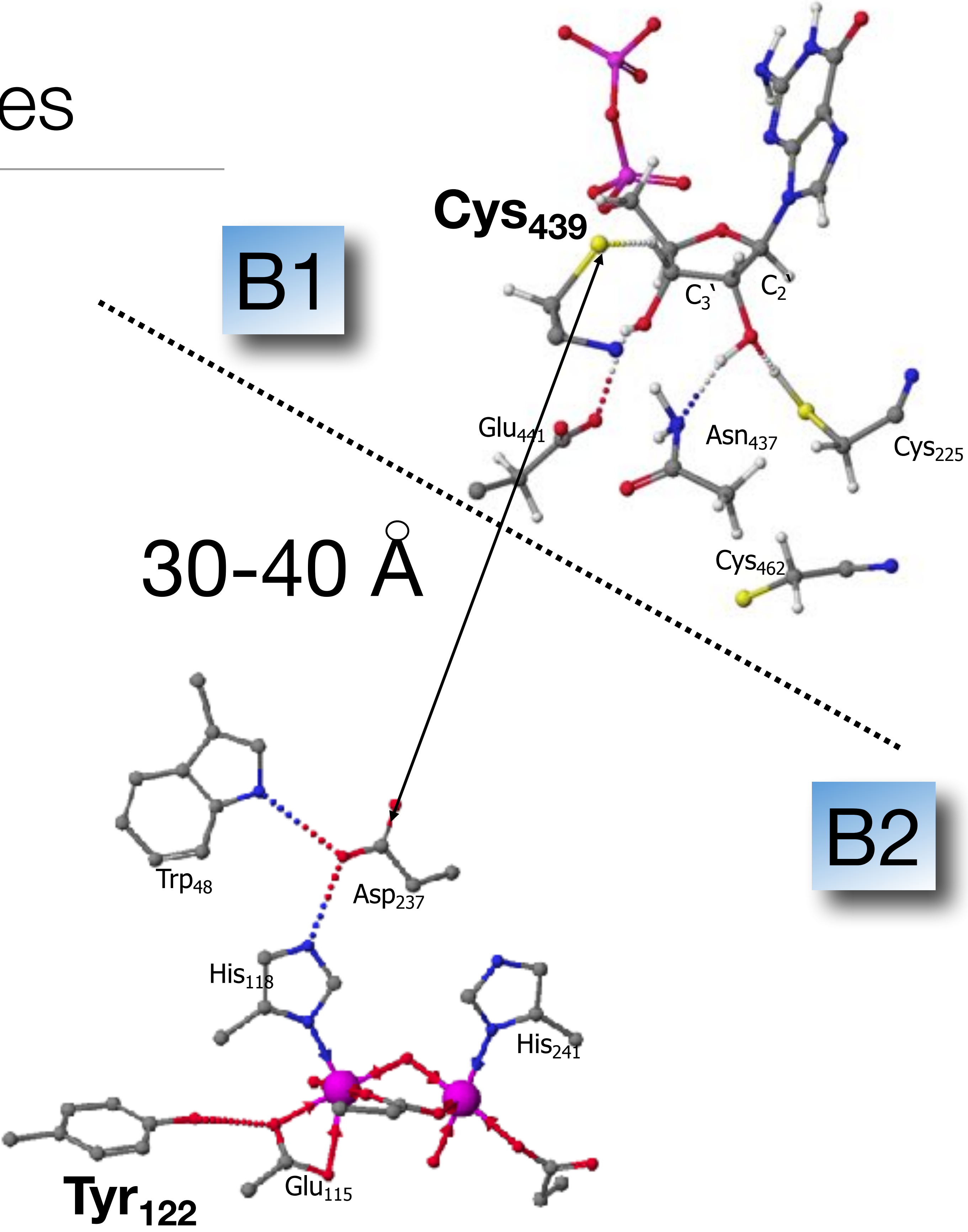
$$E^{\text{DSD-DFT}} = \underbrace{E_{\text{1-el}} + J + c_{\text{X}}E_{\text{X}}^{\text{HF}} + \left(1-c_{\text{X}}\right)E_{\text{X}}^{\text{DFT}} + c_{\text{C}}E_{\text{C}}^{\text{DFT}}}_{E^{\text{SCF}}} + \underbrace{c_{\text{O}}E_{\text{O}}^{\text{MP2}} + c_{\text{S}}E_{\text{S}}^{\text{MP2}}}_{E^{\text{SCS-MP2}}} + \underbrace{s_6E_{\text{Disp.}}}_{E^{\text{Disp.}}}$$

Grimme S. [1] JCC **2004**, *25*, 1463; [2] *JCP* **2006**, *124*, 034108. [3] Kozuch, S. et al. *JPC C* **2010**, *114*, 20801.

g-Tensors and Enzyme Active Sites: An Example

Ribonucleotide Reductases

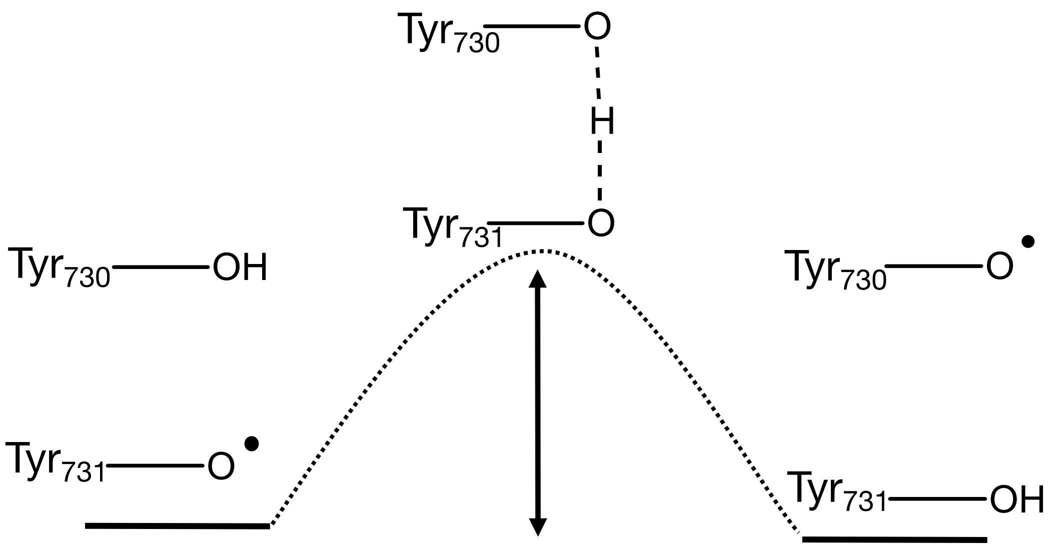




(a) Sjöberg, B.M. (1994) *Structure*, 2, 793

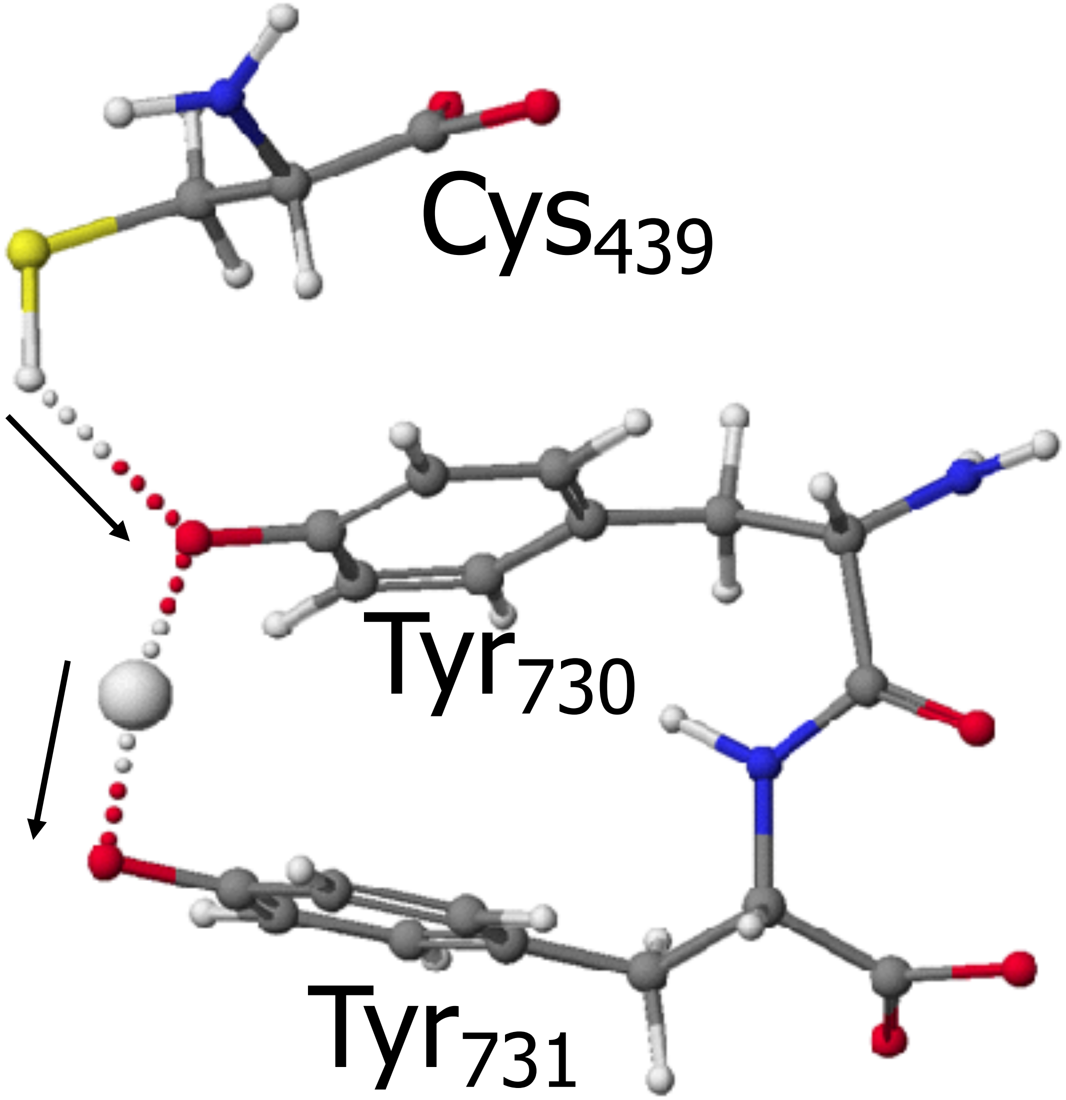
(b) Siegbahn, P.E.M. (1998) *J. Phys. Chem. B.*, 102, 10622

‚Long Range Radical Transfer‘



~4.9 kcal mol^{-1}

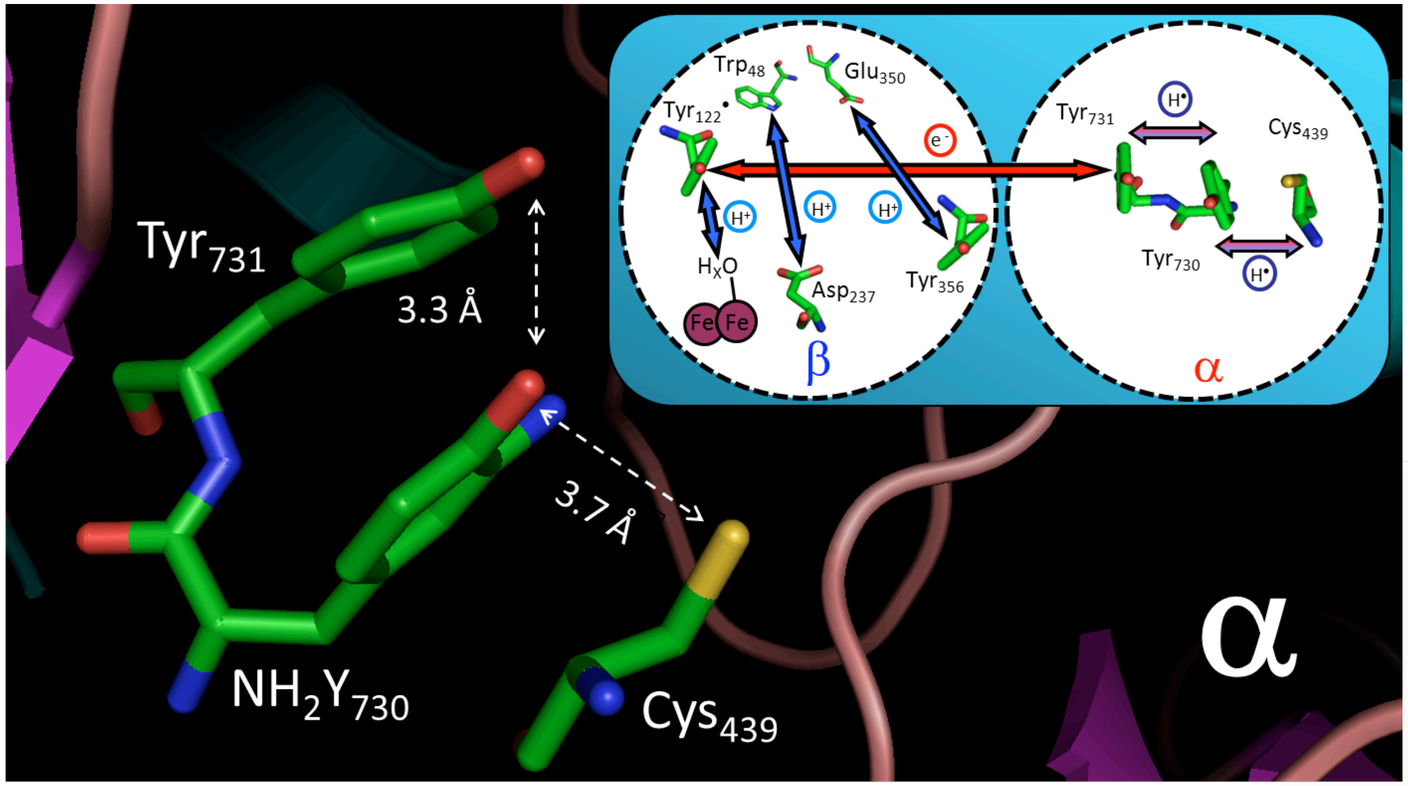
k ~ 10^9 s^{-1}

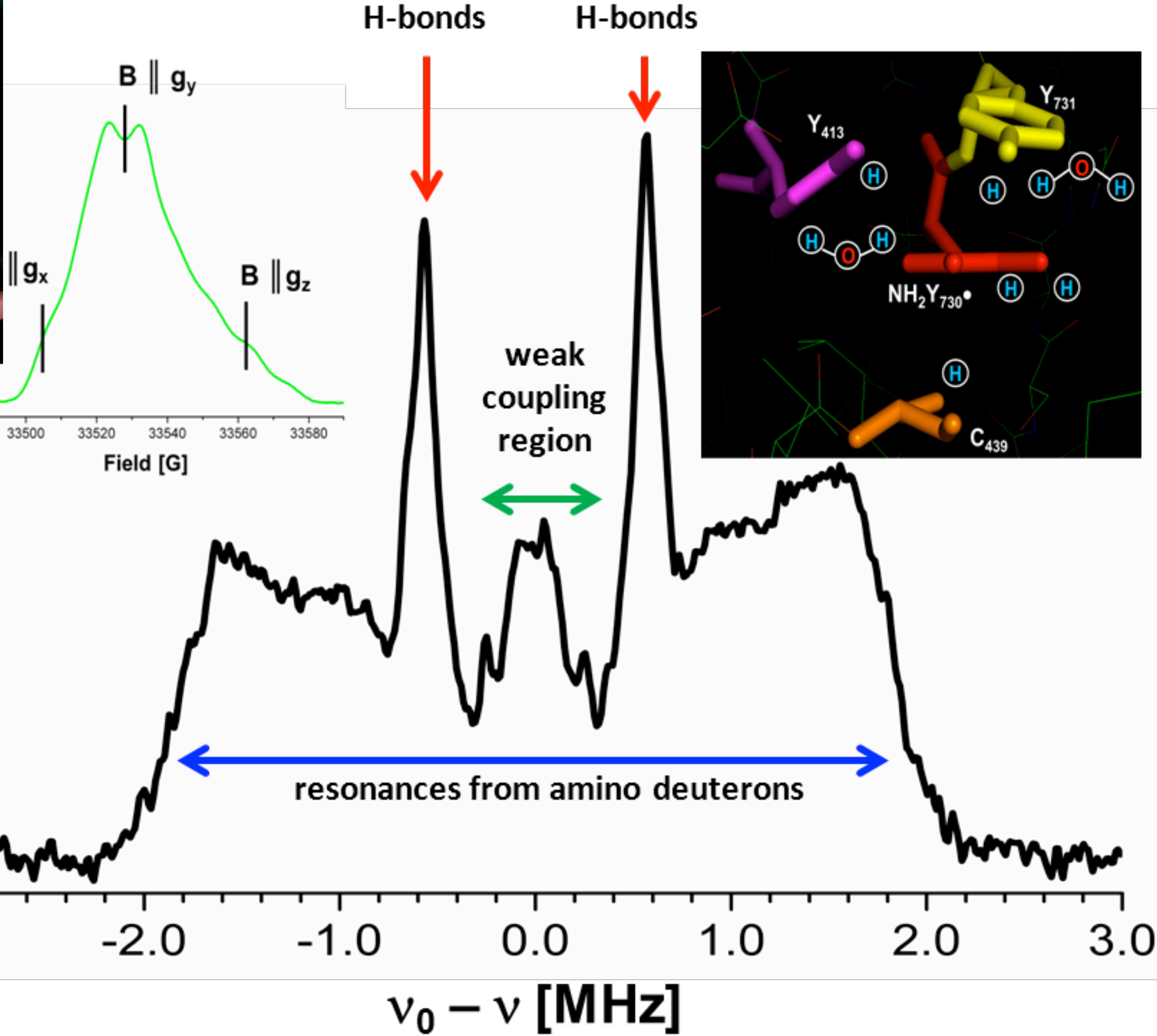


Transition state for H-atom transfer form Tyr_{730} to Tyr_{731}

Siegbahn, P.E.M. (1998) *J. Phys. Chem. B*, 102, 10622

Chasing the Electron Transfer Pathway



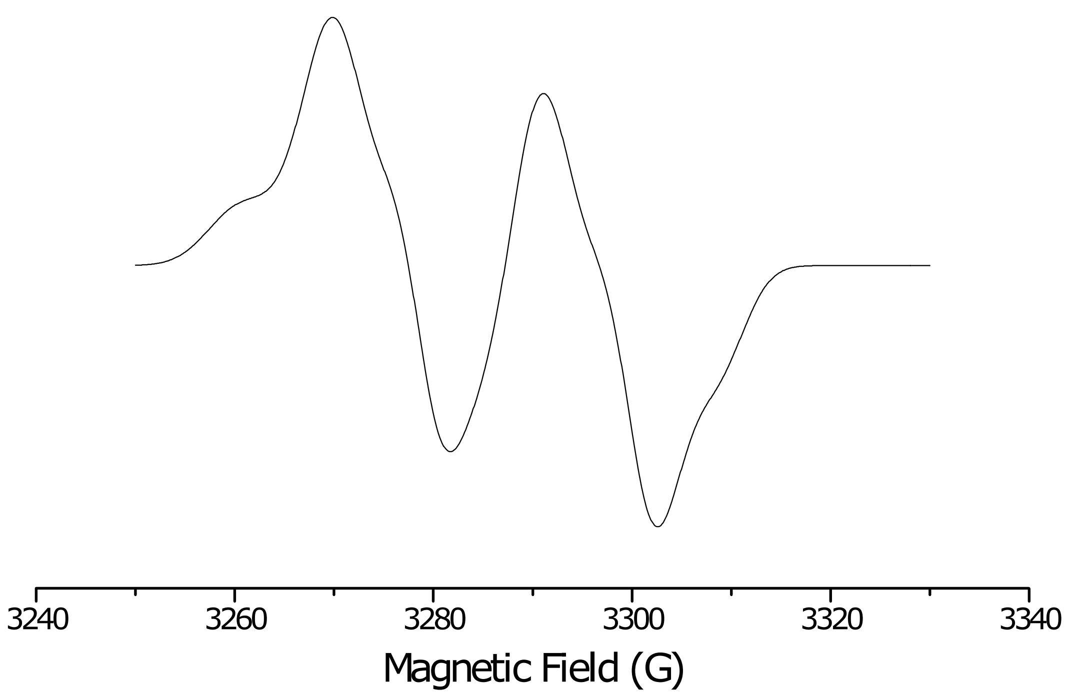


Chemical modification of Tyr 730 with an ortho NH$_2$ group impairs electron transfer to the active site and hence make the Tyr730/Tyr731 pair amenable to spectroscopic study by high-resolution EPR/ENDOR spectroscopy

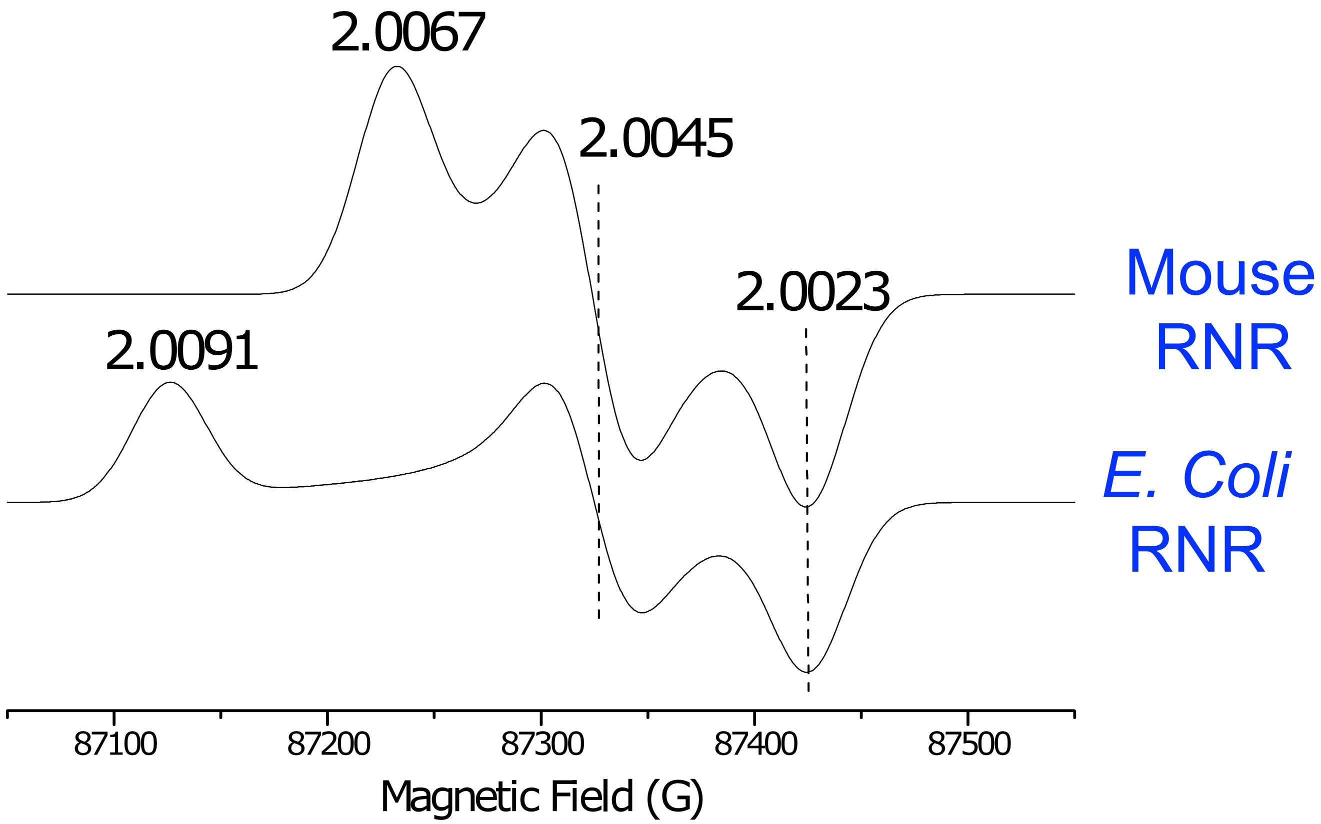
Agirevich, T.; Riplinger, C.; Stubbe, J.; FN; Bennati, M. *J. Am. Chem. Soc.*, **2012**, 134, 17661

EPR Spectroscopy of Tyrosyl Radicals

X-Band
9.2 GHz

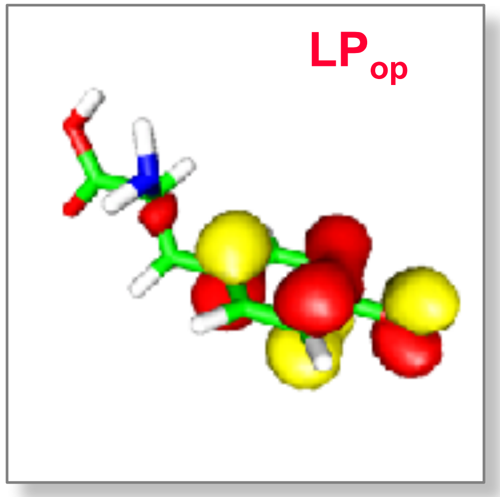


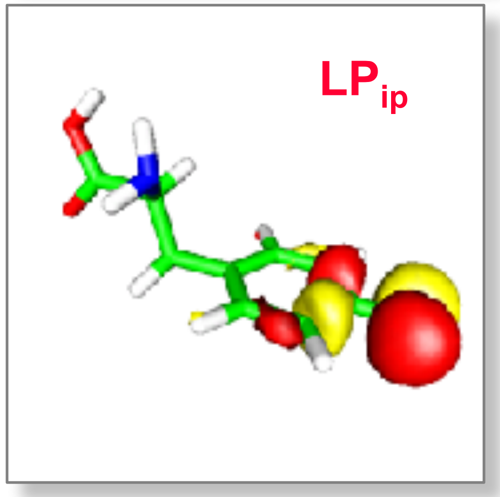
High Field
245 GHz

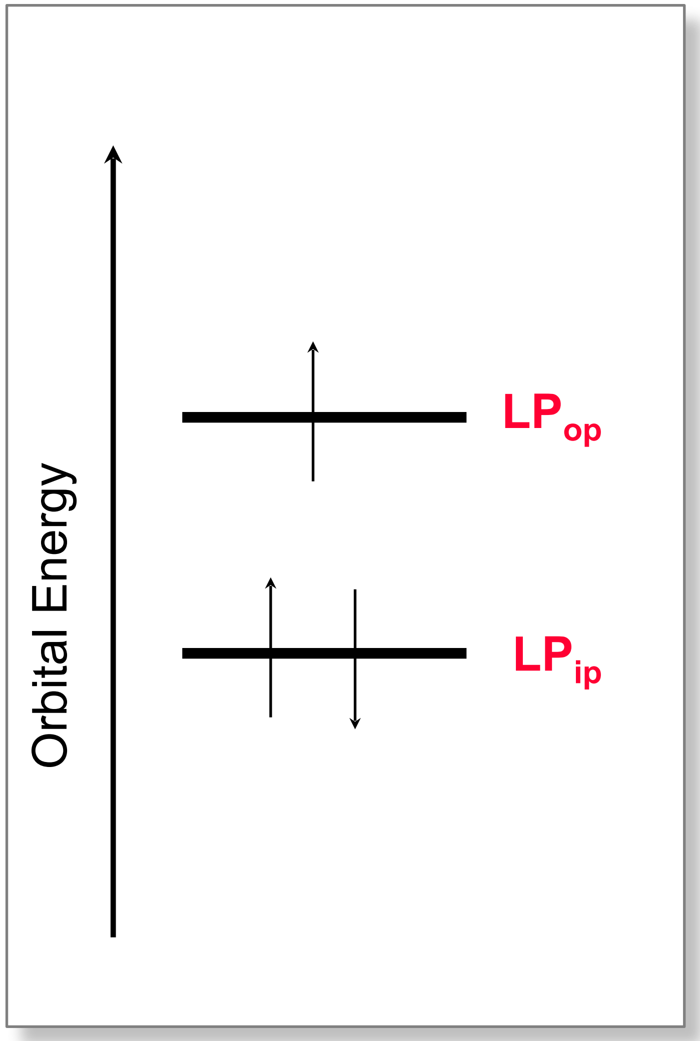


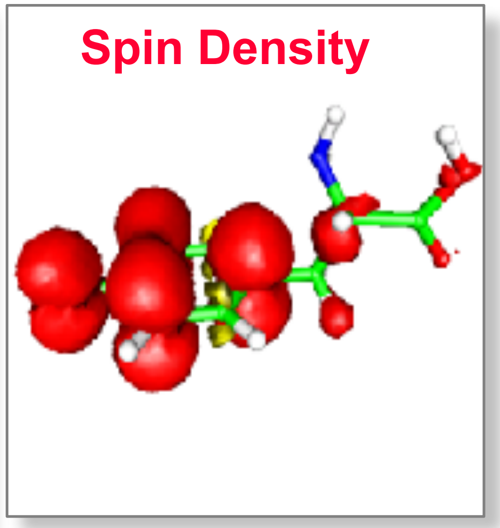
Large variation in g_{max} values reflect different protein environments and carries electronic structure information

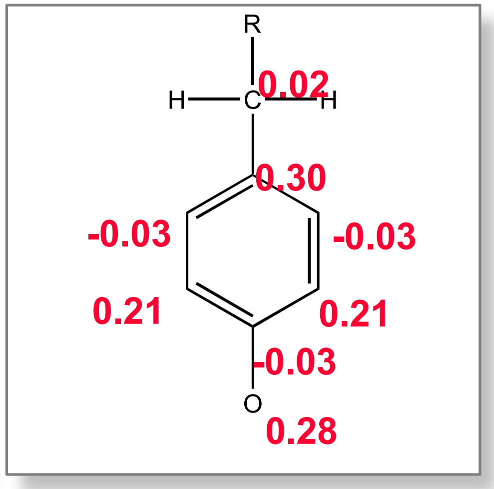
Electronic Structure of Tyrosyl Radicals


LP_{op}

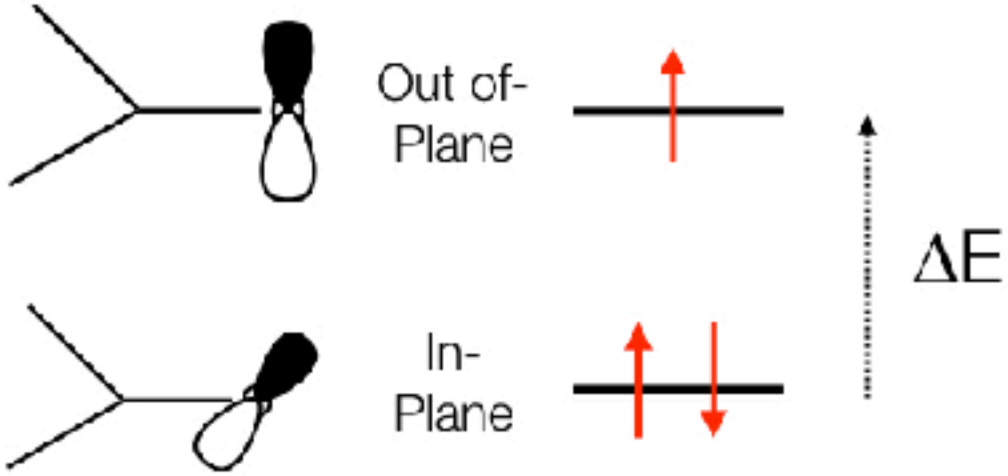

LP_{ip}

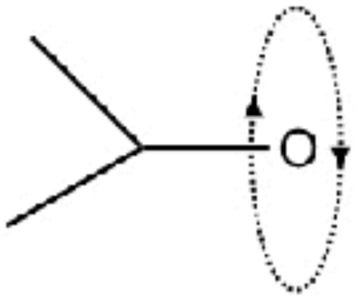



Spin Density

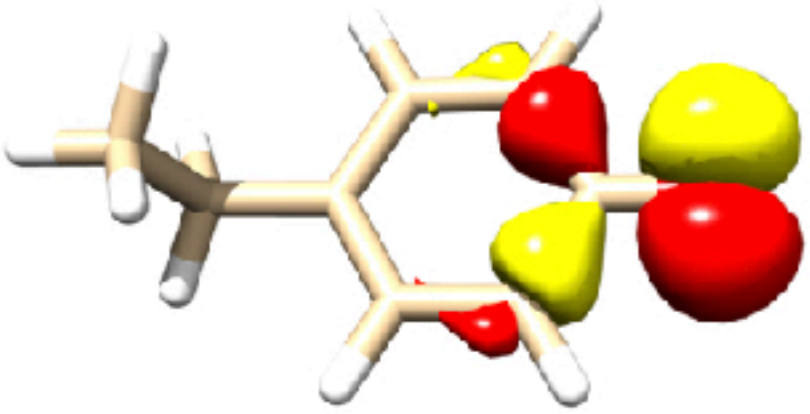


Origin of the g-tensor and H-Bonding Effects

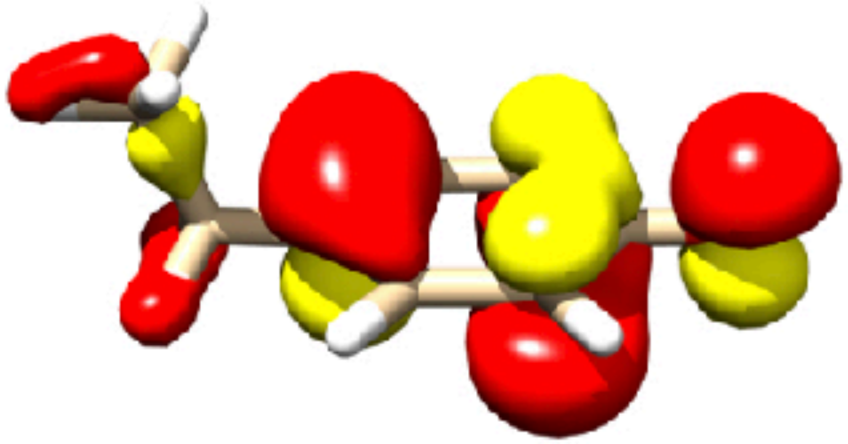




Rotation around
C-O bond axis (=,Z'')
turns in-plane and
Out-of plane
Orbitals into each other

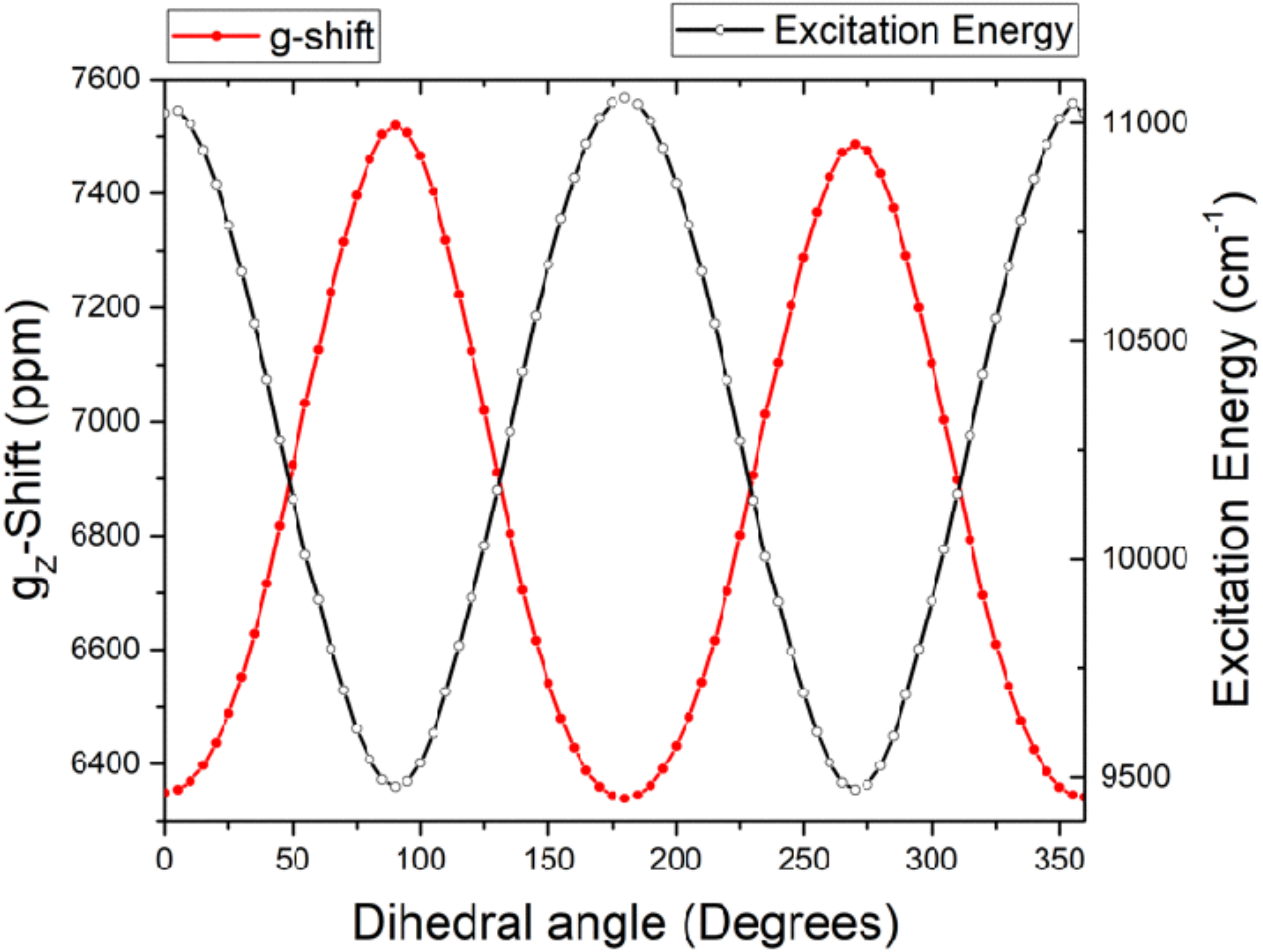


In-Plane

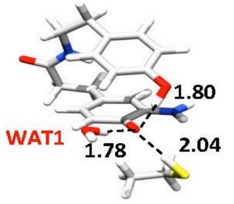
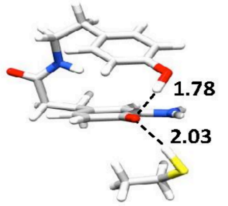
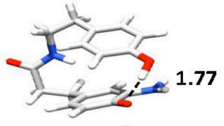
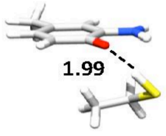
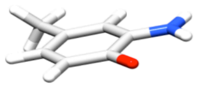


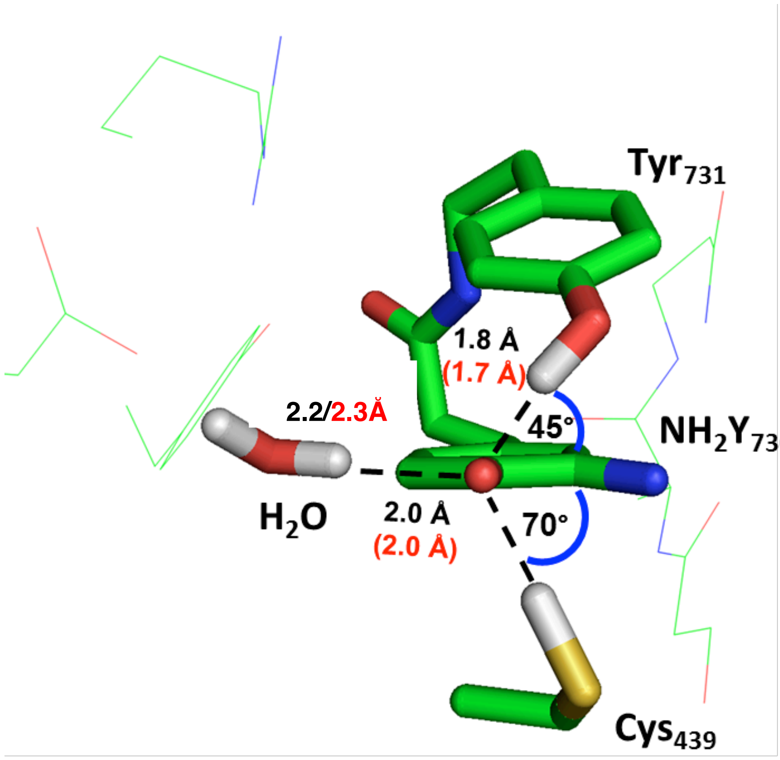
Out of-Plane (SOMO)

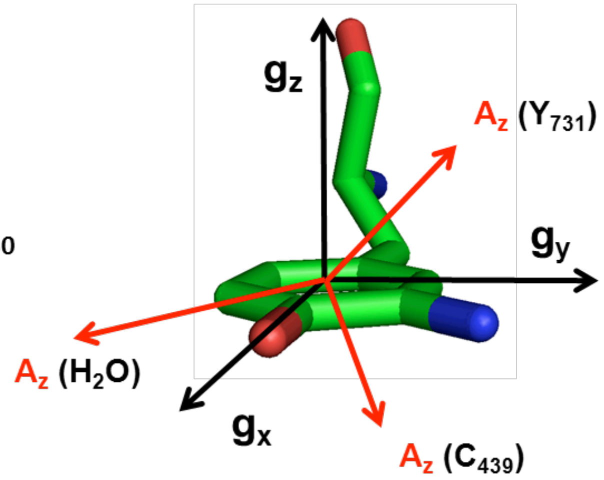
Rotation of the H-bonding Water Molecule



DFT Calculations on Large Cluster Models

		g_x	g_y	g_z
9	Experiment	2.0052	2.0042	2.0022
	DFT model	Deviation from experiment [in ppt]		
8	Model **6** (without WAT1)	-0.1	-0.1	-0.3
7	Model **4** (with WAT1)	-0.3	-0.1	-0.4
6	 $NH_2Y_{730}^{\bullet}$ - Tyr_{731} - C_{439} - WAT1	-0.6	-0.3	-0.5
5	 $NH_2Y_{730}^{\bullet}$ - Tyr_{731} - C_{439}	-0.2	-0.2	-0.4
4	 $NH_2Y_{730}^{\bullet}$ - Tyr_{731}	0.3	0.2	-0.2
3	 $NH_2Y_{730}^{\bullet}$ - Cys_{439}	0.8	0.1	-0.4
2	 2-amino-4-methyl-phenol radical (2-AMPR)	0.9	0.3	0.0
1	 2-amino-dimethyl-4-methyl-phenol radical	1.7	0.4	0.0



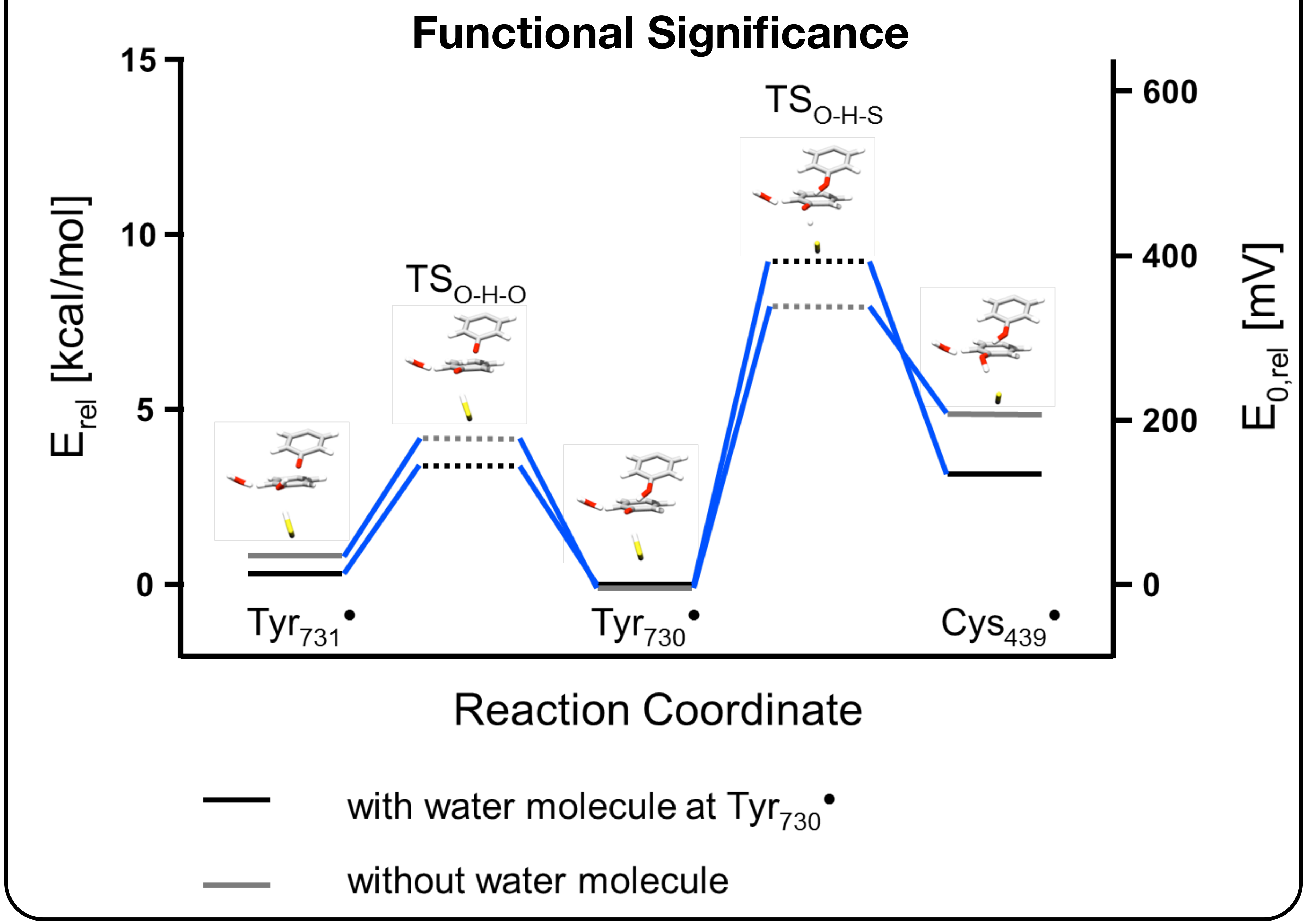


After *many* iterations between theory and experiment, the combined data demonstrate a **water molecule hydrogen bonded to Tyr_{730}**.

Agirevich, T.; et al. *J. Am. Chem. Soc.*, **2012**, 134, 17661

Functional Significance of H-Bonds

Functional Significance of H-Bonds



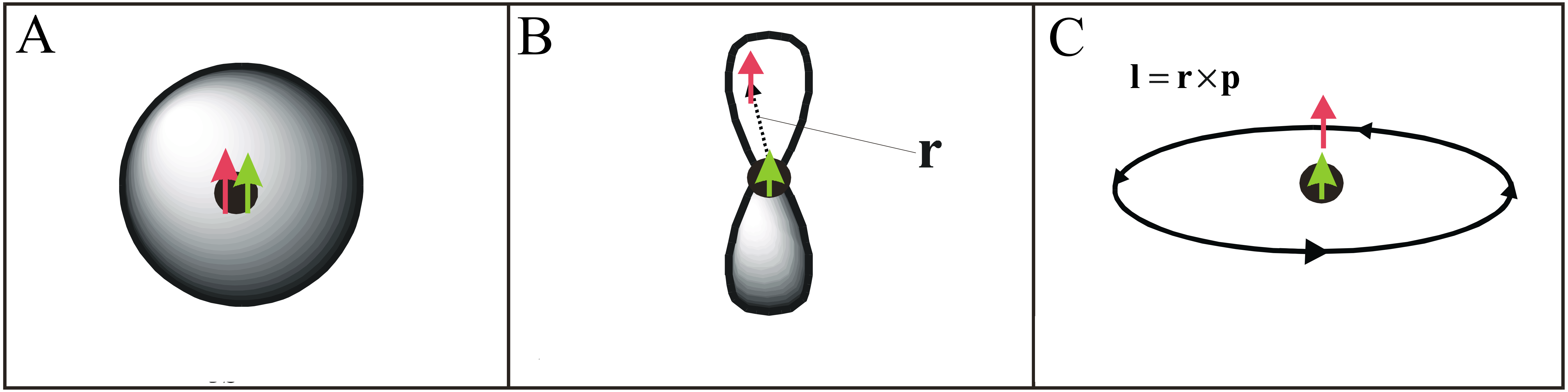
The Quantum Chemistry of Hyperfine Coupling

Hyperfine Couplings: Physical Picture

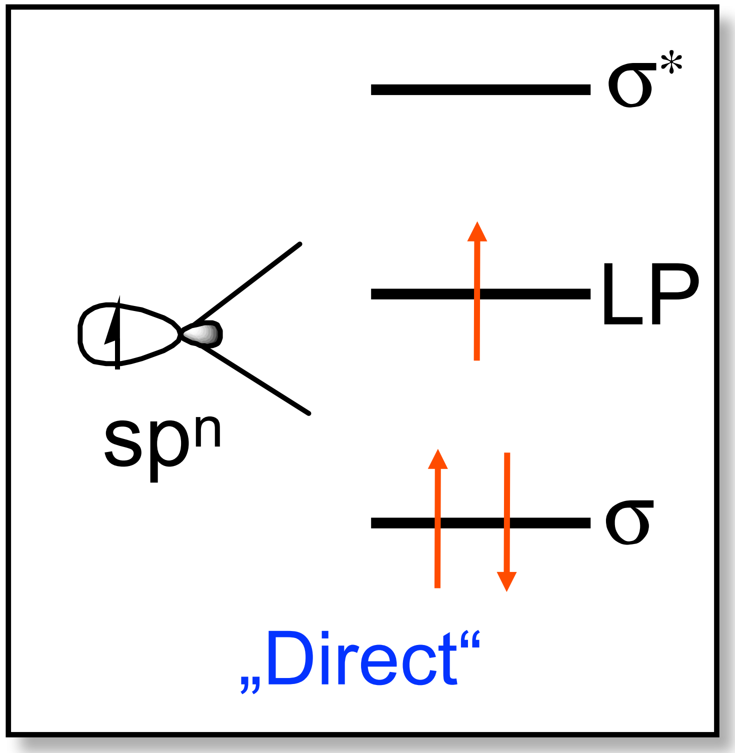
Fermi-Term

Dipole-Term

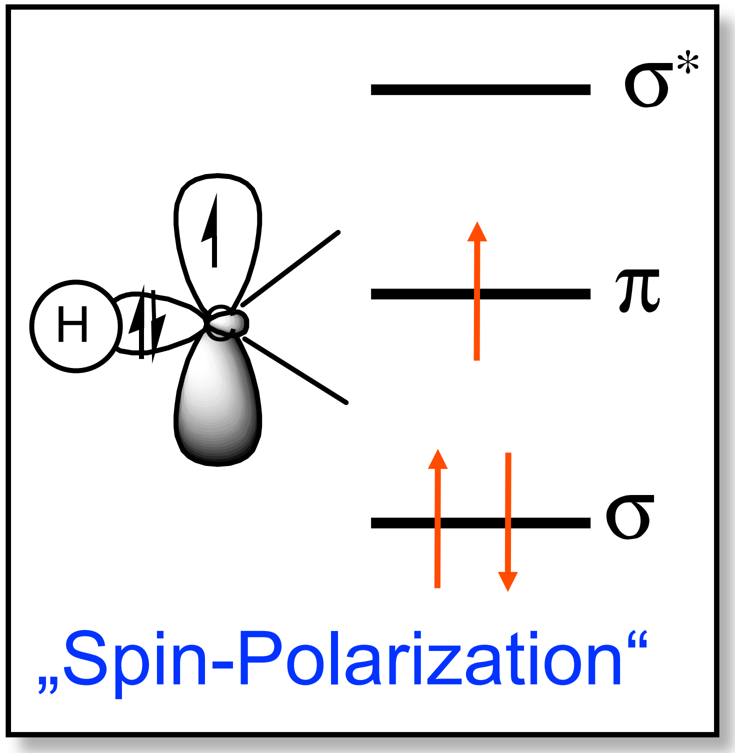
Spin-Orbit-Term



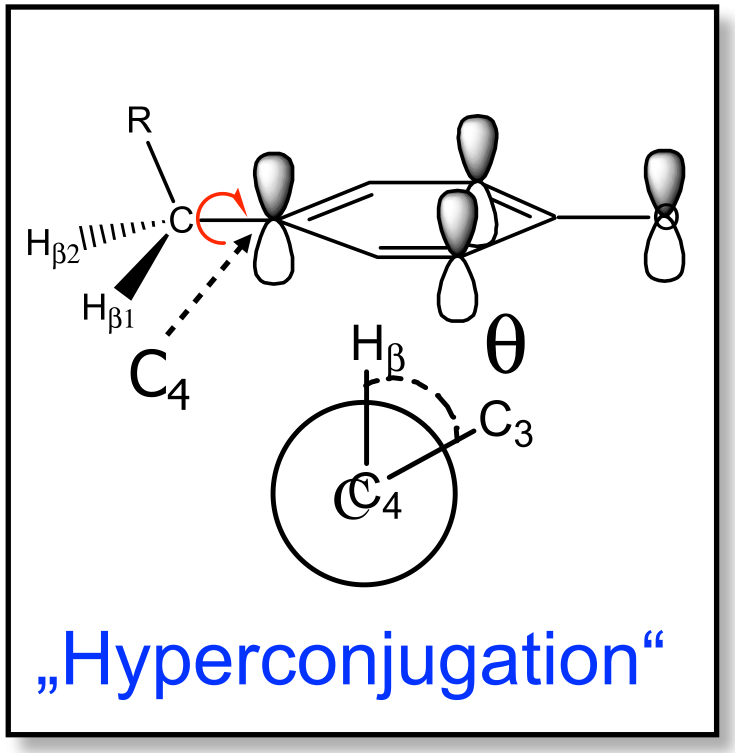
Overview: Isotropic Hyperfine Mechanisms



„Direct“



„Spin-Polarization“



„Hyperconjugation“

(easy)

(hard)

(moderate)

Valence shell spin distribution typically more or less ok with DFT

- UHF strongly overestimates SP
- DFT generally underestimates SP
- Needs relativity for metal nuclei

Overview: Dipolar Hyperfine Mechanisms

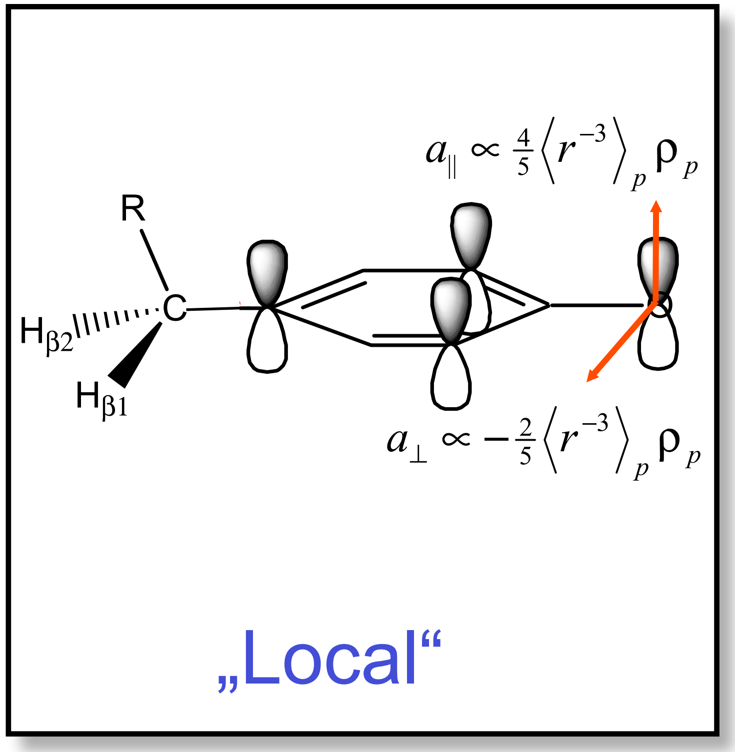
(moderate)

Depends on valence shell spin distribution and is often more or less ok with DFT
(but: tendency to give too covalent M-L bonds means too large ligand HFC, too small metal HFC

(easy)

Depends only on structure and becomes valid after a few Angström

Overview: Dipolar Hyperfine Mechanisms



$$a_{\|} \propto \tfrac{4}{5}\left\langle r^{-3}\right\rangle_{p} \rho_{p}$$

$$a_{\perp} \propto -\tfrac{2}{5}\left\langle r^{-3}\right\rangle_{p} \rho_{p}$$

„Local“

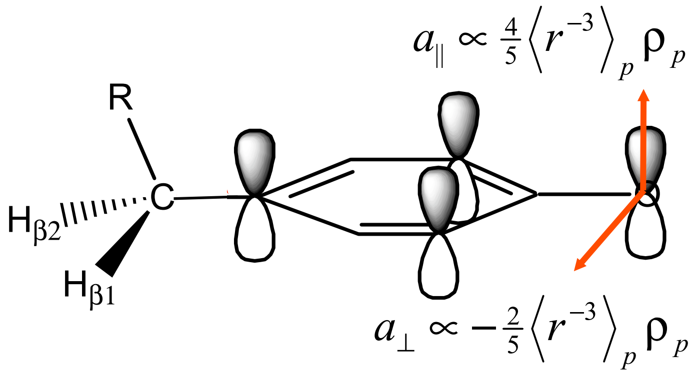
(moderate)

Depends on valence shell spin distribution and is often more or less ok with DFT
(but: tendency to give too covalent M-L bonds means too large ligand HFC, too small metal HFC

(easy)

Depends only on structure and becomes valid after a few Angström

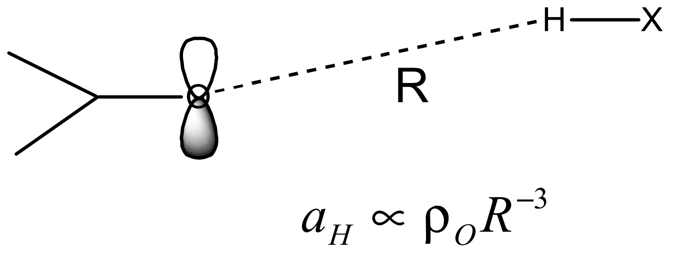
Overview: Dipolar Hyperfine Mechanisms



„Local“

(moderate)

Depends on valence shell spin distribution and is often more or less ok with DFT
(but: tendency to give too covalent M-L bonds means too large ligand HFC, too small metal HFC



„Point Dipole“

(easy)

Depends only on structure and becomes valid after a few Angström

Contributions to the Hyperfine Coupling

In general:

Spin Density

Basis functions

Spin Density Response

$$A_{KL}^{(N)} = \frac{P_N}{2S}\sum_{\mu\nu} P_{\mu\nu}^{\alpha-\beta}\left\langle \mu \mid r^{-5}(\delta_{KL}r^2 - 3(\mathbf{r}-\mathbf{R}_N)_K(\mathbf{r}-\mathbf{R}_N)_L) \mid \nu\right\rangle - \frac{P_N}{S}\sum_{\mu\nu}\frac{\partial P_{\mu\nu}^{\alpha-\beta}}{\partial I_{N;K}}\left\langle \mu \mid h_L^{SOC} \mid \nu\right\rangle$$

Fermi-contact + spin dipolar

Spin-Orbit

$$P_N = g_e g_N \beta_e \beta_N$$

Element specific constant

Let us first focus on the first order term. From the partial integration of the divergent operator, there arises the Fermi contact term:

$$A_{KL}^{(N;Fermi)} = \delta_{KL}\frac{8\pi}{3}\frac{P_N}{2S}\sum_{\mu\nu} P_{\mu\nu}^{\alpha-\beta}\left\langle \mu \mid \delta(\mathbf{r}-\mathbf{R}_N) \mid \nu\right\rangle = \delta_{KL}\frac{8\pi}{3}\frac{P_N}{2S}\rho^{\alpha-\beta}(\mathbf{R}_N)$$

The remainder (sans the Fermi term), is the spin-dipolar contribution:

$$A_{KL}^{(N;dip)} = \frac{P_N}{2S}\sum_{\mu\nu} P_{\mu\nu}^{\alpha-\beta}\left\langle \mu \mid r^{-5}(\delta_{KL}r^2 - 3(\mathbf{r}-\mathbf{R}_N)_K(\mathbf{r}-\mathbf{R}_N)_L) \mid \nu\right\rangle = \frac{P_N}{2S}\sum_{\mu\nu} P_{\mu\nu}^{\alpha-\beta}\left\langle \mu \mid F_{KL}^{N} \mid \nu\right\rangle$$

Multi-center contributions to the HFC

Our basis functions {μ} are assigned to atoms. The dipolar operator is attached to an atom N. Hence, we can decompose the HFC tensor into one-, two- and three-center contributions, e.g.:

$$A_{KL}^{(N;dip)} = \frac{P_N}{2S} \sum_{\mu_N \nu_N} P_{\mu_N \nu_N}^{\alpha-\beta} \left\langle \mu_N \mid F_{KL}^{N} \mid \nu_N \right\rangle$$

1-Center

$$+ \frac{P_N}{2S} \sum_{N' \neq N} \sum_{\mu_{N'} \nu_{N'}} P_{\mu_{N'} \nu_{N'}}^{\alpha-\beta} \left\langle \mu_{N'} \mid F_{KL}^{N} \mid \nu_{N'} \right\rangle$$

2-Center Point charge

$$+ \frac{P_N}{S} \sum_{N' \neq N} \sum_{\mu_N \nu_{N'}} P_{\mu_N \nu_{N'}}^{\alpha-\beta} \left\langle \mu_N \mid F_{KL}^{N} \mid \nu_{N'} \right\rangle$$

2-Center bond (small-ish)

$$+ \frac{P_N}{2S} \sum_{N' \neq N} \sum_{N'' \neq N,N'} \sum_{\mu_{N'} \nu_{N''}} P_{\mu_{N'} \nu_{N''}}^{\alpha-\beta} \left\langle \mu_{N'} \mid F_{KL}^{N} \mid \nu_{N''} \right\rangle$$

3-Center (small)

Physical Interpretation of HFC Contributions

$$A_{KL}^{(N;local-dip)} = \frac{P_N}{2S} \sum_{\mu_N \nu_N} P_{\mu_N \nu_N}^{\alpha-\beta} \left\langle \mu_N \mid F_{KL}^{N} \mid \nu_N \right\rangle \approx \rho_N^{\alpha-\beta} \qquad A_{KL}^{N;dip}$$

Atomic Spin POPULATION

Intrinsic Atomic HFC

Hence, by studying the HFC's of various nuclei in the molecule, one can get an idea about the spin-distribution in the system (famous: Weissman/McConnel relation).

!!!! ***BUT BE CAREFUL- this is a crude approximation !!!!***

$$A_{KL}^{(N;pc-dip)} \approx \frac{P_N}{2S} \sum_{N' \neq N} \rho_{N'}^{\alpha-\beta} \left\{ R_{NN'}^{-5} (\delta_{KL} R_{NN'}^{2} - 3(\mathbf{R}_N - \mathbf{R}_{N'})_K (\mathbf{R}_N - \mathbf{R}_{N'})_L \right\}$$

Point dipole form. This gives HFC's to „remote" atoms that may not carry much spin population themselves

!!!! ***Physical basis for ‚measuring' distances with EPR HFC's !!!!***

Multicenter Contributions: ^{14}N-HFC in $[Cu(NH_3)_4]^{2+}$

	A_{iso}	$A_D(\perp)$	$A_D(\|\|)$
1-Center	34.96	-4.93	9.87
2-Center			
Point ‚Charge‘	-0.02	-0.68	1.21
Bond	2.76	+0.47	-0.91
3-Center	0.06	<0.01	<0.01
Total	37.76	-5.09	10.12

FN (**2001**) *J. Phys. Chem. A*, 105, 4290

The „Point Charge“ Term

$$A_{KL}^{(N;PD)} = \frac{P_N}{2S} \sum_{N' \neq N} \sum_{\mu_{N'}\nu_{N'}} P_{\mu_{N'}\nu_{N'}}^{\alpha-\beta} \left\langle \mu_{N'} \mid F_{KL}^{N} \mid \nu_{N'} \right\rangle$$

From a sufficient distance, the angular form of the atomic orbitals is not important anymore. Hence, let us replace us all of them by delta functions $\mu_{N'}(\mathbf{r}) \rightarrow \delta(\mathbf{r} - \mathbf{R}_{N'})$

Then: $$A_{KL}^{(N;PD)} \approx \frac{g_e g_N \beta \beta_N}{2S} \sum_{N' \neq N} R_{NN'}^{-5} \left\{ \delta_{KL} R_{NN'}^{2} - 3(\mathbf{R}_N - \mathbf{R}_{N'})_K (\mathbf{R}_N - \mathbf{R}_{N'})_L \right\} \underbrace{\sum_{\mu_{N'}\nu_{N'}} P_{\mu_{N'}\nu_{N'}}^{\alpha-\beta}}_{\approx \rho_{N'}}$$

That is a „**distributed dipole**“ formula (need to know the spin population of all centers!)

The „Point Charge“ Term

$$A_{KL}^{(N;PD)} = \frac{P_N}{2S} \sum_{N' \neq N} \sum_{\mu_{N'}\nu_{N'}} P_{\mu_{N'}\nu_{N'}}^{\alpha-\beta} \left\langle \mu_{N'} \mid F_{KL}^{N} \mid \nu_{N'} \right\rangle$$

From a sufficient distance, the angular form of the atomic orbitals is not important anymore. Hence, let us replace us all of them by delta functions $\mu_{N'}(\mathbf{r}) \rightarrow \delta(\mathbf{r} - \mathbf{R}_{N'})$

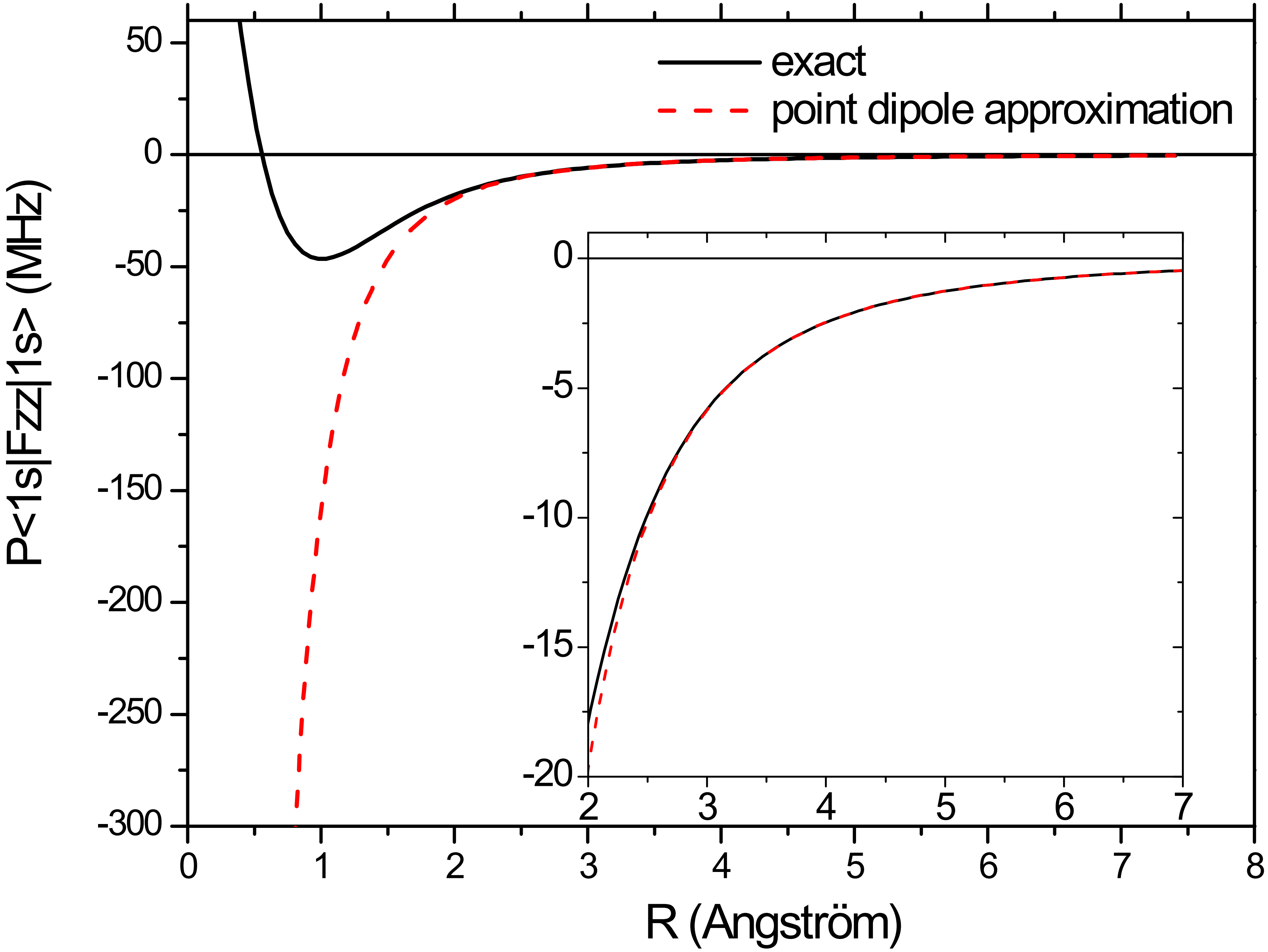
Then: $$A_{KL}^{(N;PD)} \approx \frac{g_e g_N \beta \beta_N}{2S} \sum_{N' \neq N} R_{NN'}^{-5} \left\{ \delta_{KL} R_{NN'}^{2} - 3(\mathbf{R}_N - \mathbf{R}_{N'})_K (\mathbf{R}_N - \mathbf{R}_{N'})_L \right\} \underbrace{\sum_{\mu_{N'}\nu_{N'}} P_{\mu_{N'}\nu_{N'}}^{\alpha-\beta}}_{\approx \rho_{N'}}$$

That is a „**distributed dipole**“ formula (need to know the spin population of all centers!)

IMPORTANT NOTES:

- ➡ There is **no g-tensor** is that formula (only g_e)! And there shouldn’t be. The literature is wrong in this respect.
- ➡ It is a **really bad idea** to condense the spin only to the metal center and neglect other nuclei. Short distances are amplified by the R^{-3} dependence!
- ➡ You can not expect to obtain accurate spin populations from inverting this equation on the basis of measured HFCs, only ballpark numbers

When is the delta-function replacement justified?



FN; Solomon, EI (**2003**) in: Miller, JS; Drillon, M „Molecular Magnetism“ Vol. IV

Spin Density vs Spin Population

The **spin-density** is a three dimensional function of space. It is well defined, physically observable and integrates to the number of unpaired electrons

$$\rho^{\alpha-\beta}(\mathbf{r}) = \left\langle \Psi_0 \,\middle|\, \sum_i 2s_{zi}\delta(\mathbf{r}-\mathbf{r}_i) \,\middle|\, \Psi_0 \right\rangle \approx \sum_{k(SOMO)} 2\int \psi_k(\mathbf{r}')s_z\delta(\mathbf{r}'-\mathbf{r})\psi_k(\mathbf{r}')\,d\mathbf{r}'$$

$$= \sum_{k(SOMO)} \left|\psi_k(\mathbf{r})\right|^2$$

$$= \sum_{\mu\nu} P_{\mu\nu}^{\alpha-\beta}\mu(\mathbf{r})\nu(\mathbf{r})$$

The **spin-population** is a intuitively appealing but more or less arbitrary division of spin-density onto atoms. It is *not* physically observable

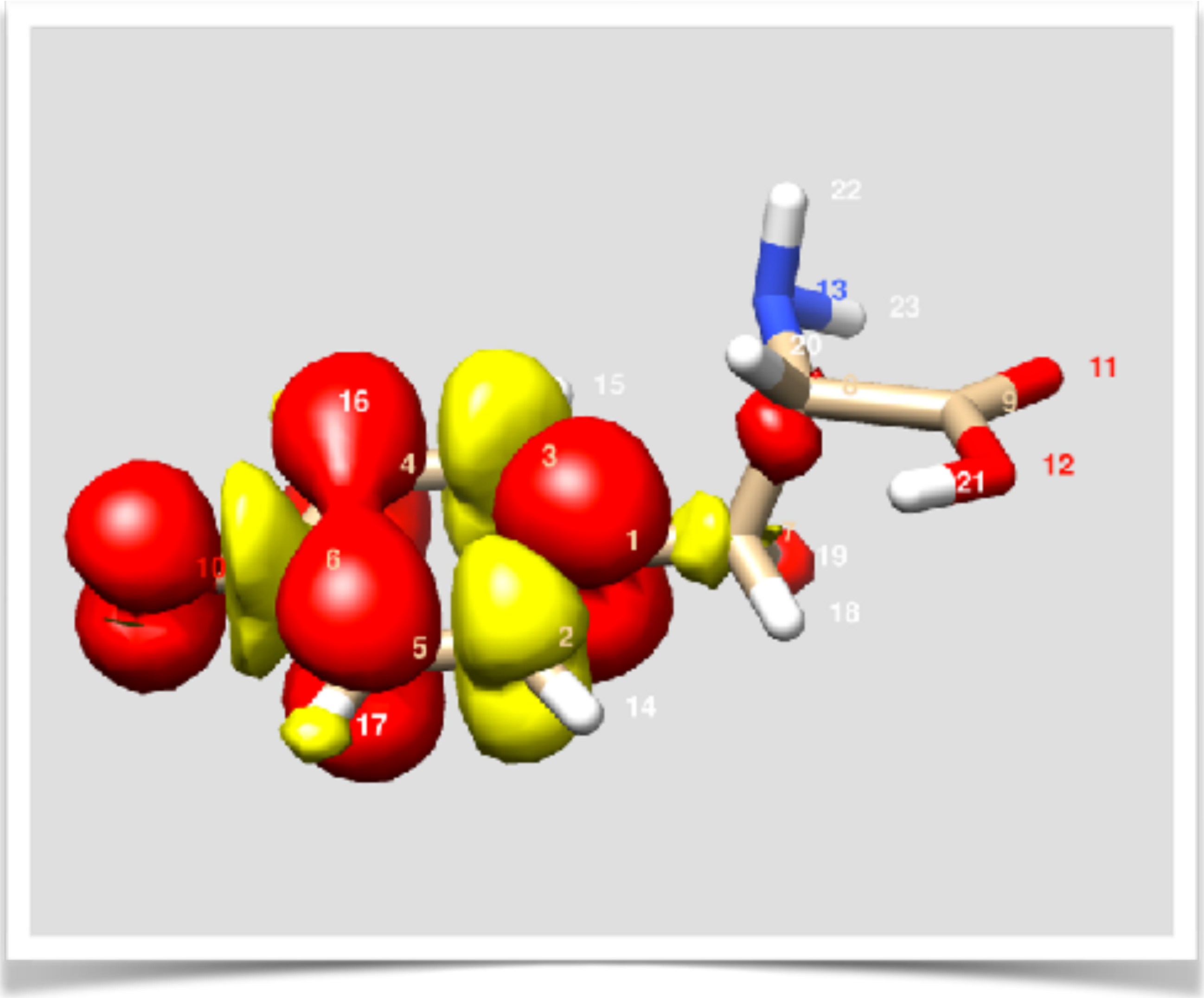
$$\int \rho^{\alpha-\beta}(\mathbf{r})d\mathbf{r} = N_{unpaired} = \sum_{\mu\nu} P_{\mu\nu}^{\alpha-\beta} S_{\mu\nu}$$

$$= \underbrace{\sum_A \sum_{\mu_A\nu_A} P_{\mu_A\nu_A}^{\alpha-\beta} S_{\mu_A\nu_A}}_{LOCAL-Spin-Population} + \underbrace{2\sum_A \sum_{B\neq A} \sum_{\mu_A\nu_{B\neq A}} P_{\mu_A\nu_B}^{\alpha-\beta} S_{\mu_A\nu_B}}_{BOND-Spin-Population;\ divide\ equally}$$

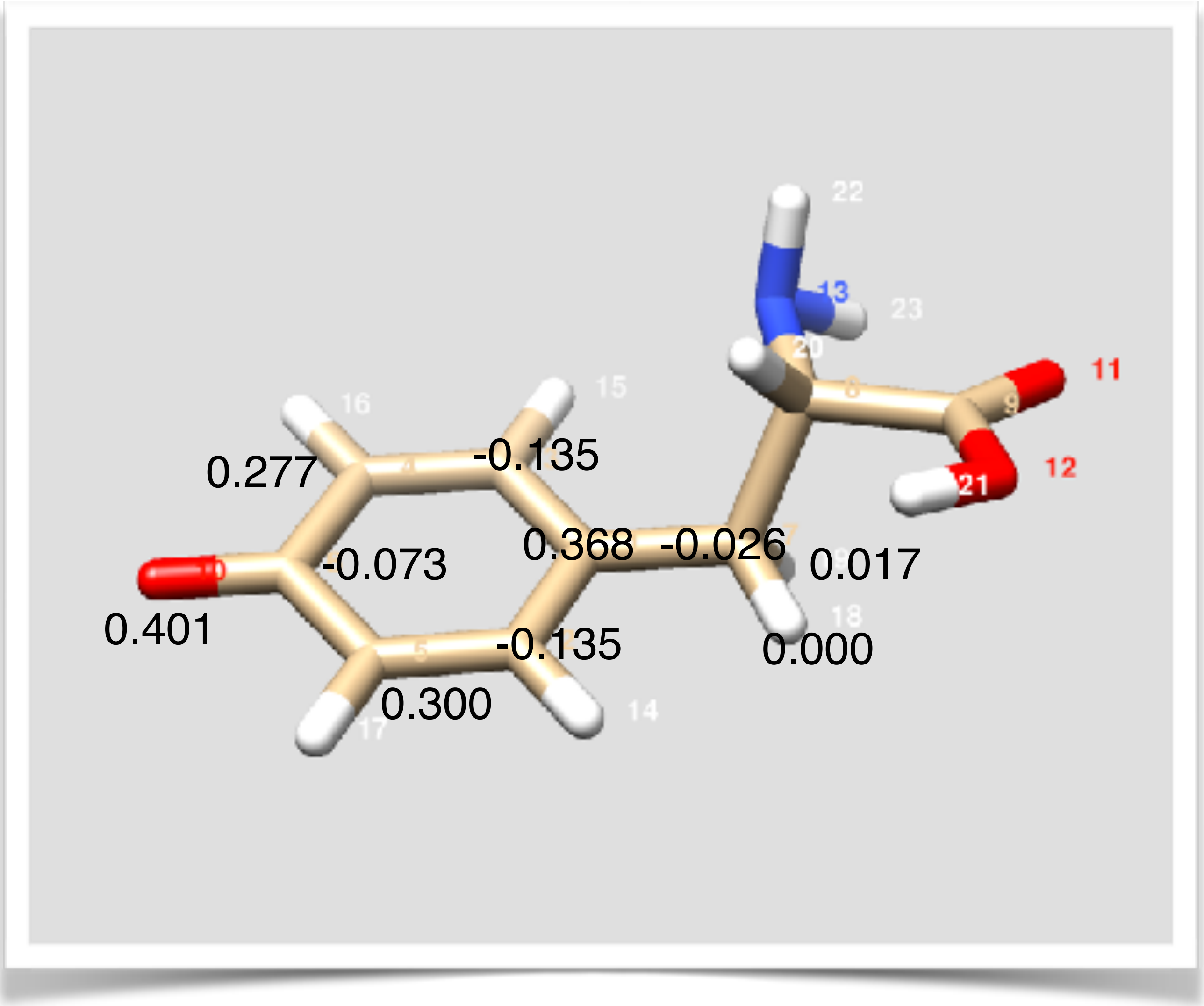
$$= \sum_A \rho_A^{\alpha-\beta}$$

Example: Tyrosine Radical

Spin Density



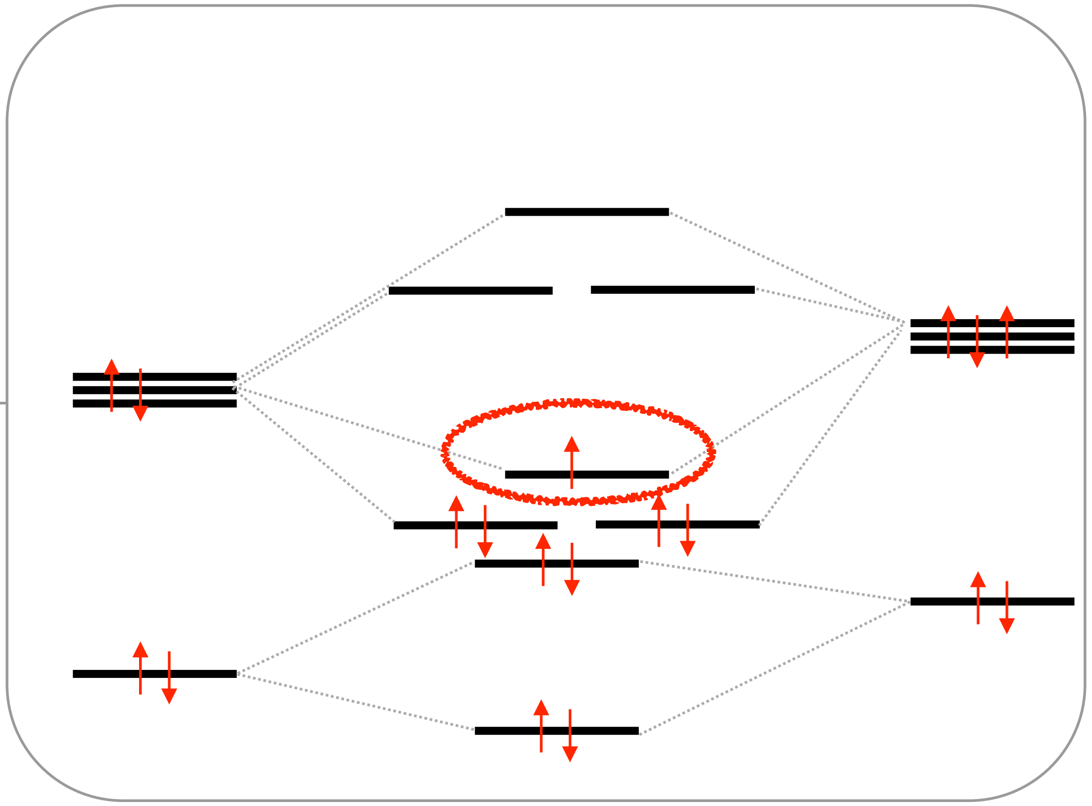
Spin Population

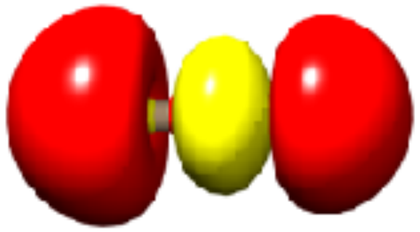
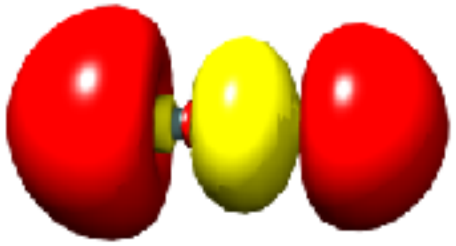
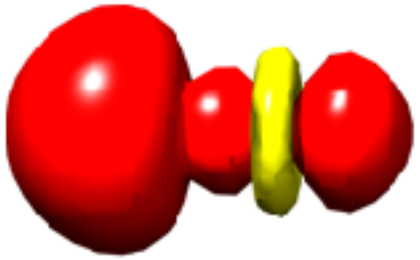
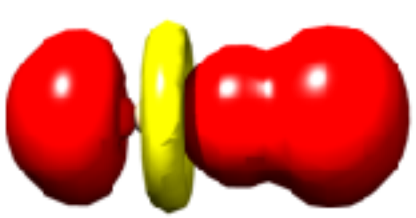
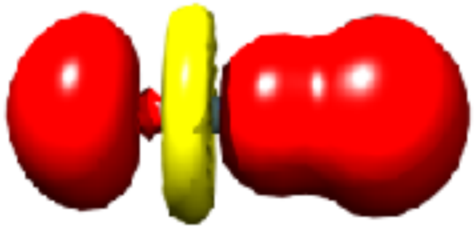


<u>Note</u>: the spin-population takes no account of *how* exactly the spin density is distributed among the available orbitals of the atom it is assigned to!

Spin Distribution and Bonding

Example: XN$^{\cdot}$ $^2\Sigma$–radicals (X= C, Si, Ge, Sn)



	CN	**SiN**	**GeN**	**SnN**
SOMO				
Spin-Dens				
ρ(N)	**13.0%**	**87.2%**	**89.2%**	**97.8%**
A^N(MHz)	**21.5**	**53.7**	**46.6**	**9.1**

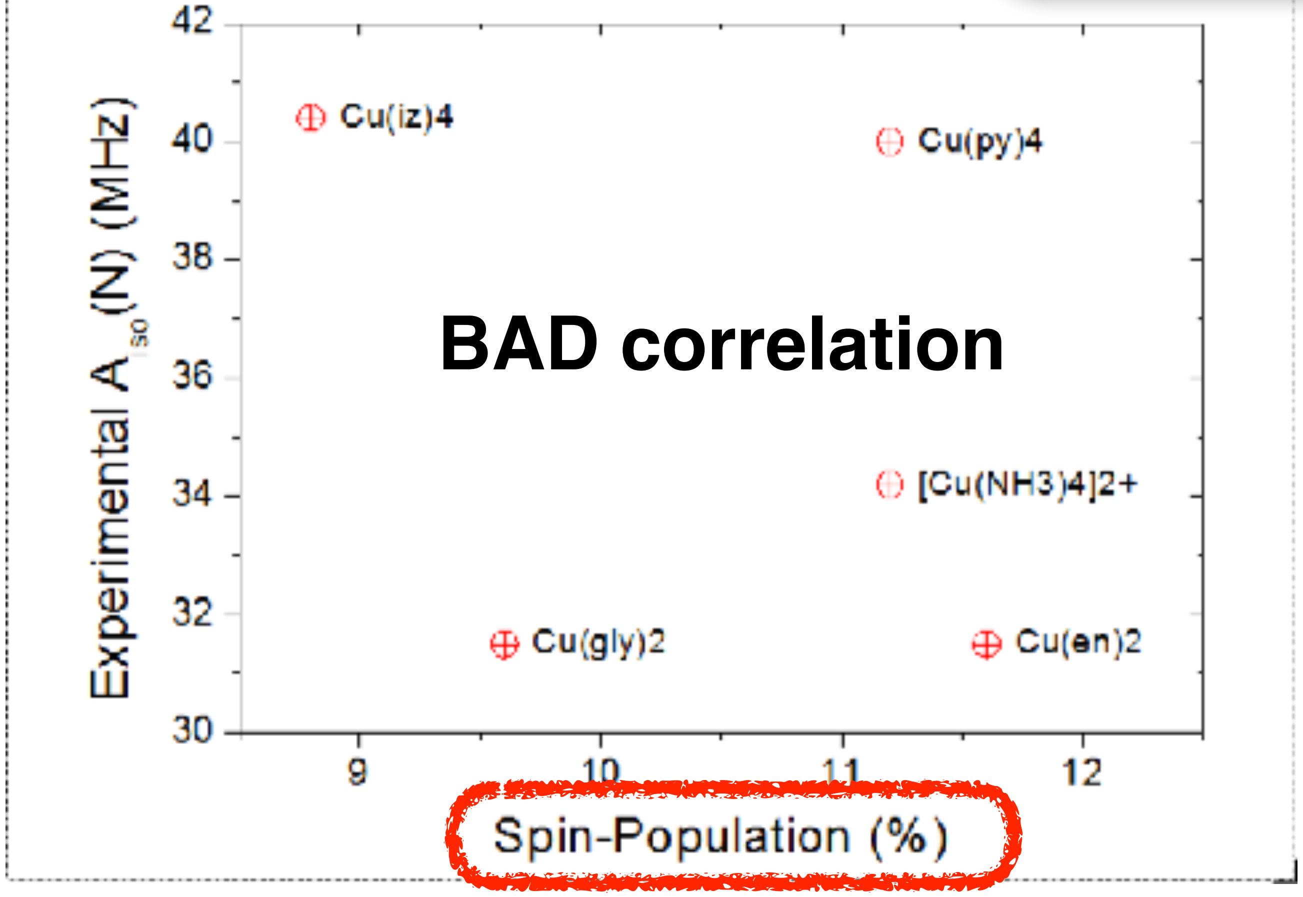
Spin *Density* and *Population* are NOT synonymous

The equation: $A_{KL}^{(N;local-dip)} \approx \rho_N^{\alpha-\beta} A_{KL}^{N;dip}$

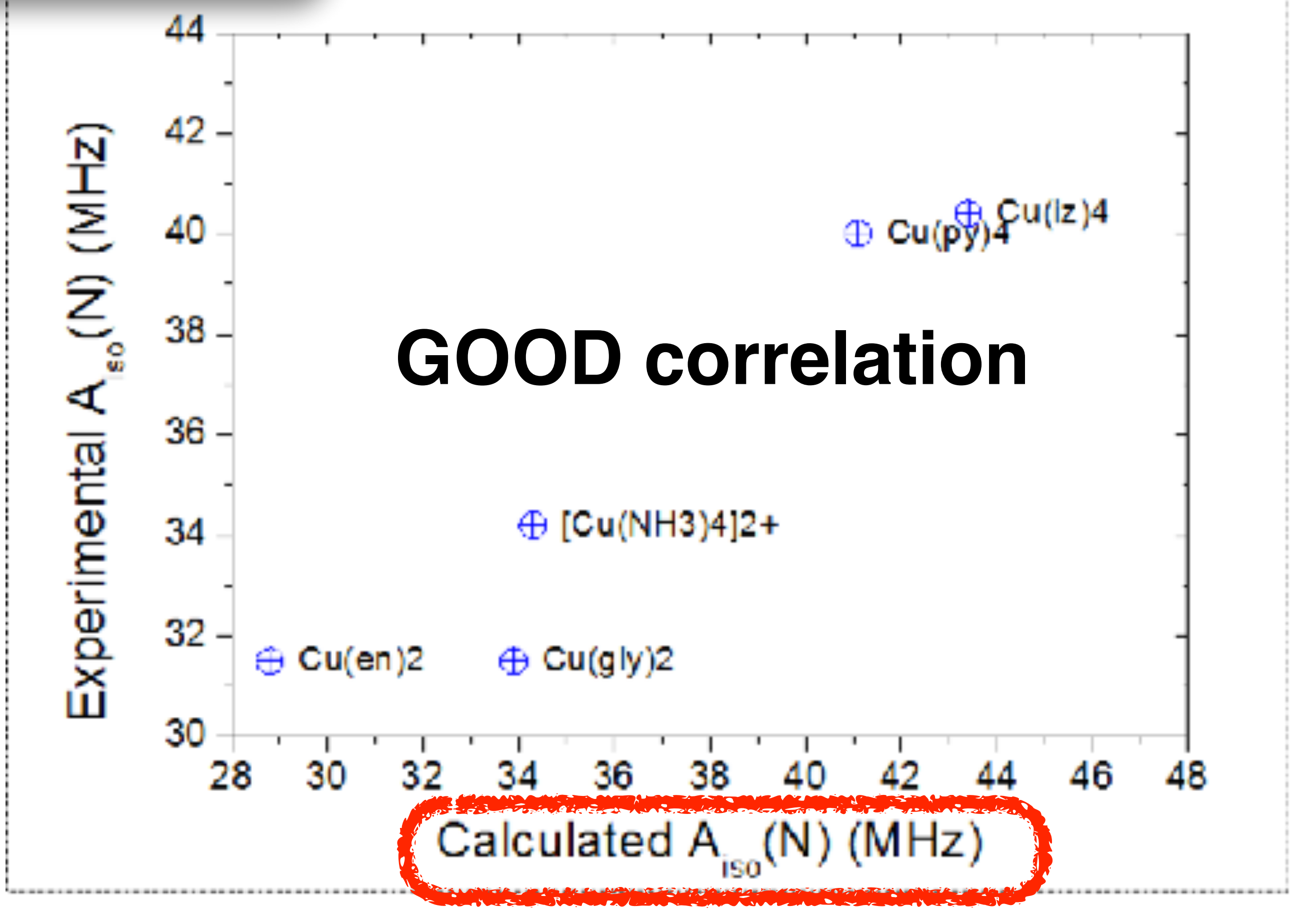
Is very attractive and has been used for decades in EPR

… but it is not rigorous - example:

Cu^{II}(NR)$_4$ complexes

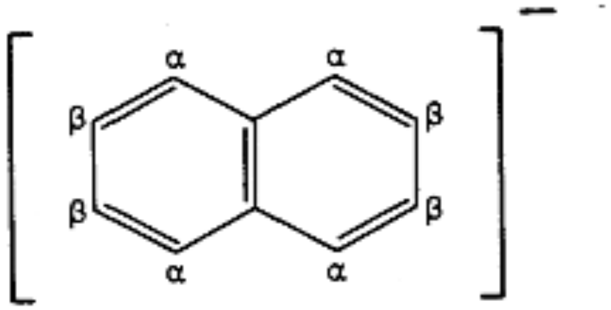


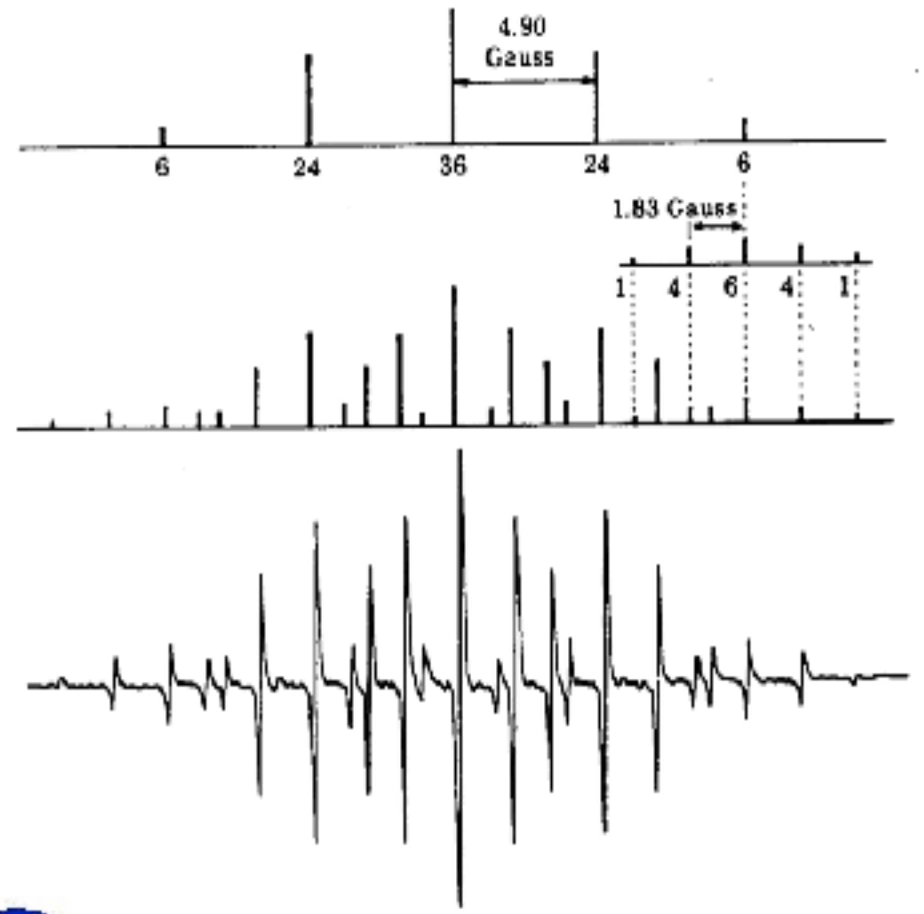
BAD correlation

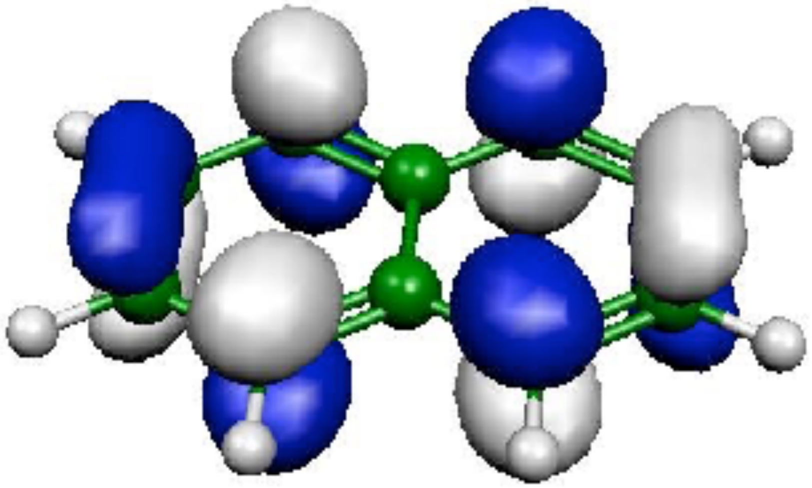


GOOD correlation

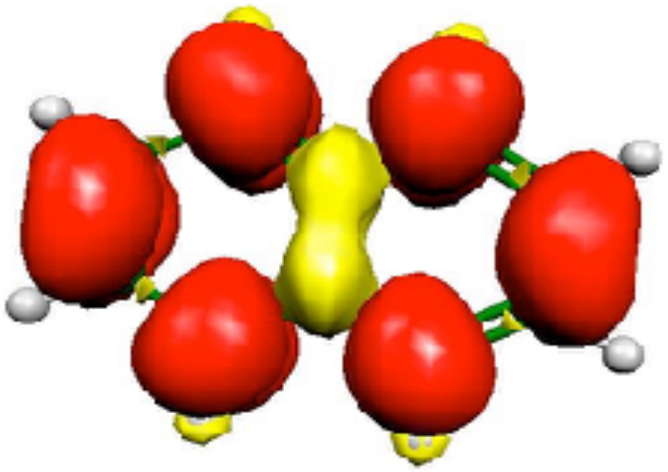
Example: Naphtalene Anion Radical







Singly Occupied MO



Spin Density
(red=positive,
yellow=negative)

Calc. vs. Exp. Hyperfine Couplings

a_α = 5.6 Gauss (exp= 4.9 Gauss)

a_β = 1.7 Gauss (exp=1.8 Gauss)

Spin Polarization

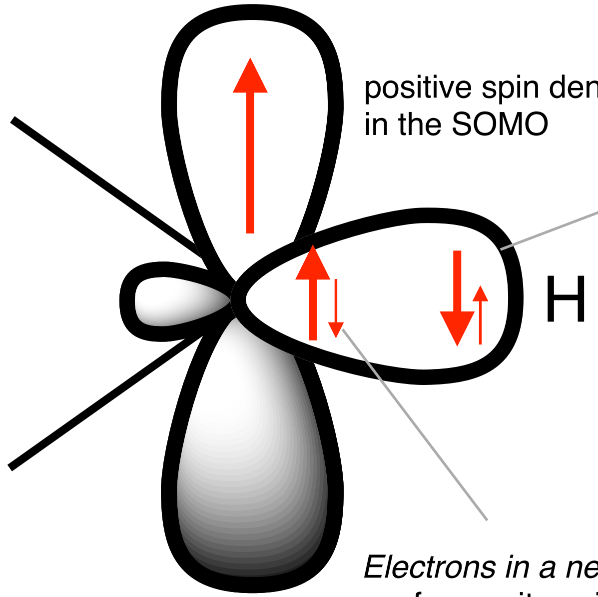
The **Electron Density** is intrinsically positive $\rho(\mathbf{r}) = \rho^{\alpha}(\mathbf{r}) + \rho^{\beta}(\mathbf{r}) > 0 \quad (all\ \mathbf{r})$

The **Spin Density** can have either sign: $\rho^{\alpha-\beta}(\mathbf{r}) = \rho^{\alpha}(\mathbf{r}) - \rho^{\beta}(\mathbf{r})$

The way we normalize the spin density ensures that it's integral is equal the number of unpaired electrons

$$\int \rho^{\alpha-\beta}(\mathbf{r})\, d\mathbf{r} = 2S$$

However, *locally* the spin density can be negative. This occurs due to the **‚spin-polarization‘**. It is particularly importantat places, where the SOMO's have nodes



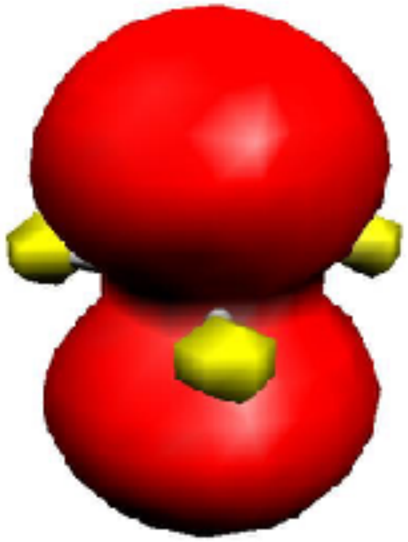
positive spin density
in the SOMO

Electrons in a nearby sigma bond.
Due to e^- of the same spin are being ‚drawn’ closer to the e^- in the SOMOs, there is a net surplus of spin-down electrons a bit further away.

Electrons in a nearby sigma bond.
e^- of opposite spin are more strongly repelled by the unpaired e^- than e^- of same spin

Origin: The „**Fermi-hole**“:
The quantum mechanical exchange creates a ‚hole‘ around a reference electrons inside which the probability of finding another electron with the same spin is reduced.

Calculating Spin Polarization



Example: CH_3 radical $^1H/^{13}C$ couplings (MHz)

- Both isotropic HFC's arise from spin polarization

Basis set dependence (B3LYP):

	^1H	^{13}C
Extended	**-61.0**	**83.7**
Quadruple-ζ	-63.0	83.0
Triple-ζ	-59.5	82.3
Double-ζ	-57.1	76.0
EPR-II	-	-

Method dependence

Method	^1H	^{13}C
B3LYP	-66.6	84.7
PBE0	-72.5	80.6
BP86	-67.6	60.7
PW91	-66.0	60.7
UHF	-122.1	162.8
CCSD(T)	-72.6	79.7
Exp	**-70**	**+76**

- Very difficult for theory! Hartree-Fock is useless, DFT sometimes erratic. Need high-level ab initio (e.g. coupled-cluster theory)
- Basis convergence is hard to achieve and very slow. Need core region well!

Transition Metal Hyperfine Couplings

For the metal nuclei, we need all three parts of the HFC

$$A(M) = A_{iso}(M) + A_{dip}(M) + A_{SOC}(M)$$

All coming from core-level spin-polarization since the spin is in the metal d-orbitals

DFT-bad
(underestimates)

Is mostly affected by metal-ligand covalency

DFT-reasonable
(underestimates)

Depends on excited states and covalence prop to Δg

DFT-mediocre
(underestimates)

The three parts have different signs and can have comparable magnitude

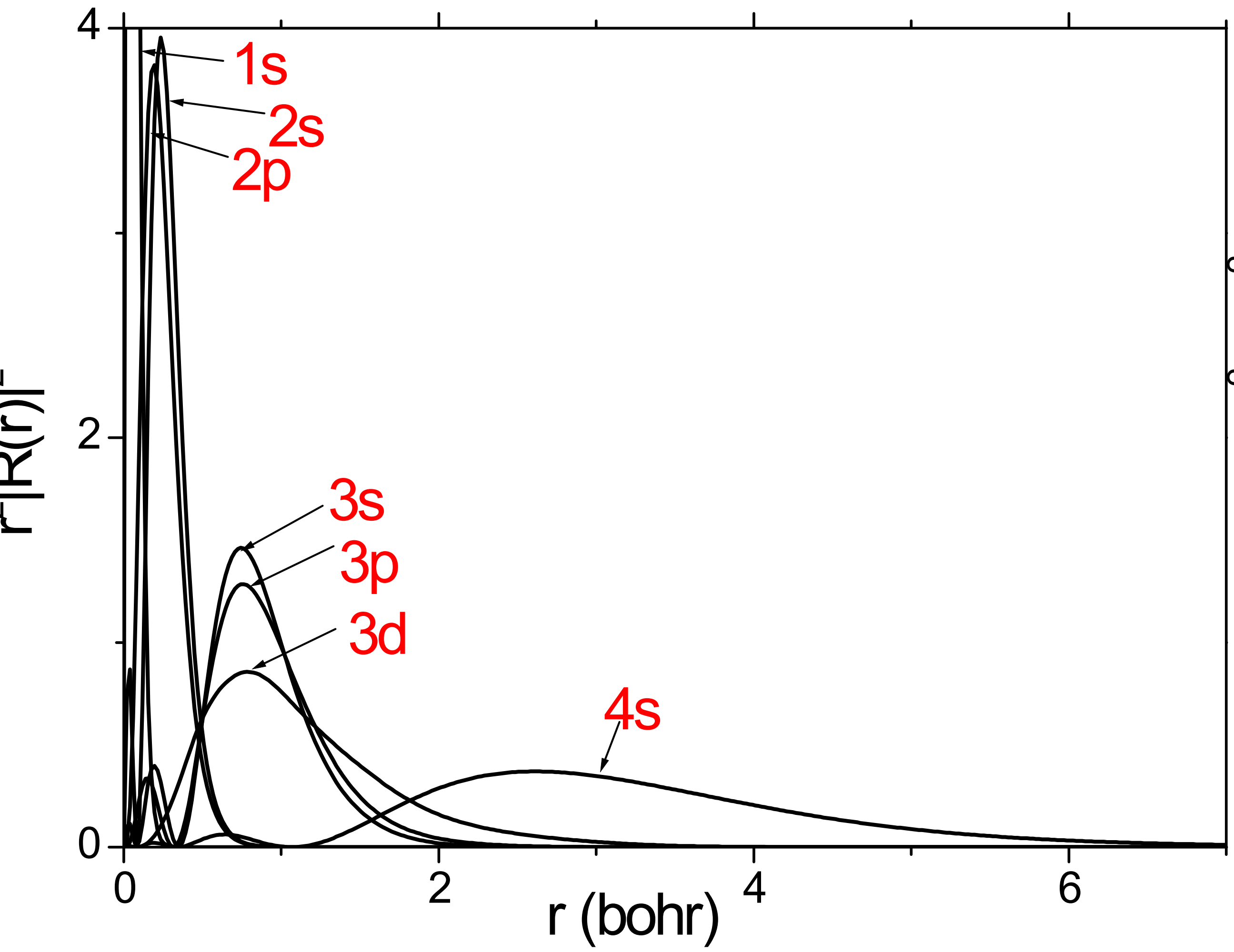
			iso	dip	SOC	Total
e.g. $[Cu(NH_3)_4]^{2+}$	$A_{\|\|}(MHz)$	A.I.	-362	-577	+348	-591
		B3LYP	-336	-485	+210	-611
	$A_{\perp}(MHz)$	A.I.	-362	+287	+78	~0
		B3LYP	-336	+243	+59	-34

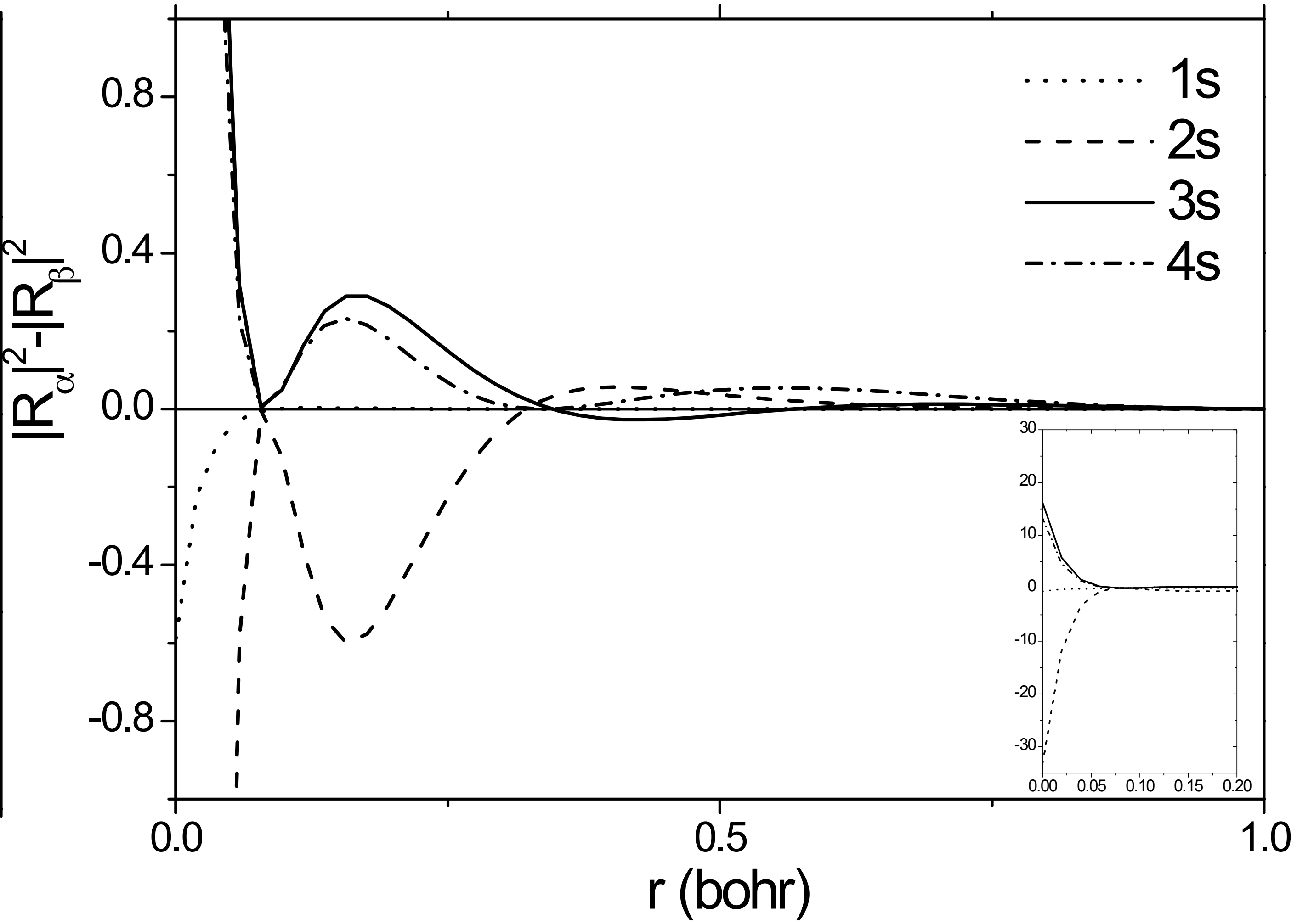
FN *Mag. Res. Chem.*, **2004**, 42, S187-S198

Fermi Term: Core-Level Spin Polarization

Radial Functions

Spin Polarization

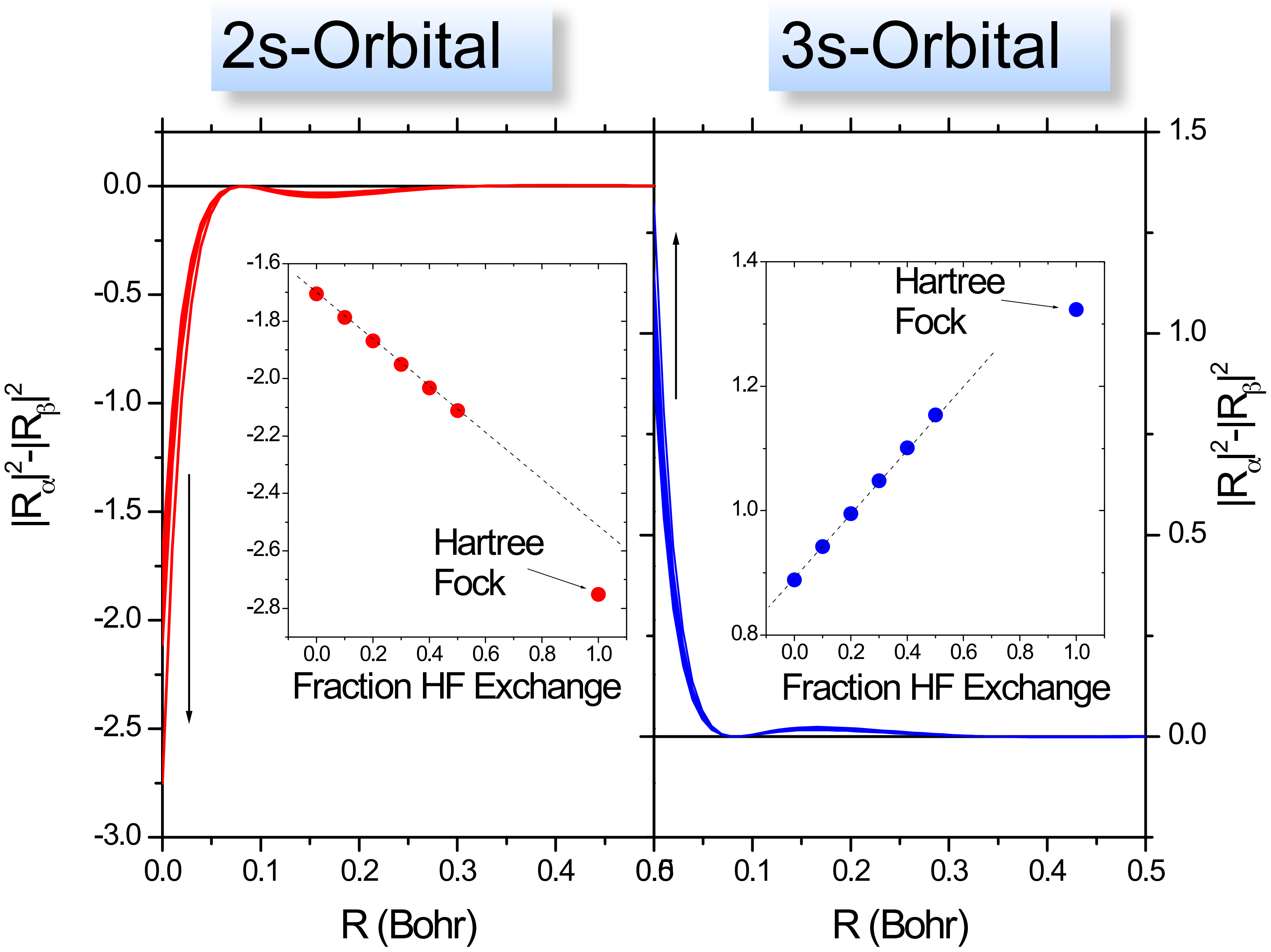




FN; Solomon, EI (**2003**) in: Miller, JS; Drillon, M „Molecular Magnetism“ Vol. IV

HF Calculation on ^6S of Mn(II)

Core-Level Spin-Polarization: DFT

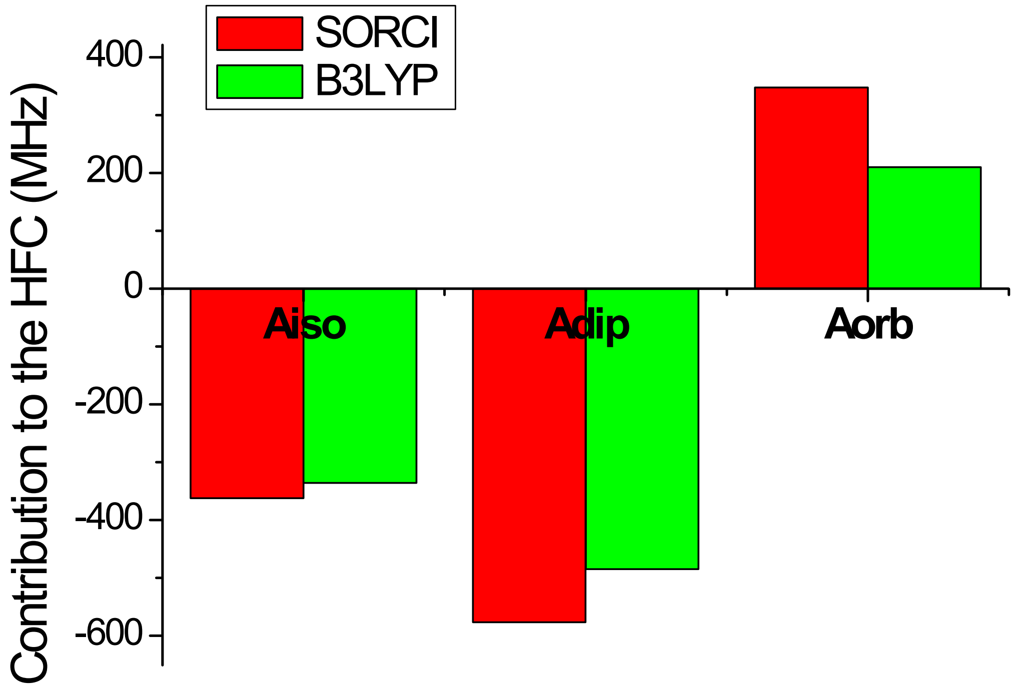


Munzarova, ML; Kubacek, P; Kaupp, M (**2000**) *J. Am. Chem. Soc.*, 122, 11900

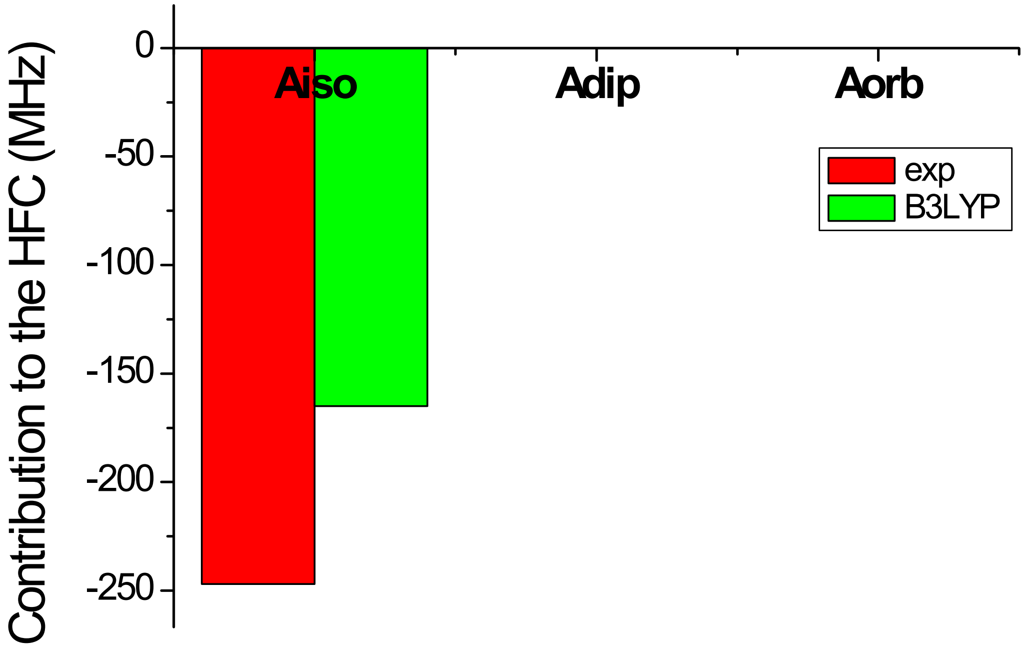
FN; Solomon, EI (**2003**) in: Miller, JS; Drillon, M „Molecular Magnetism“ Vol. IV

Performance of DFT for Metal HFCs

$[Cu(NH_3)_4]^{2+}$



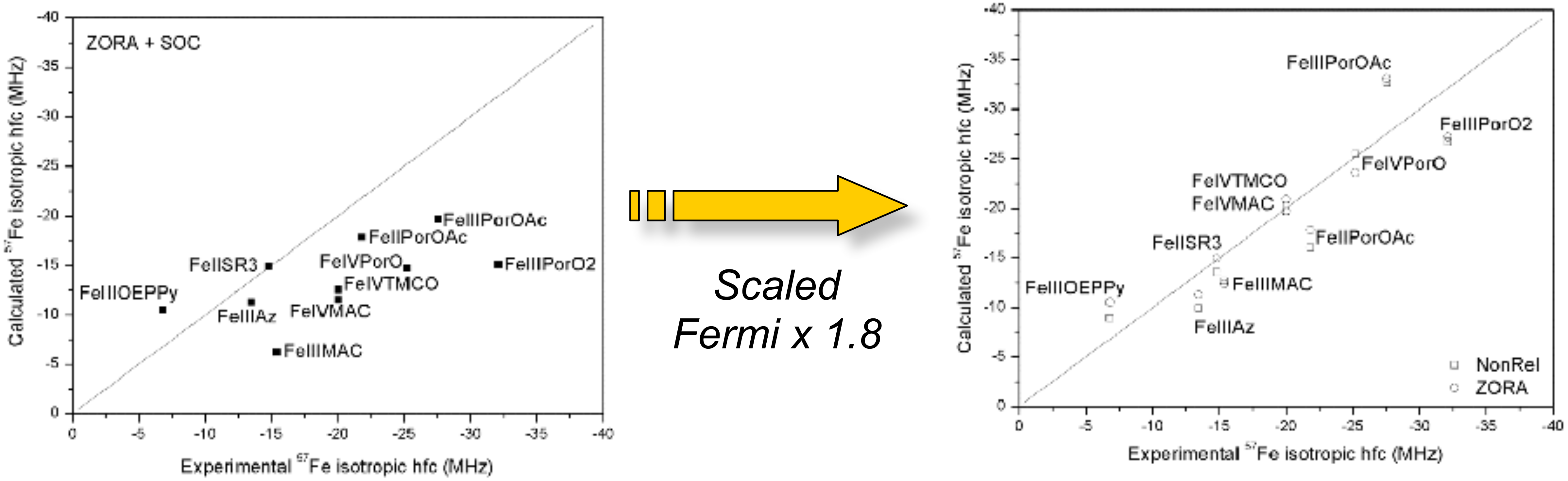
$[Mn(H_2O)_6]^{2+}$



- Isotropic coupling underestimated (too positive)
- Spin-Orbit contribution underestimated (not positive enough $\propto \Delta g$)
- Dipolar part usually underestimated in magnitude (too covalent)

FN *J. Chem. Phys.* (**2003**), 3039-3048

Results for Iron Hyperfine Structure



- Conclusions:
  - Isotropic HFCs underestimated by DFT by 80% on average for systems with **small SOC** (hs-Fe^{III}, ls-Fe^{IV}) (→ Scaling factor 1.8)
  - The SOC contribution can be large (up to 50%) and its accuracy is doubtful
  - In cases with **large SOC** (ls-Fe^{III}, hs-Fe^{II}) one obtains better agreement without scaling of the isotropic part (→ Error compensation)
  - With some ‚educated guess' to the system RMS~3-4 MHz (NonRel or ZORA)

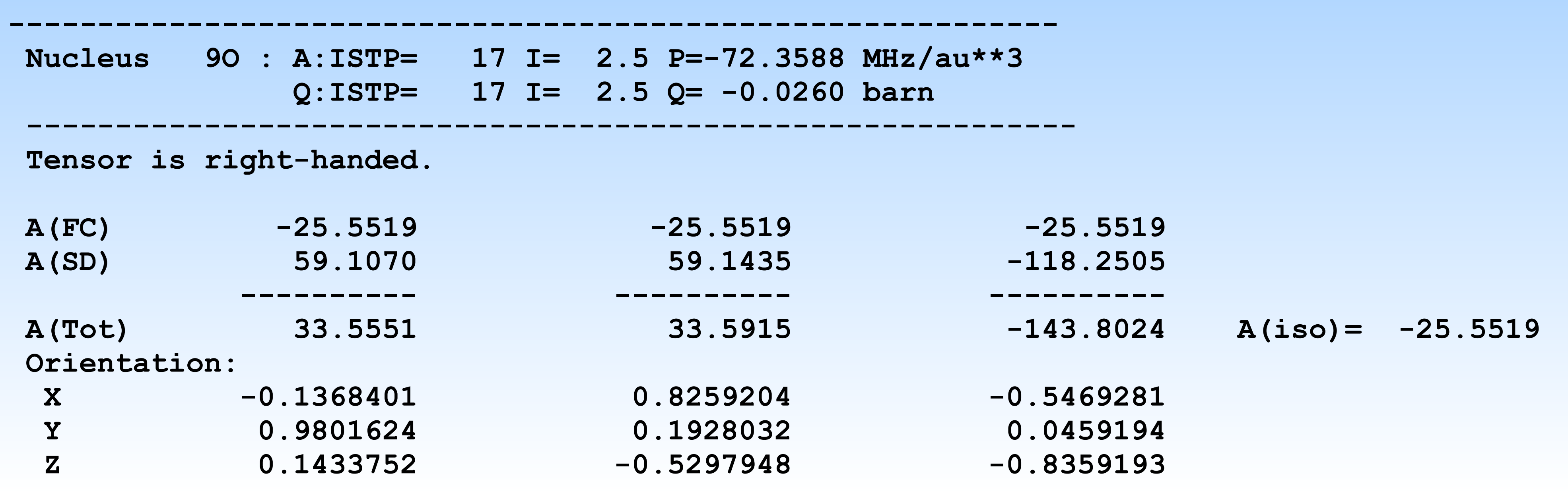
Sinnecker, S.; Slep, L.; Bill, E.; FN (**2005**) *Inorg. Chem.*, 44, 2245

Hyperfine-Tensors in ***ORCA***

- Only for HF, DFT, MP2 and CCSD/OOCCD via the %eprnmr command

```
%eprnmr nuclei = all H {aiso, adip}
        nuclei = all N {aiso, adip, fgrad}
        nuclei = all Cu{aiso, adip, aorb, fgrad}
        end
```

- NOTE: You have to have to block AFTER the coordinates. Otherwise the program doesn‘t know the nuclei
- NOTE: only one *type* of nucleus per ‚Nuclei‘ command“
- NOTE: it makes no sense to calculate the expensive SOC correction for light nuclei but for the metal you need it!
- **Output**



```
-----------------------------------------------------------
 Nucleus    9O : A:ISTP=   17 I=  2.5 P=-72.3588 MHz/au**3
                 Q:ISTP=   17 I=  2.5 Q= -0.0260 barn
 -----------------------------------------------------------
 Tensor is right-handed.

 A(FC)        -25.5519          -25.5519          -25.5519
 A(SD)         59.1070           59.1435         -118.2505
             ----------        ----------        ----------
 A(Tot)        33.5551           33.5915         -143.8024     A(iso)=   -25.5519
 Orientation:
  X           -0.1368401         0.8259204        -0.5469281
  Y            0.9801624         0.1928032         0.0459194
  Z            0.1433752        -0.5297948        -0.8359193
```

Using ORCA to Create Simulation Input

Input

```
%eprnmr gtensor true
        nuclei = all H  {aiso,adip,fgrad}
        nuclei = all C  {aiso,adip,fgrad}
        nuclei = all O  {aiso,adip,fgrad}
        end
```

Output

```
-------------------------------------------------------------------------
          Euler rotation of hyperfine tensor to g-tensor
-------------------------------------------------------------------------


-------------------------------------------------------------------
 Atom  |   Alpha    Beta    Gamma   |   Ax       Ay       Az
       |          [degrees]         |           [MHz]
-------------------------------------------------------------------
 13H      -39.1     88.9     -1.2      11.56     6.71     4.91
 14H        7.3     49.6     77.3      11.91     5.32     6.84
 15H       -0.6     23.9     89.6      -8.37   -22.13   -28.42
 16H       24.1     89.6     -0.8     -30.81    -9.08   -23.70
 17H       26.8     88.4     -0.6       4.75    -0.82    -0.35
 18H       -4.2     67.4    -27.4      43.36    37.65    38.30
...
```

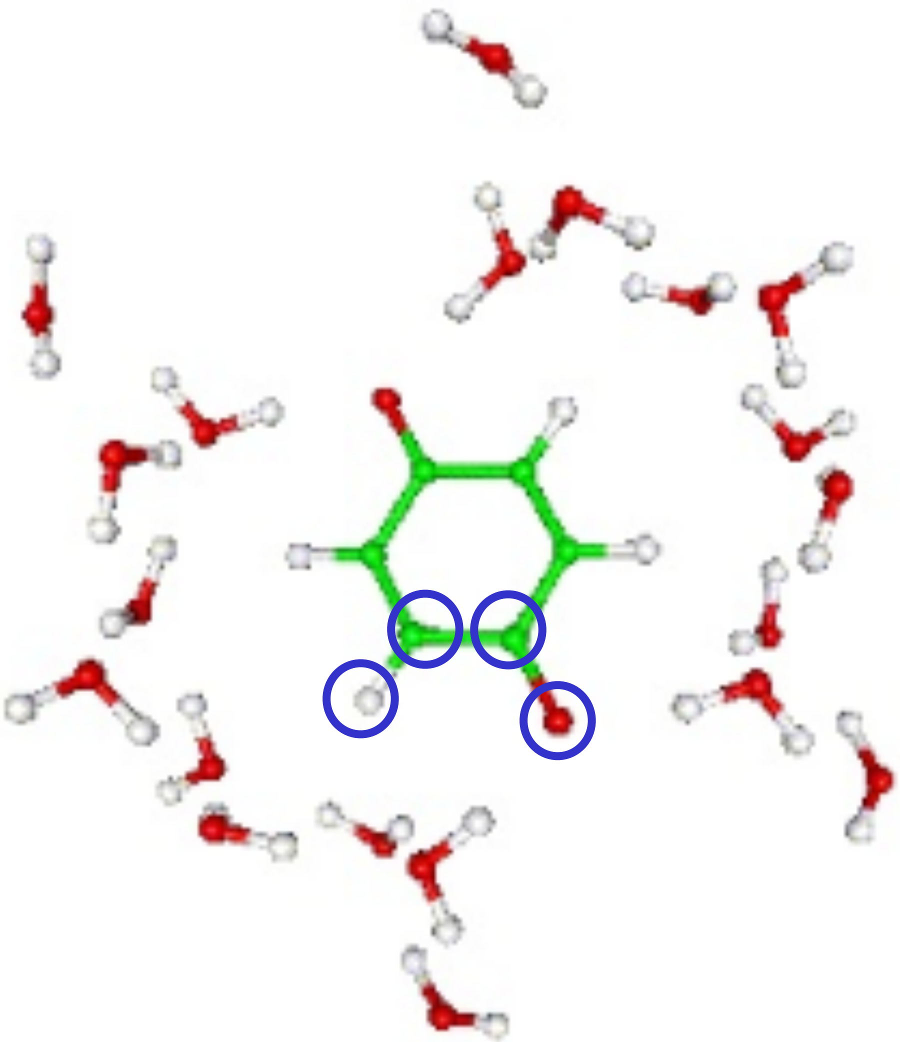
Euler angles

Projection of HFC tensor on g-tensor axes

- ✓ Can be directly fed into **EasySpin**
- ✓ Good strategy: Leave Euler Angles at their calculated values and fit principal HFC values. Allow 10-30% variation

Combining Theory and Experiment

... If everything goes well and you do it as carefully as you can, this is what can be achieved in a number of cases:



S. Sinnecker *et al*., *JACS,* **2004**, 126, 3280

Combining Theory and Experiment

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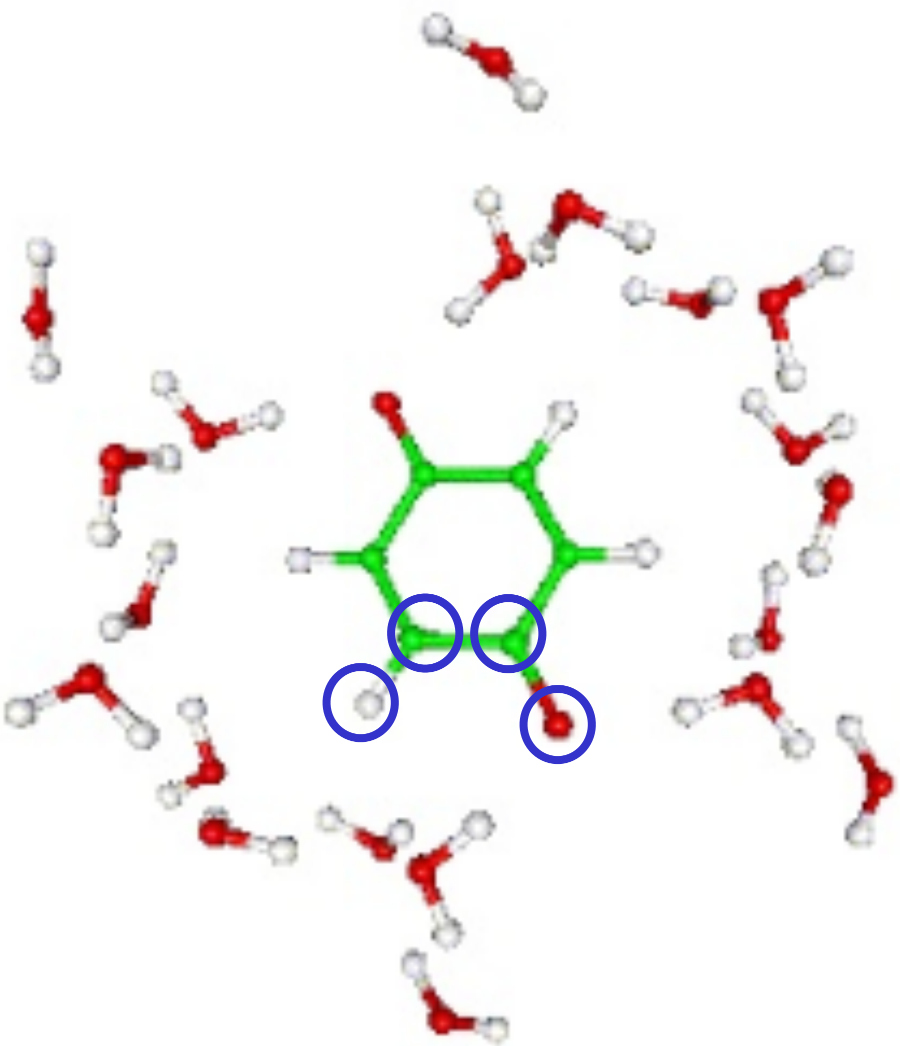
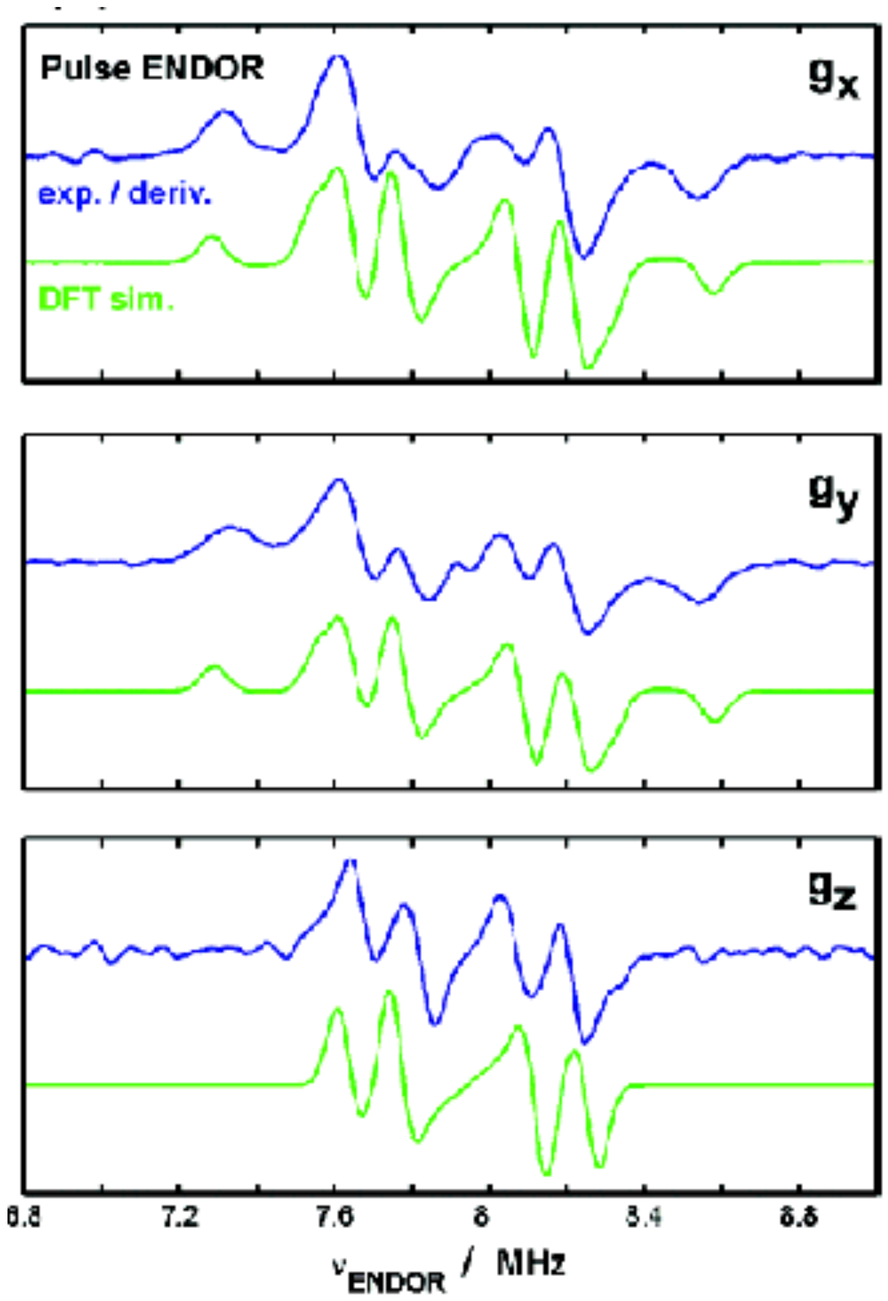




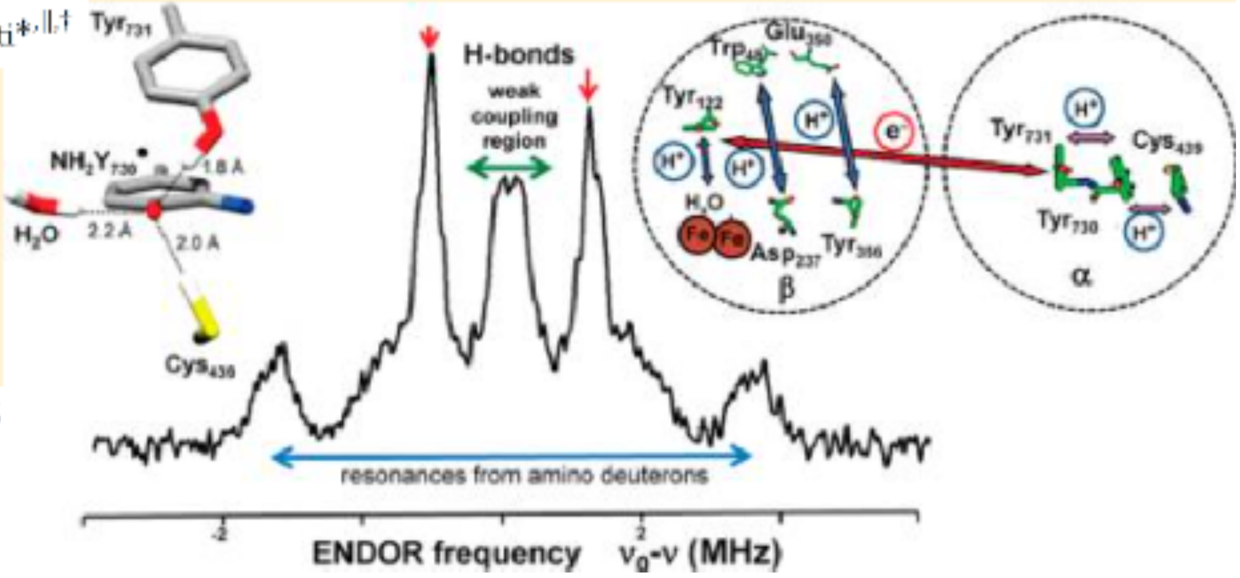
S. Sinnecker *et al.*, *JACS,* **2004**, 126, 3280

Applications

ENDOR Spectroscopy and DFT Calculations: Evidence for the Hydrogen-Bond Network Within $\alpha 2$ in the PCET of *E. coli* Ribonucleotide Reductase

Tomislav Argirević,[†] Christoph Riplinger,[‡] JoAnne Stubbe,[§] Frank Neese,[*,‡] and Marina Bennati[*,∥,†]

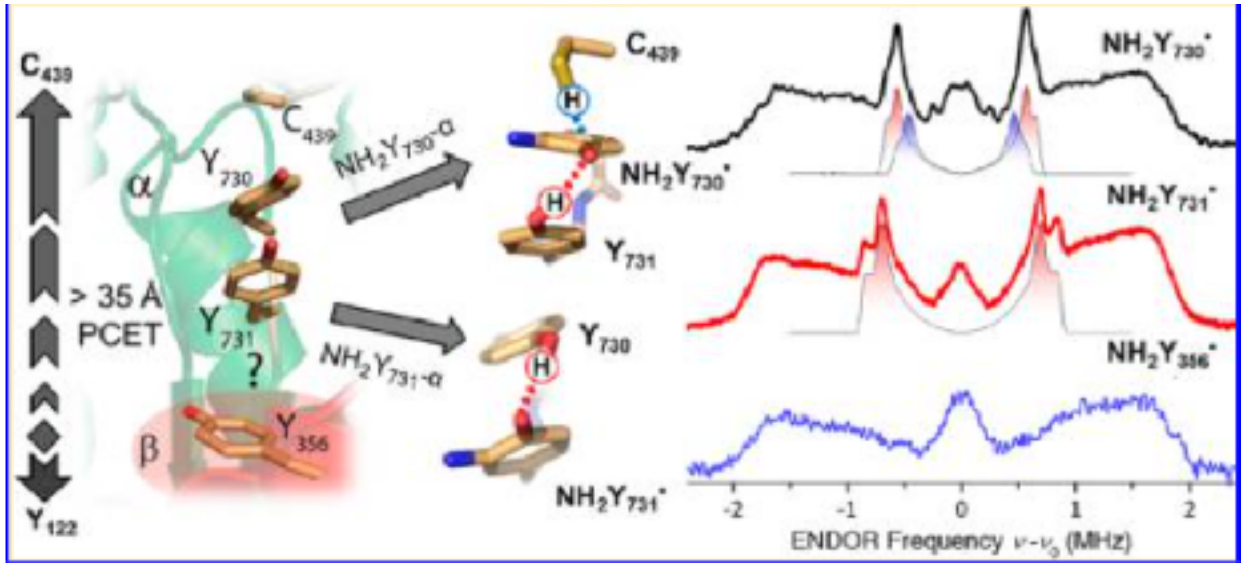
J. Am. Chem. Soc. 2012, 134, 17661−17670



Hydrogen Bond Network between Amino Acid Radical Intermediates on the Proton-Coupled Electron Transfer Pathway of *E. coli* $\alpha 2$ Ribonucleotide Reductase

Thomas U. Nick,[†] Wankyu Lee,[‡] Simone Koßmann,[§] Frank Neese,[*,§] JoAnne Stubbe,[*,‡] and Marina Bennati[*,†,∥]

J. Am. Chem. Soc. 2015, 137, 289−298



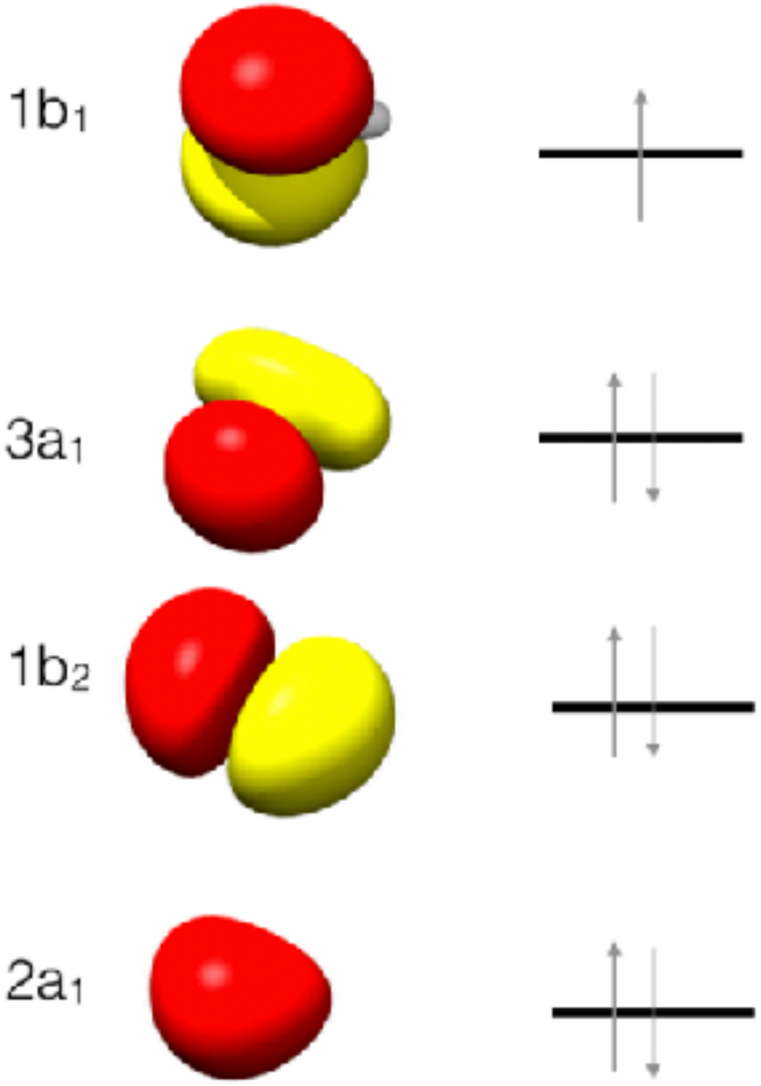
Current State of the Art in Hyperfine Calculations

Challenges in HFC Calculations


SOMO


Spin Density

H_2O^+




Spin density

	$A_{\mathrm{iso}}(\mathrm{O})$
CCSD	-78.5
UHF	-140.5
LDA	7.0
BP86	-22.0
PBE	-37.1
TPSS	-35.5
TPSSh	-44.4
B3LYP	-57.1
M06L	-194.9
M06-2X	-134.1
B2PLYP	-76.1
CAM-B3LYP	-49.7
Exp.[57]	-83

The Coupled Cluster Density

- ✓ Lagrangian formulation:

$$E_{DLPNO-CCSD} + \sum_{\mu} \lambda_{\mu} r_{\mu} = \left\langle \Psi_0 \,|\, (1+\Lambda) e^{-T} H e^{T} \,|\, \Psi_0 \right\rangle \qquad \mu = S, D \equiv \left({}^{a}_{i}, {}^{ab}_{ij}\right)$$

- ✓ Linear equations for determining the λ's

$$\frac{\partial L}{\partial t_{\mu}} = 0 = \left\langle \Psi_0 \,|\, (1+\Lambda)(e^{-T} H e^{T} - E_{DLPNO-CCSD}) \,|\, \Psi_{\mu} \right\rangle$$

- ✓ **IMPORTANT**: Take derivative of ACTUAL DLPNO-CCSD residual, do **NOT** apply DLPNO approximations to the canonical λ-equations!

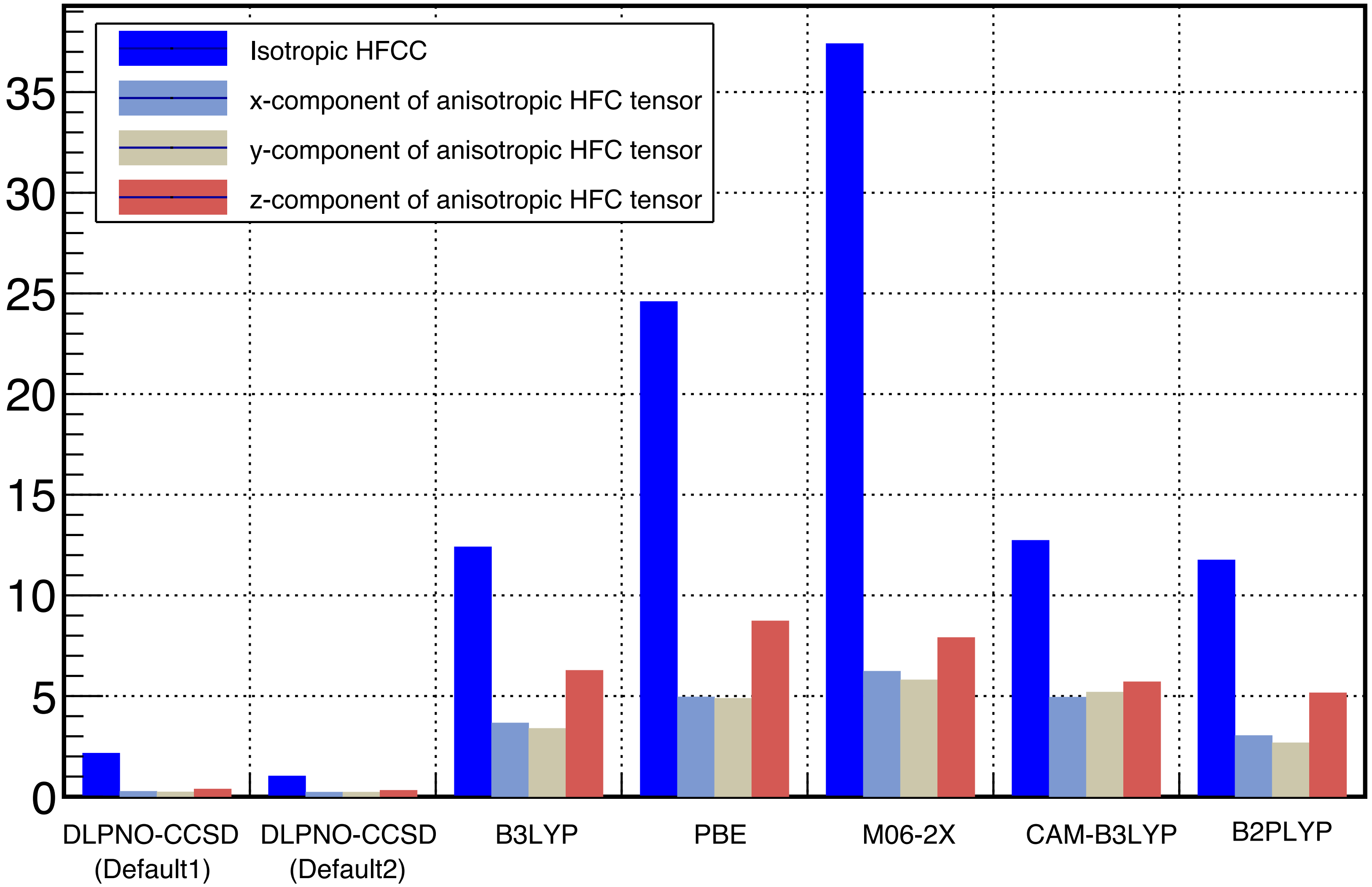
- ✓ One particle density defined through derivative w.r.t. perturbation c:

$$\frac{\partial L}{\partial \chi} = \sum_{pq} D^{CC}_{pq}(t, \lambda) \frac{\partial h_{pq}}{\partial \chi}$$

- ✓ where D_{pq} accounts for the response of the CCSD wave function to the external perturbation. (vide infra for orbital-response contributions)

DLPNO-CCSD vs DFT

58 atoms in 28 small radicals



PBE

B3LYP

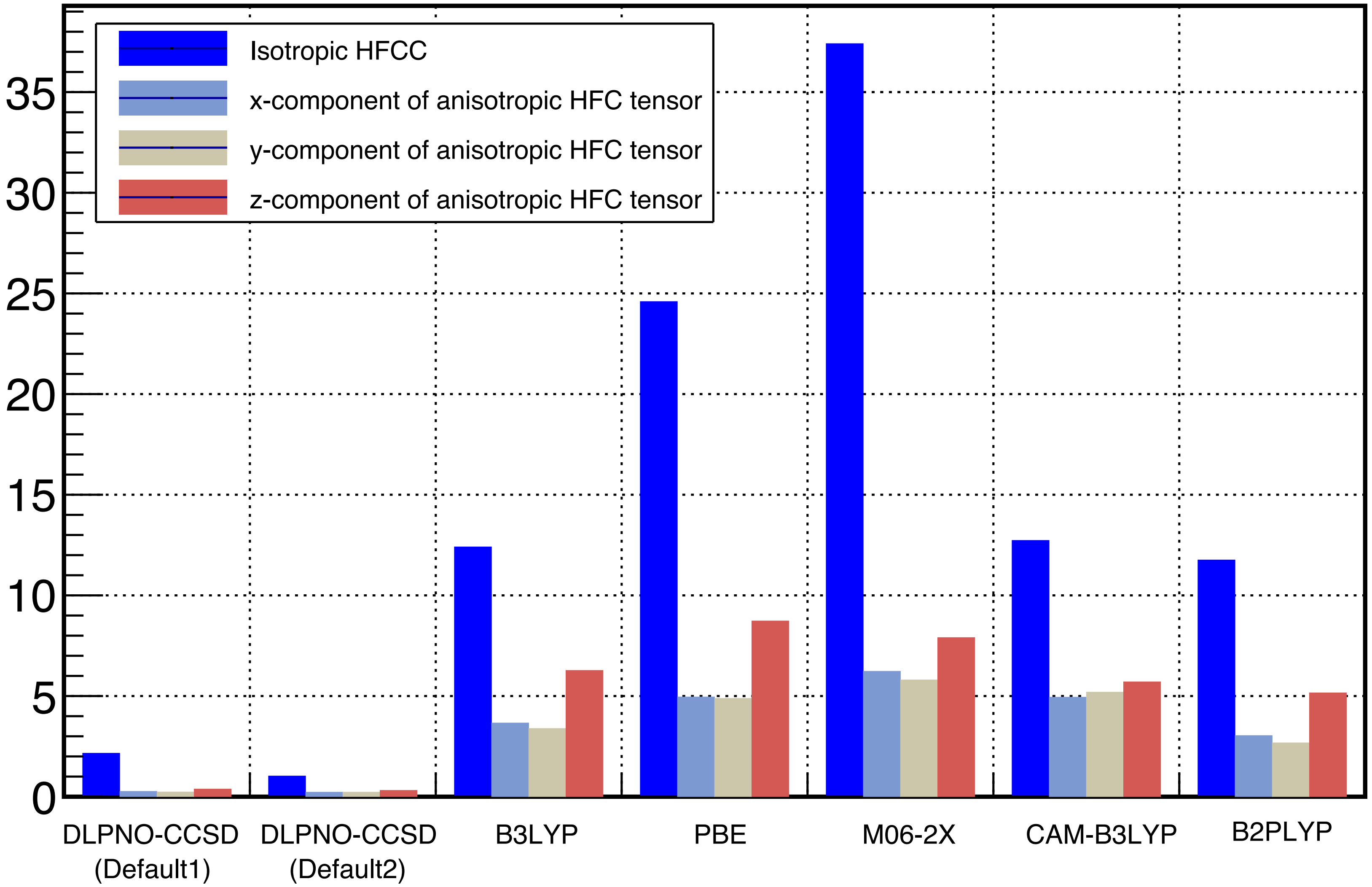
B2PLYP

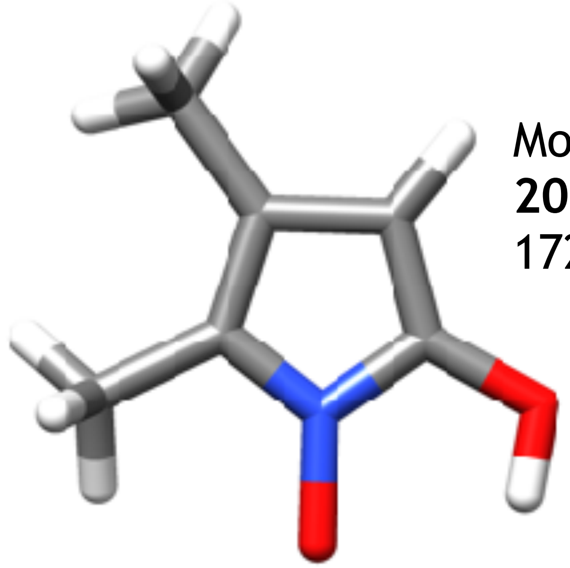
cc-pwCVQZ basis/ no frozen core

[1] S. Kossmann FN, *J. Phys. Chem. A* 114, 11768 (**2010**).

DLPNO-CCSD vs DFT

58 atoms in 28 small radicals





Molecules **2014**, 19, 17279

Experimental $\vec{a}_N = 41.2 \text{ MHz}$

DLPNO-CCSD $\vec{a}_N = 39.2 \text{ MHz}$

PBE $\vec{a}_N = 3.2 \text{ MHz}$

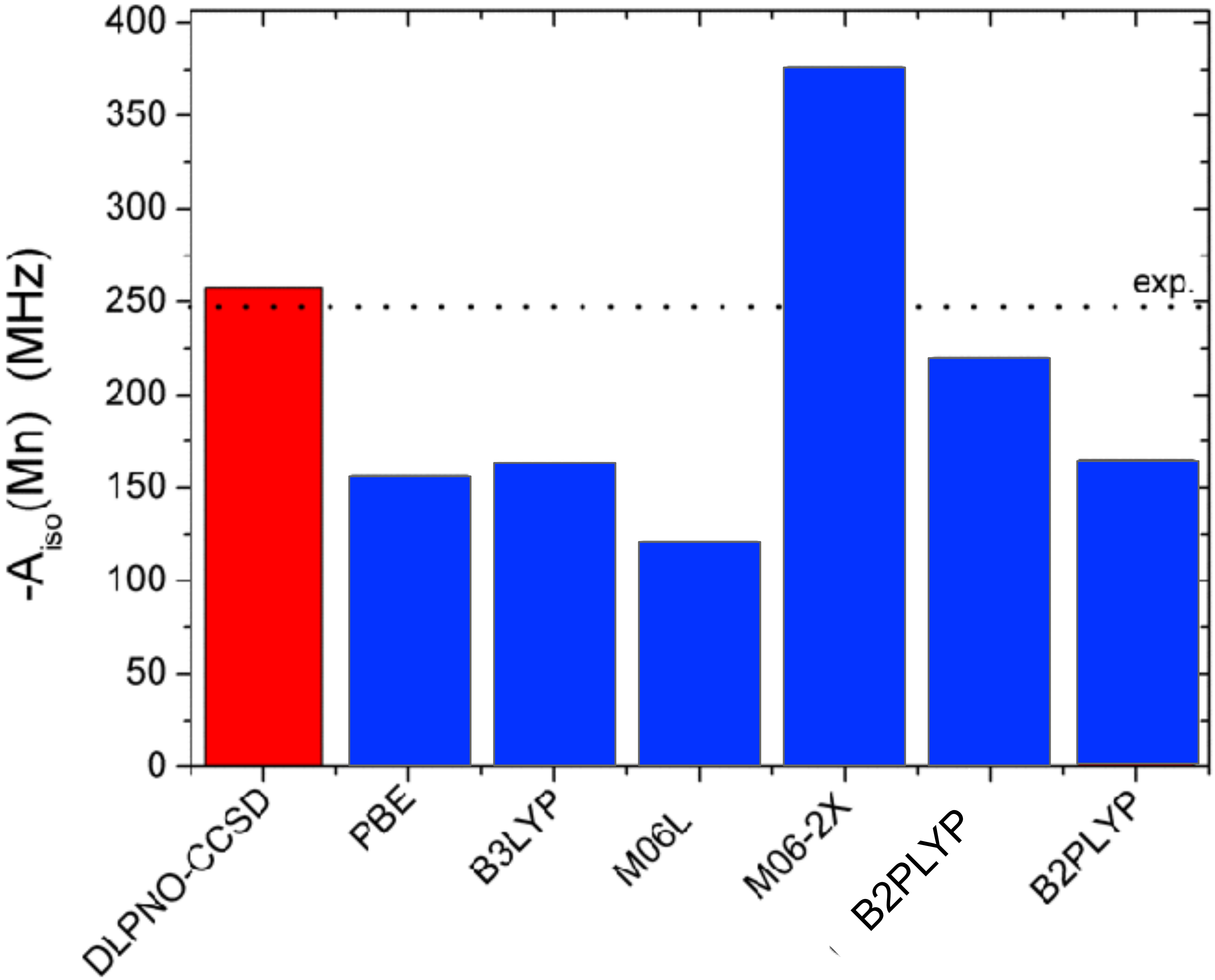
B3LYP $\vec{a}_N = 8.6 \text{ MHz}$

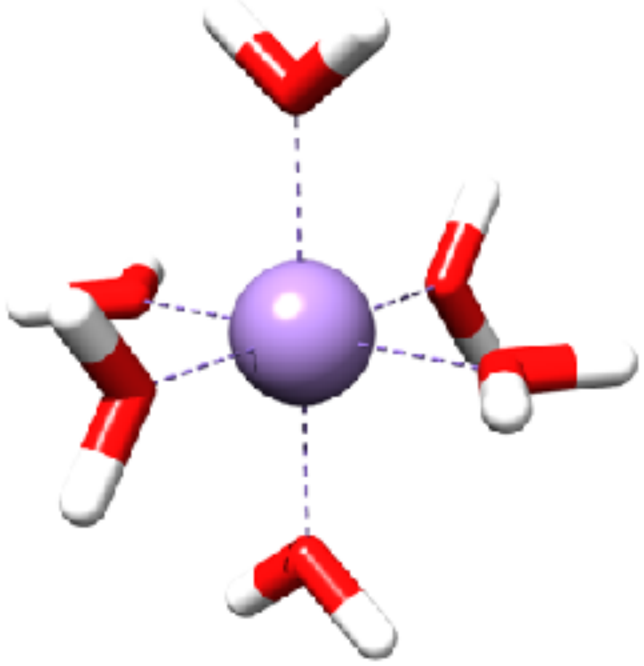
B2PLYP $\vec{a}_N = 19.2 \text{ MHz}$

cc-pwCVQZ basis/ no frozen core

[1] S. Kossmann FN, *J. Phys. Chem. A* 114, 11768 (**2010**).

Transition Metal Hyperfine Couplings: Example

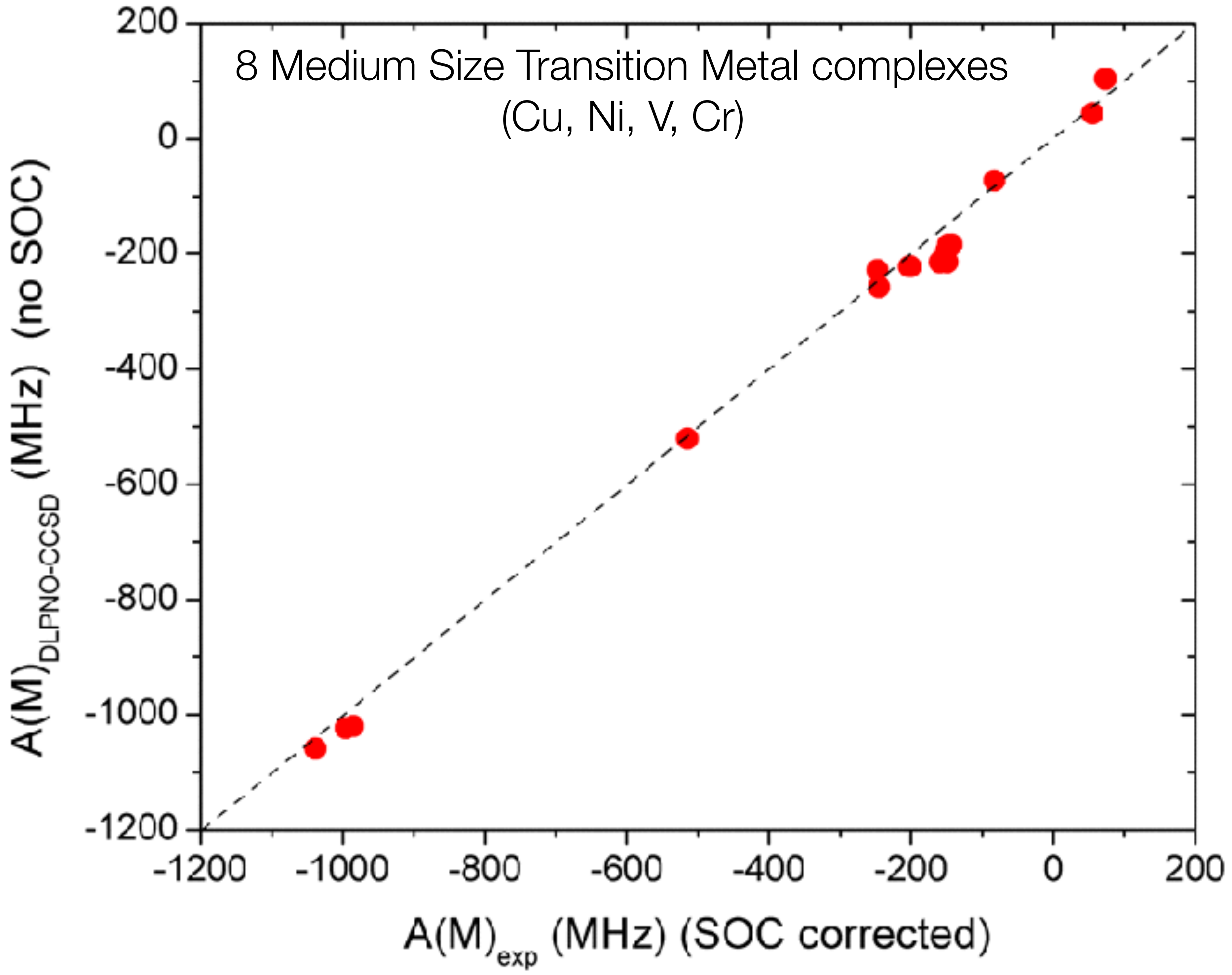




$[Mn(H_2O)_6]^{2+}$

DKH-def2-TZVPP/ DKH2/ Finite Nucleus/ Picture Change

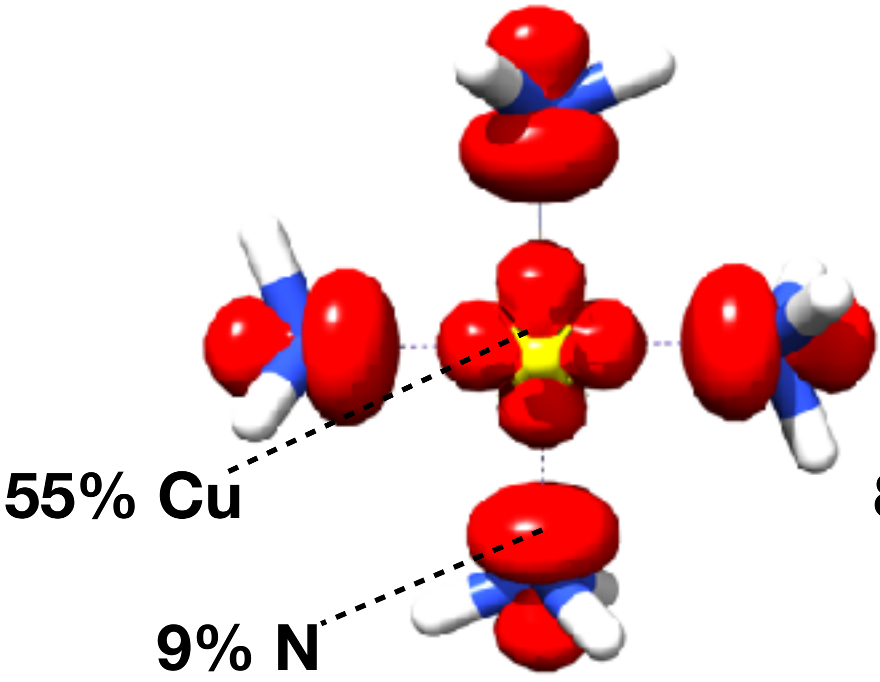
Transition Metal Hyperfine Couplings



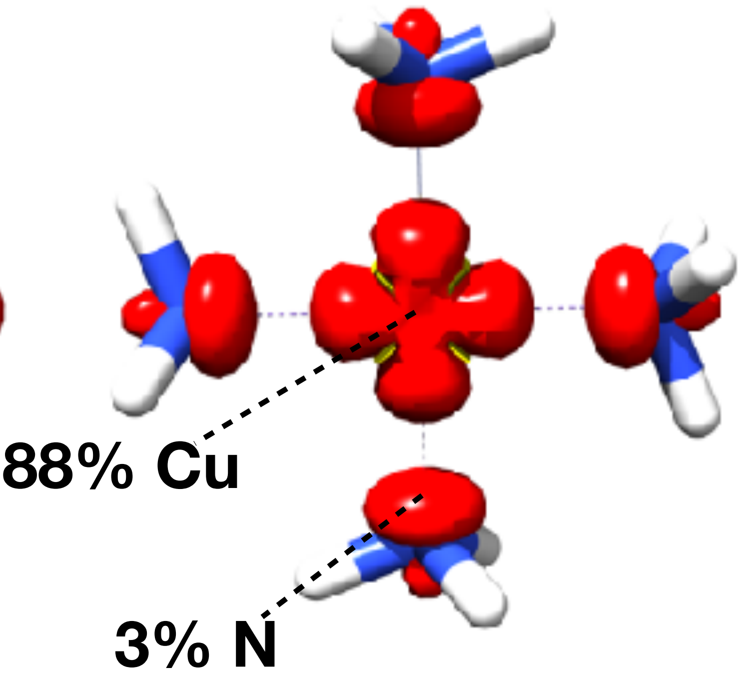
DKH-def2-TZVPP/ DKH2/ Finite Nucleus/ Picture Change

Ligand HFC, Covalency and Spin-Density

DFT *(BP86)*

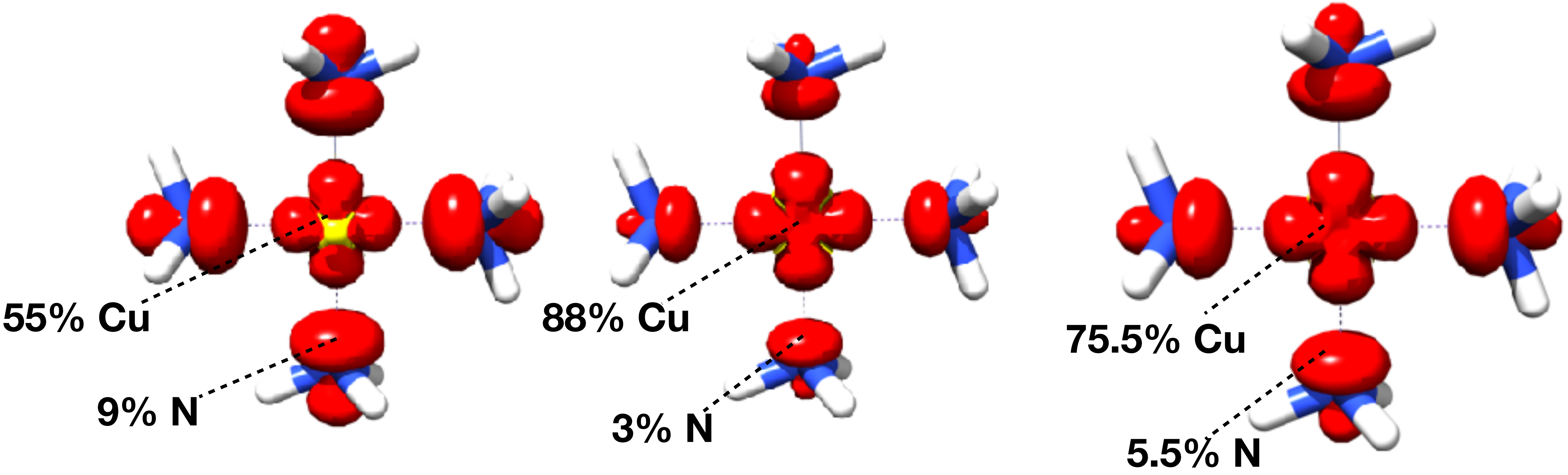


UHF



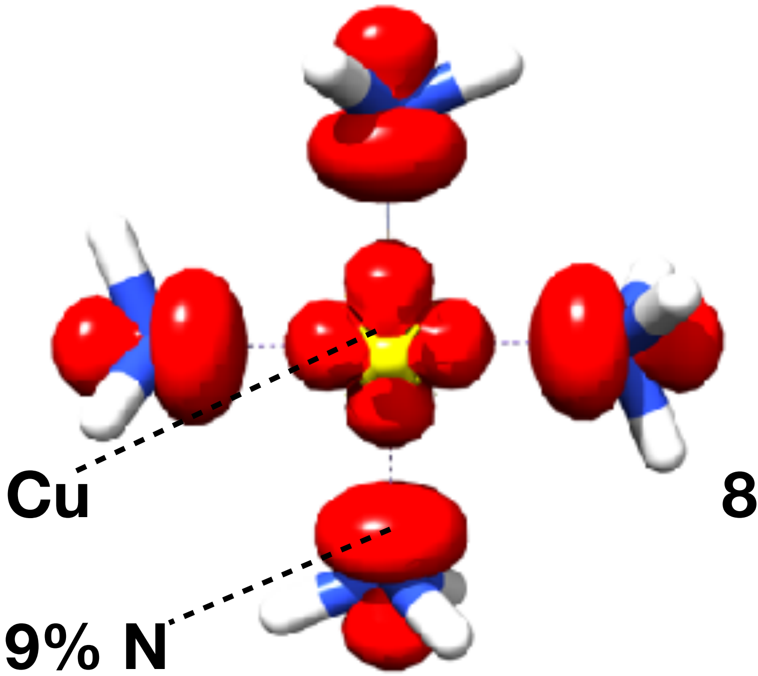
Ligand HFC, Covalency and Spin-Density

DFT *(BP86)* **UHF** **DLPNO-CCSD**



Ligand HFC, Covalency and Spin-Density

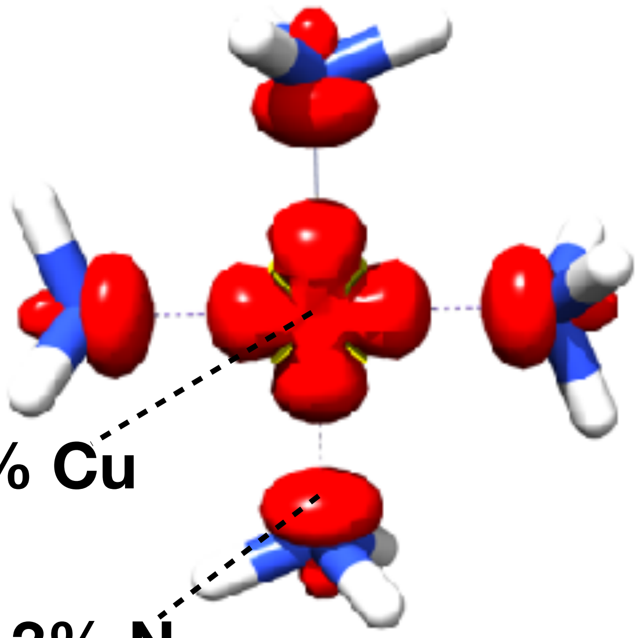
DFT *(BP86)*



much too covalent

$A_{\parallel}$(N)= 50 MHz
A_(N)= 33 MHz

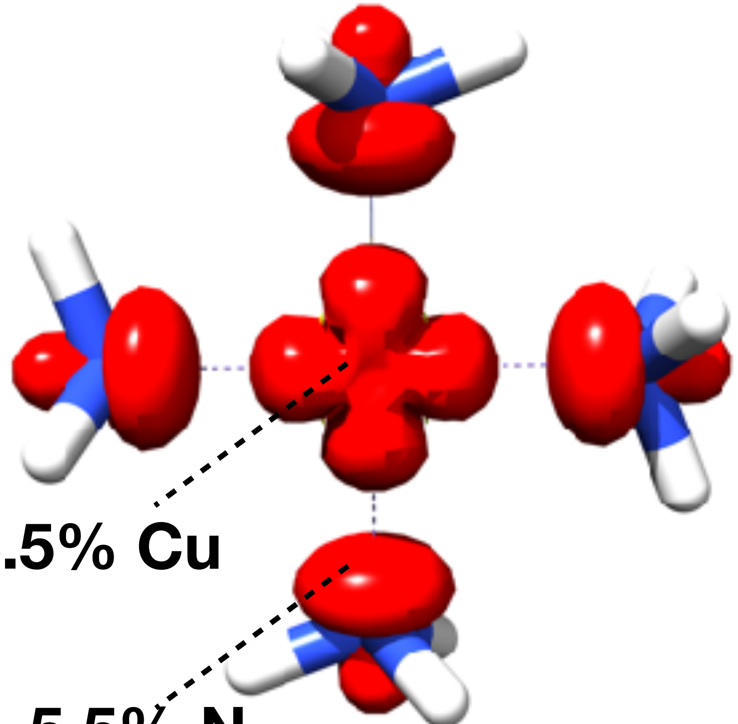
UHF



much too ionic

$A_{\parallel}$(N)= 27 MHz
A_(N)= 20 MHz

DLPNO-CCSD



about right

$A_{\parallel}$(N)= 39 MHz
A_(N)= 28 MHz

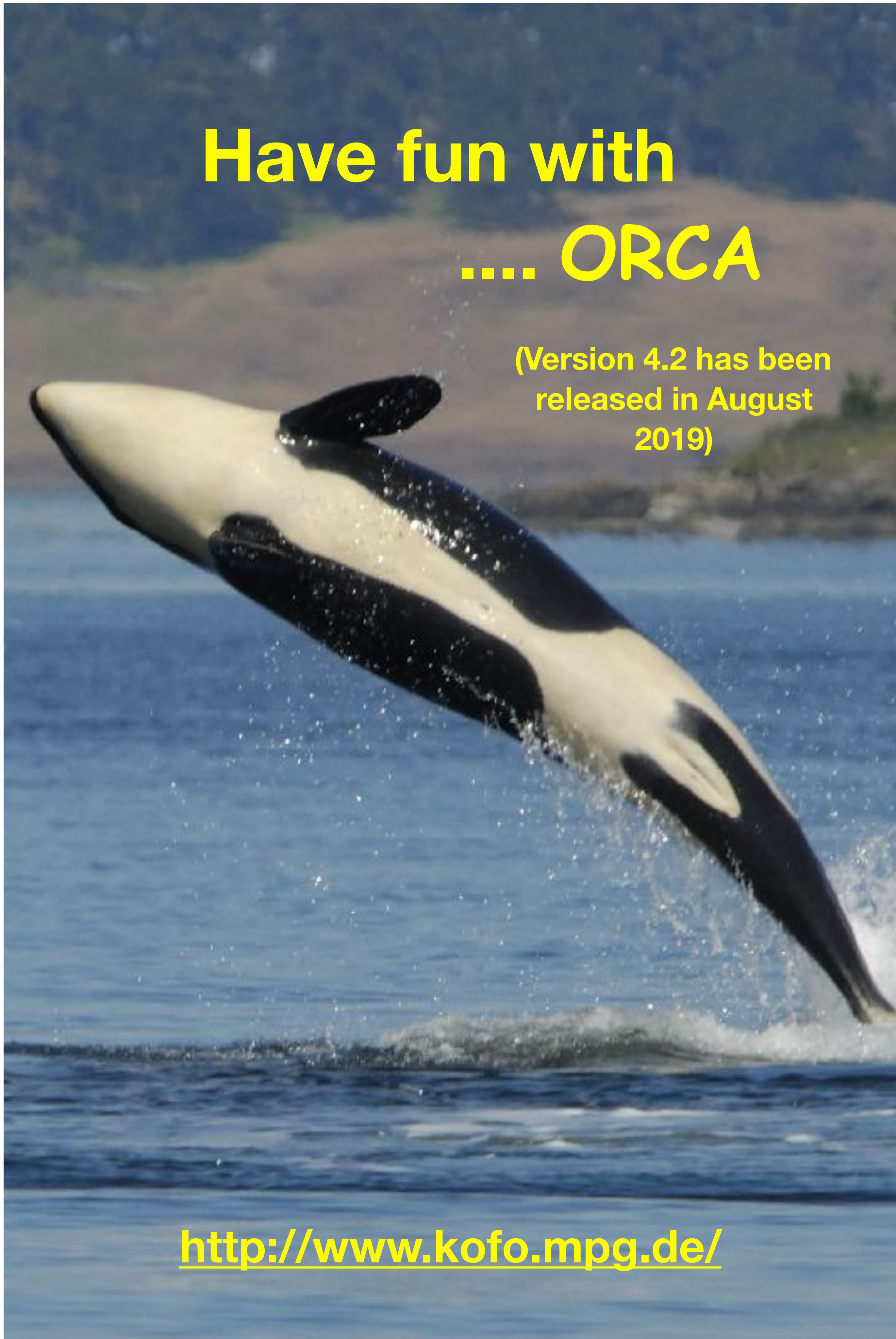
EXP: **$A_{\parallel}$(N)= 39 MHz**
A_(N)= 32 MHz

→

Dynamic correlation effects are HUGE in TM chemistry: CC gets it right!

Summary & Conclusions

- Methods to calculate magnetic resonance parameters are well established
- DFT provides moderate/good accuracy for organic molecules but not for transition metals.
- DLPNO Coupled Cluster methods are the most accurate approaches and can now be applied to large molecules (not yet for NMR or g-tensors).
- Applications to large molecules, enzymes and solids are emerging and provide a powerful partnership with experiment.



Have fun with

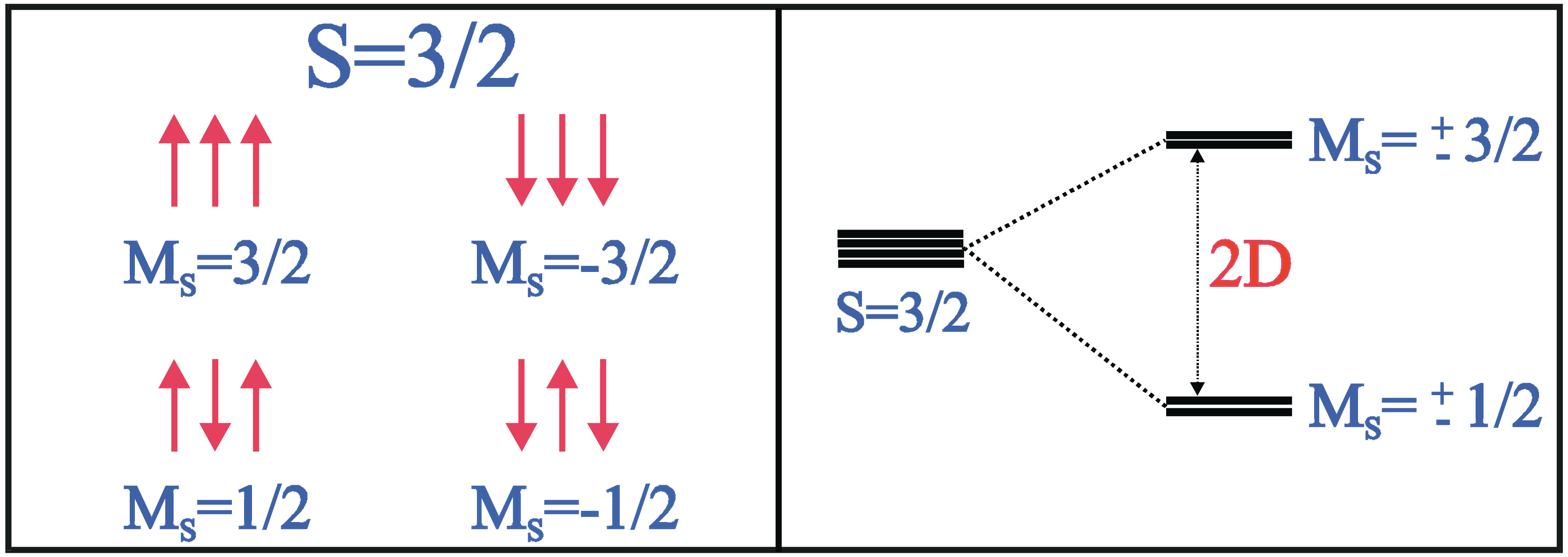
.... ORCA

(Version 4.2 has been released in August 2019)

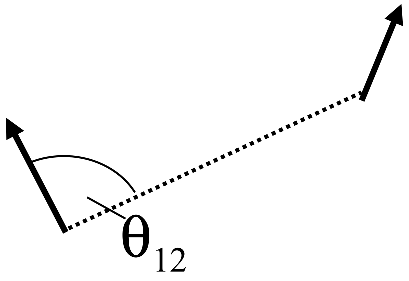
http://www.kofo.mpg.de/

The Quantum Chemistry of Zero-Field Splitting

Physical Origin of the ZFS

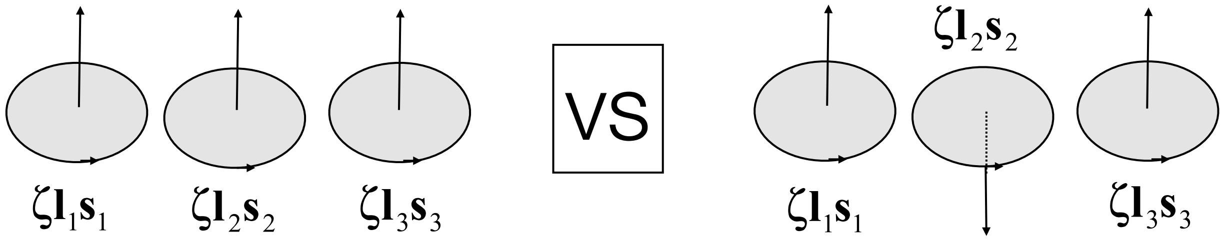


Direct Spin-Spin Coupling



$$\propto 3\cos^2\theta_{12} - 1$$

Spin-Orbit Coupling



FN(**2004**) Zero-Field Splitting. In: Kaupp, M.; Bühl, M.; Malkin, V. (Eds) *Calculation of NMR and EPR Parameters. Theory and Applications*. Wiley-VCH,

Two Common Misconceptions about ZFS

„The Zero-Field Tensor is Traceless“

No: the ZFS tensor may have a trace that is 1-2 orders of magnitude larger than the D-value itself

Only the dipolar spin-spin interaction is traceless and this only because the spin-spin „contact“ term is dropped without warning

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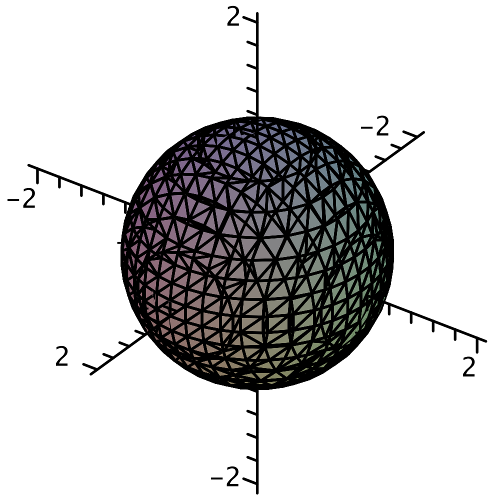
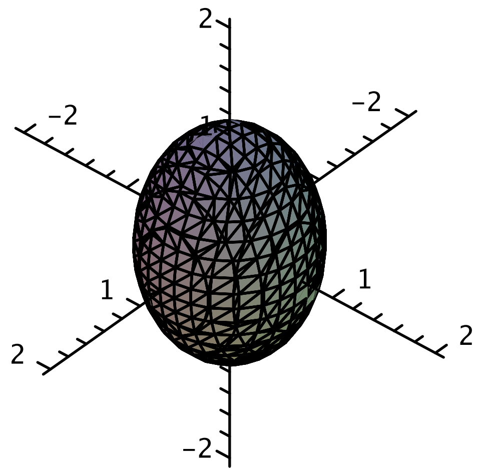
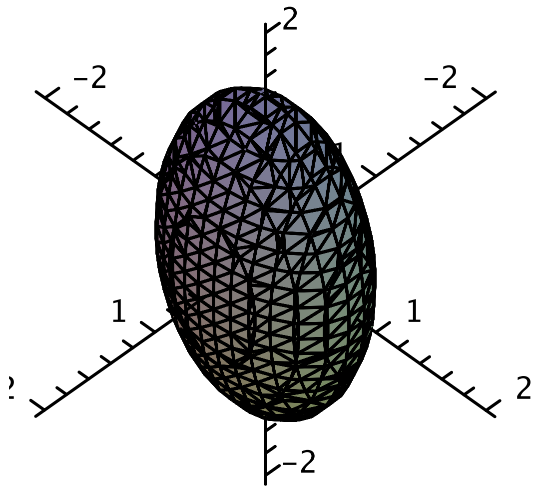


$$D_{xx} = D_{yy} = D_{zz}$$



$$D_{xx} = D_{yy} \neq D_{zz}$$



$$D_{xx} \neq D_{yy} \neq D_{zz}$$

$$\hat{H}_{ZFS} = D\left[S_z^2 - \tfrac{1}{3}S(S+1)\right] + \frac{E}{D}\left[S_x^2 - S_y^2\right]$$

$$D = D_{zz} - \tfrac{1}{2}(D_{xx} + D_{yy})$$

$$E = \tfrac{1}{2}(D_{xx} - D_{yy})$$

$$0 \leq E / D \leq 1/3$$

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„The D-tensor is proportional to the g-tensor“

$$\left.\begin{aligned} D_{kl} &= \lambda^2 \Lambda_{kl} \\ \Delta g &= 2\lambda \Lambda_{kl} \end{aligned}\right\} \Lambda_{kl} = \sum_{n \neq 0} \frac{\left\langle 0 \,|\, L_k \,|\, n \right\rangle \left\langle n \,|\, L_l \,|\, 0 \right\rangle}{E_n - E_0}$$

No: *The g-tensor contains contributions from only the excited states of the same multiplicity while the D tensor may contain up to three different multiplicities*

Counter example: High-spin d^5 (Mn^{2+}, Fe^{3+}) systems have negligible g-shifts but may have large D-values

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Counter example: High-spin d^5 (Mn^{2+}, Fe^{3+}) systems have negligible g-shifts but may have large D-values

The Spin-Orbit Coupling Contribution to the ZFS

The spin-orbit contribution to D is very complicated since it arises from the twice the SOC which mixes states of different multiplicity. The fundamental equations have been derived in 1998:

$$D_{kl}^{SOC-(0)} = -\frac{1}{S^2} \sum_{\substack{b \\ (S'=S)}} \Delta_{bS'}^{-1} \left\langle \Psi_0^{SS} \middle| \sum\nolimits_i h_k^{SOC}(i) s_z(i) \middle| \Psi_b^{SS} \right\rangle \left\langle \Psi_b^{SS} \middle| \sum\nolimits_i h_l^{SOC}(i) s_z(i) \middle| \Psi_0^{SS} \right\rangle$$

$$D_{kl}^{SOC-(-1)} = -\frac{1}{S(2S-1)} \sum_{\substack{b \\ (S'=S-1)}} \Delta_{bS'}^{-1} \left\langle \Psi_0^{SS} \middle| \sum\nolimits_i h_k^{SOC}(i) s_{+1}(i) \middle| \Psi_b^{S-1S-1} \right\rangle \left\langle \Psi_b^{S-1S-1} \middle| \sum\nolimits_i h_l^{SOC}(i) s_{-1}(i) \middle| \Psi_0^{SS} \right\rangle$$

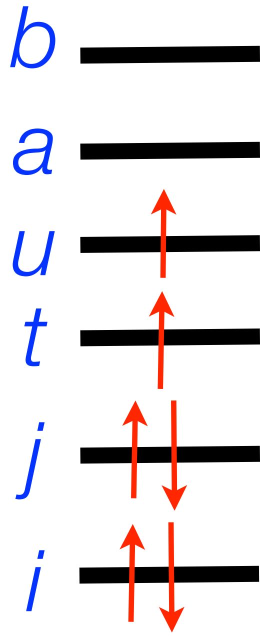
$$D_{kl}^{SOC-(+1)} = -\frac{1}{(S+1)(2S+1)} \sum_{\substack{b \\ (S'=S+1)}} \Delta_{bS'}^{-1} \left\langle \Psi_0^{SS} \middle| \sum\nolimits_i h_k^{SOC}(i) s_{-1}(i) \middle| \Psi_b^{S+1S+1} \right\rangle \left\langle \Psi_b^{S+1S+1} \middle| \sum\nolimits_i h_l^{SOC}(i) s_{+1}(i) \middle| \Psi_0^{SS} \right\rangle$$

- ✓ Formulated as an infinite sum over exact many electron states
- ✓ States with up to three different multiplicities contribute
- ✓ Only the ‚standard components‘ of each multiplet with $M_S = S$ are required

FN; EI Solomon (**1998**) *Inorg. Chem.*, 37, 6568

Spin-Orbit Processes Contributing to the ZFS

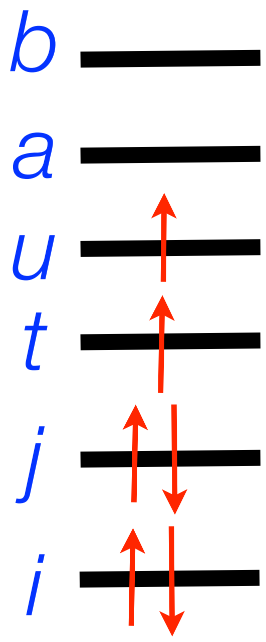
Same Spin Excitations (|0SS>→|aSS>)



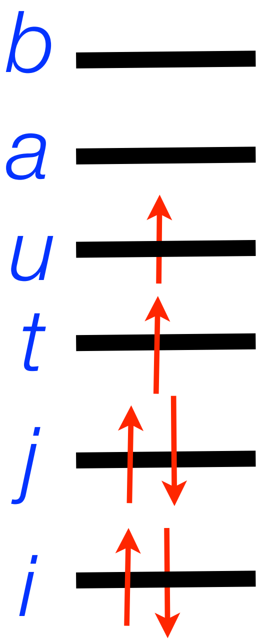
Ground State |0>

Spin-Orbit Processes Contributing to the ZFS

Same Spin Excitations ($|0SS\rangle \rightarrow |aSS\rangle$)



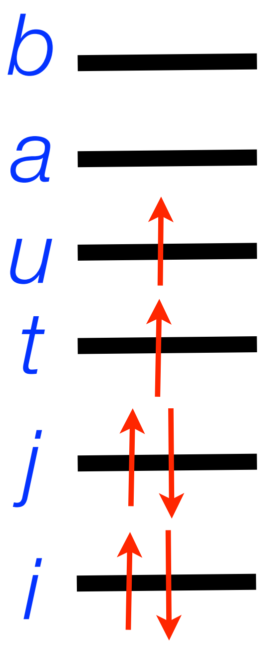
Ground State $|0\rangle$



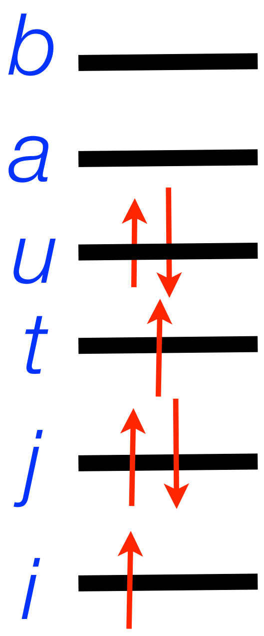
i*→*t

Spin-Orbit Processes Contributing to the ZFS

Same Spin Excitations (|0SS>→|aSS>)



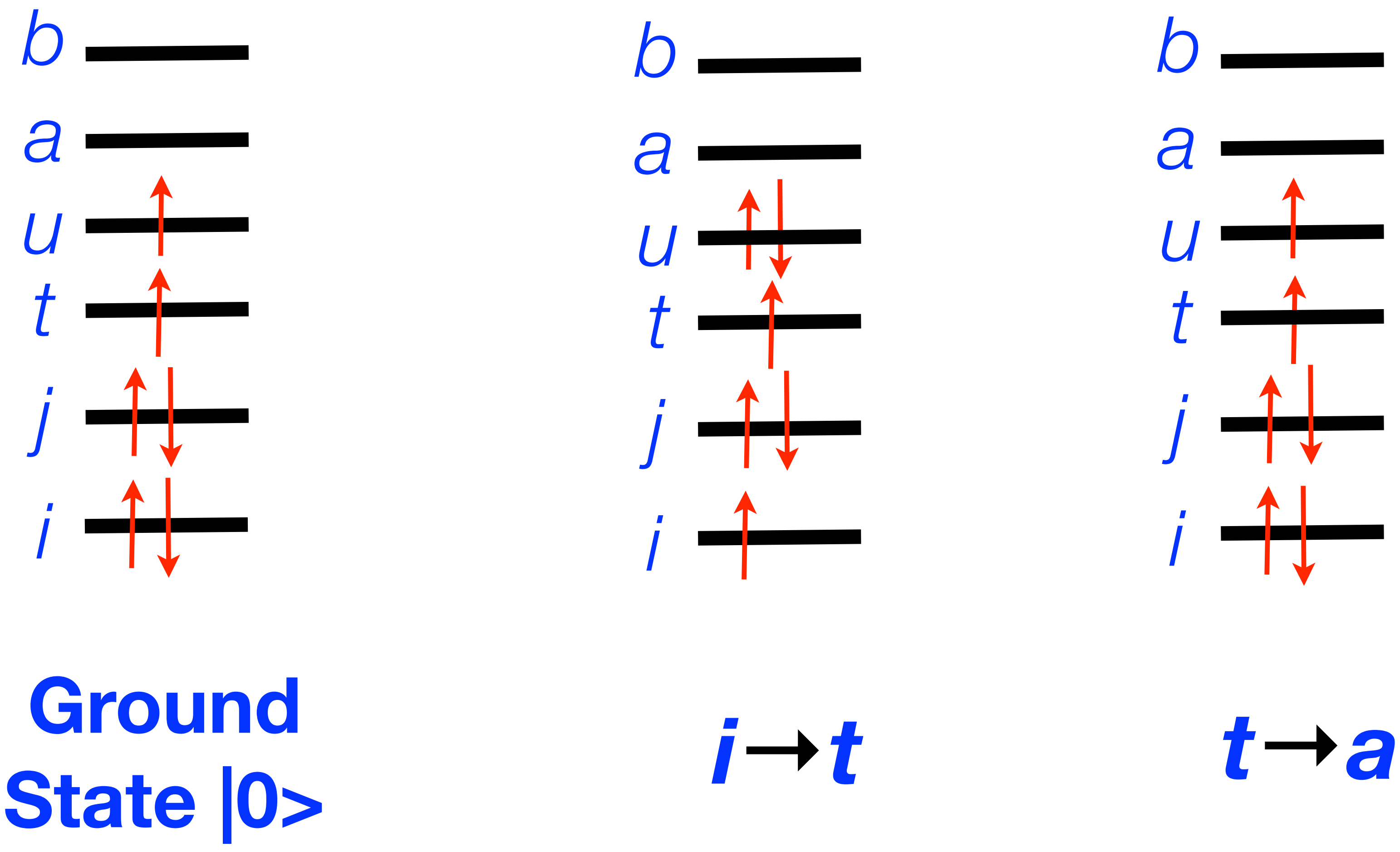
Ground State |0>



i→t

Spin-Orbit Processes Contributing to the ZFS

Same Spin Excitations (|0SS>→|aSS>)



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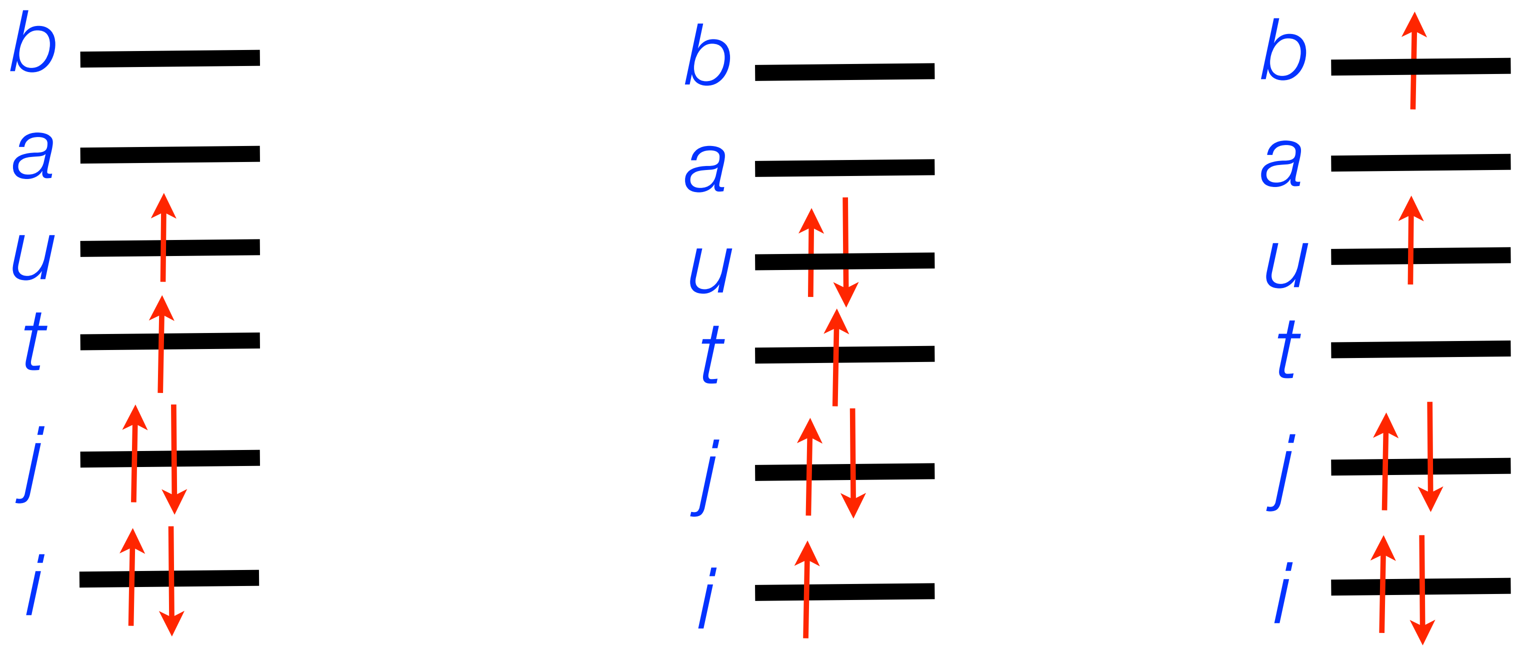


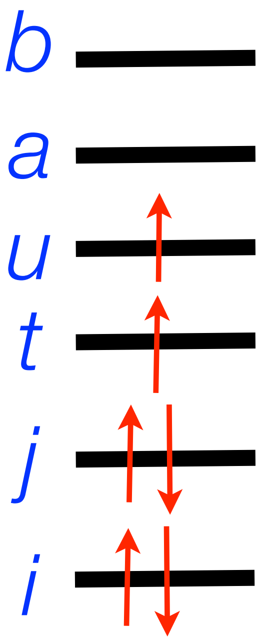
Ground State |0>

$i \rightarrow t$

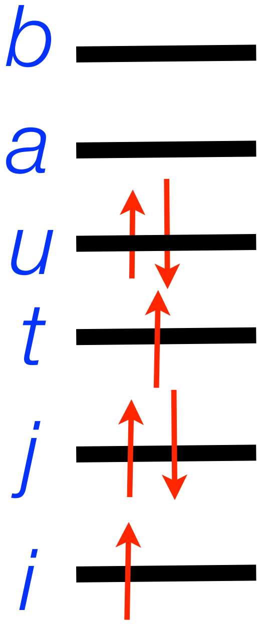
$t \rightarrow a$

Spin-Orbit Processes Contributing to the ZFS

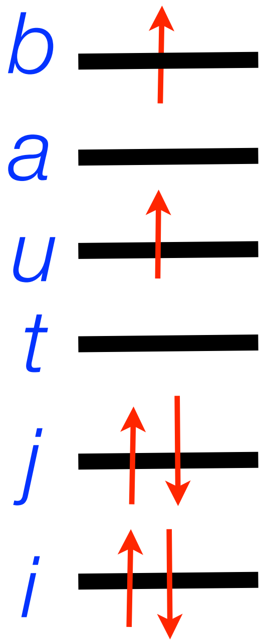
Same Spin Excitations (|0SS>→|aSS>)



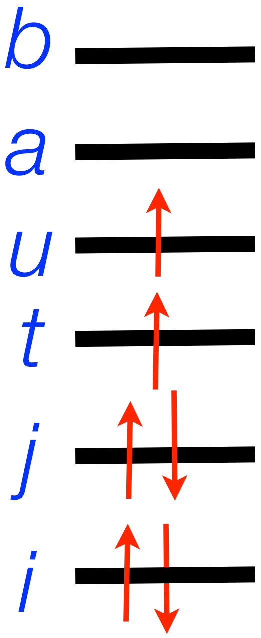
Ground State |0>



i→t



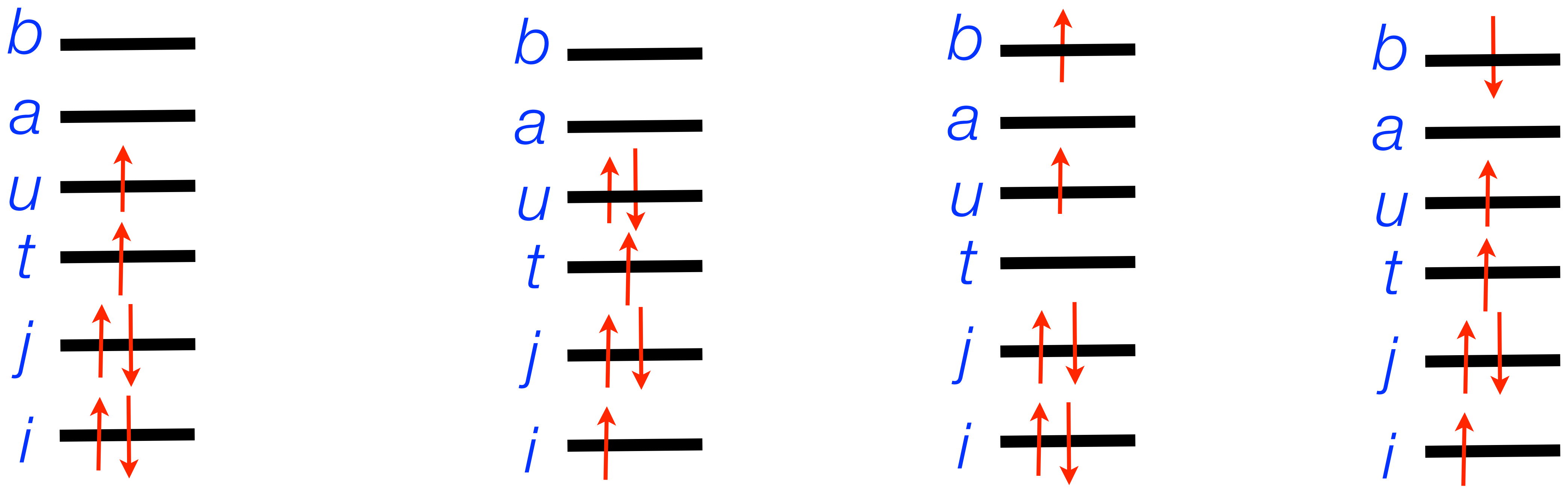
t→a



i→a

Spin-Orbit Processes Contributing to the ZFS

Same Spin Excitations (|0SS>→|aSS>)



Ground State |0>

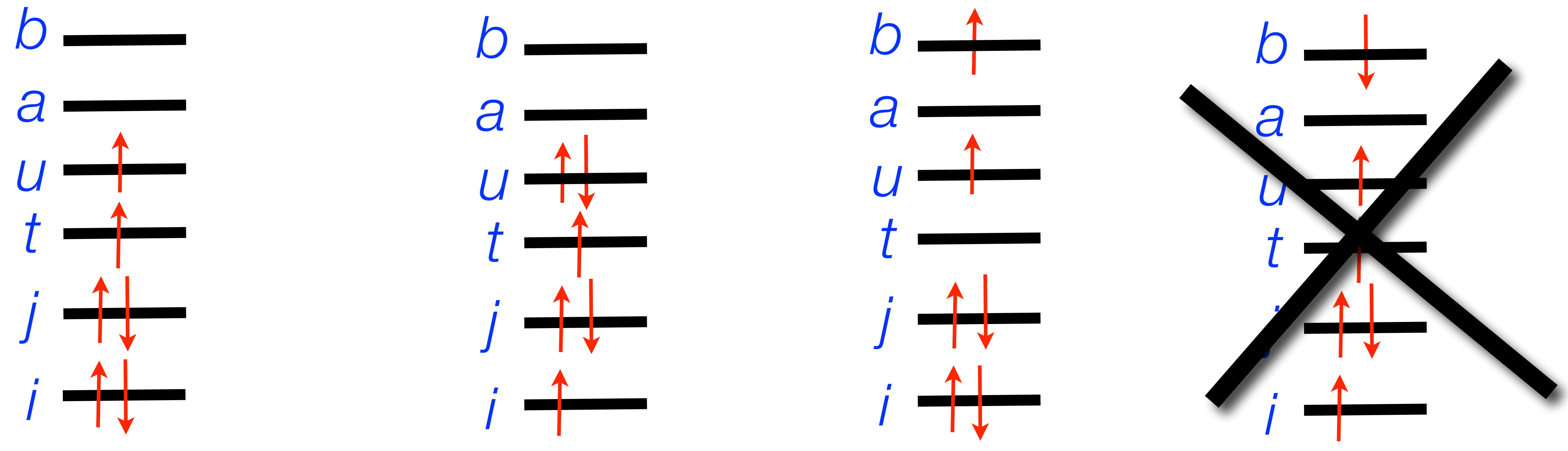
i→t

t→a

i→a

Spin-Orbit Processes Contributing to the ZFS

Same Spin Excitations (|0SS>→|aSS>)



Ground State |0>

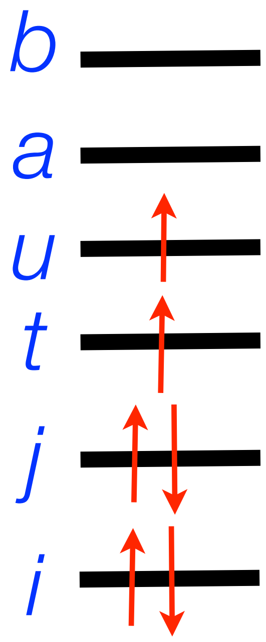
i→t

t→a

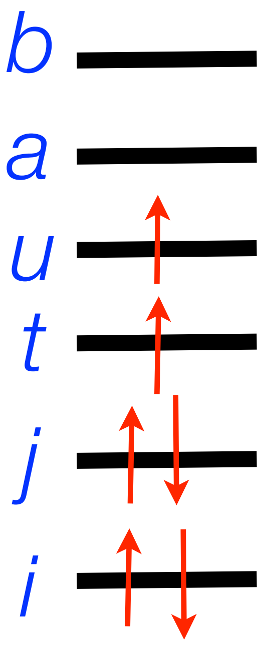
i→a

Spin-Orbit Processes Contributing to the ZFS

Spin Raising Excitations (|0SS>→|aS+1S+1>)



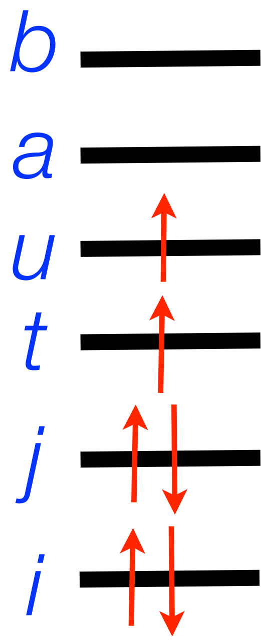
Ground State |0>



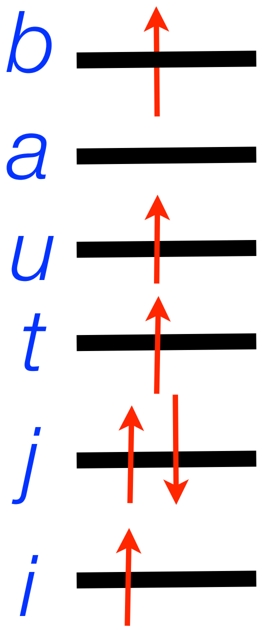
i→a

Spin-Orbit Processes Contributing to the ZFS

Spin Raising Excitations (|0SS>→|aS+1S+1>)



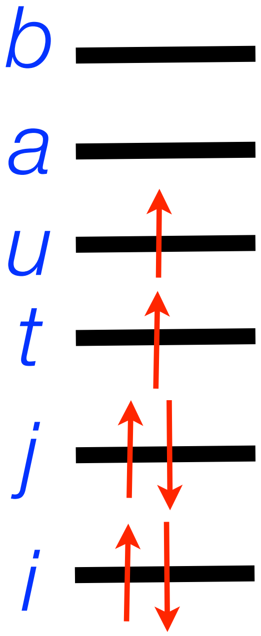
Ground State |0>



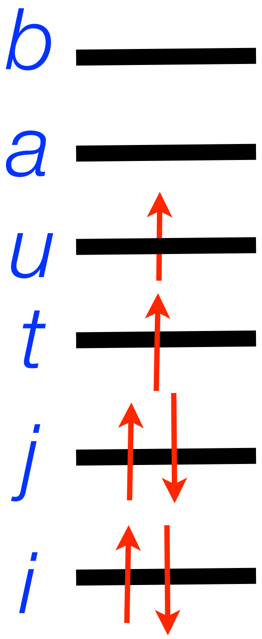
i→a

Spin-Orbit Processes Contributing to the ZFS

Spin Lowering Excitations (|0SS>→|aS-1S-1>)



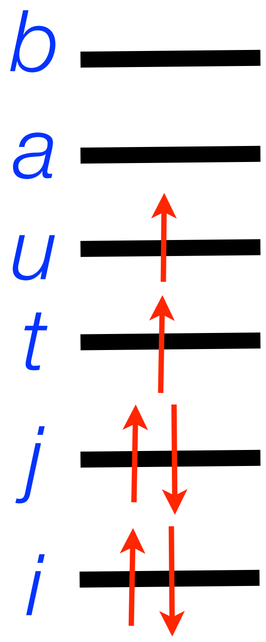
Ground State |0>



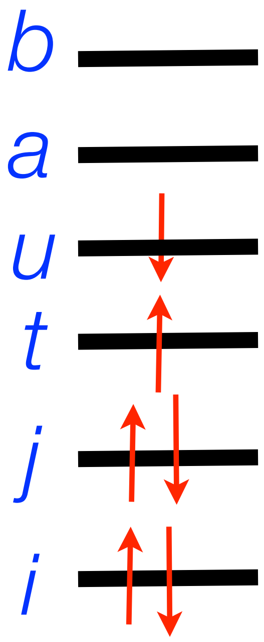
t→t

Spin-Orbit Processes Contributing to the ZFS

Spin Lowering Excitations (|0SS>→|aS-1S-1>)



Ground State |0>



t→t

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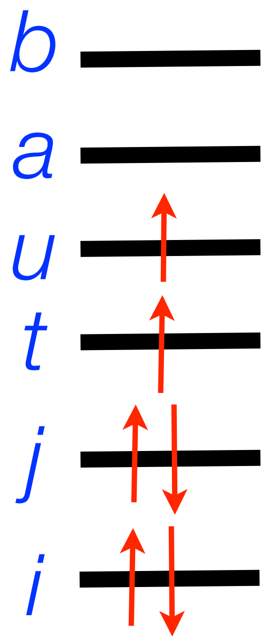

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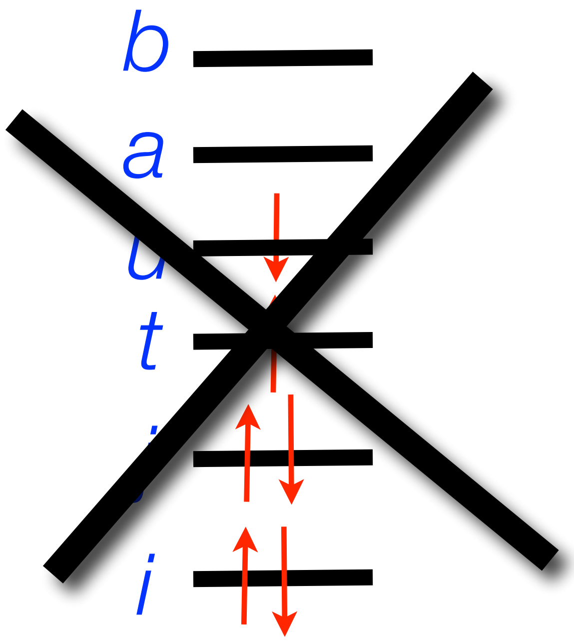

t→t

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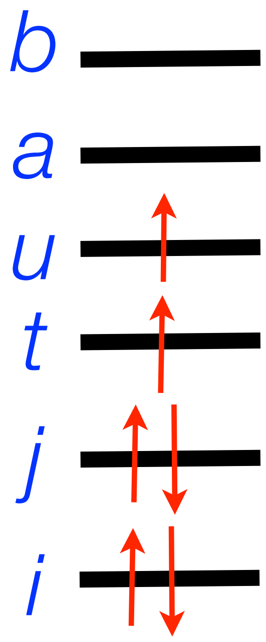
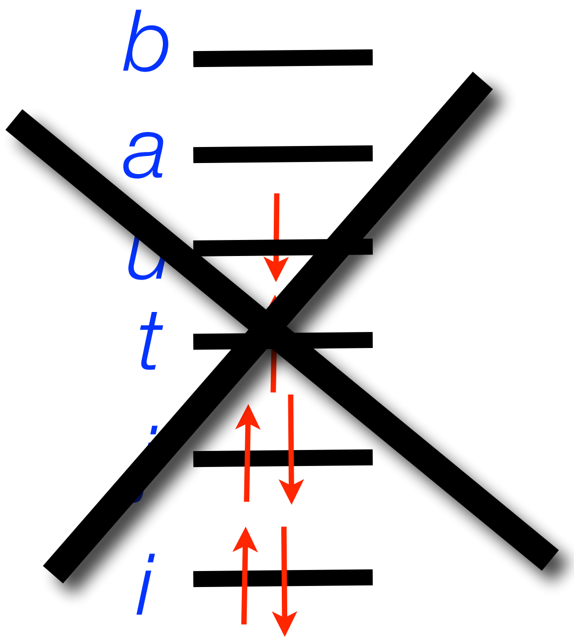
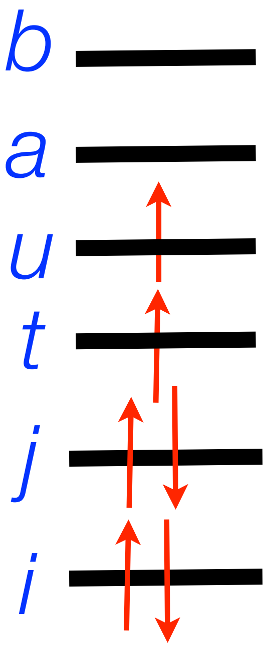
Spin Lowering Excitations (|0SS>→|aS-1S-1>)



Ground State |0>



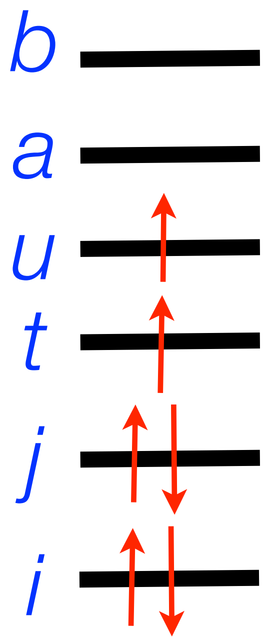
t→t



t→u

Spin-Orbit Processes Contributing to the ZFS

Spin Lowering Excitations (|0SS>→|aS-1S-1>)



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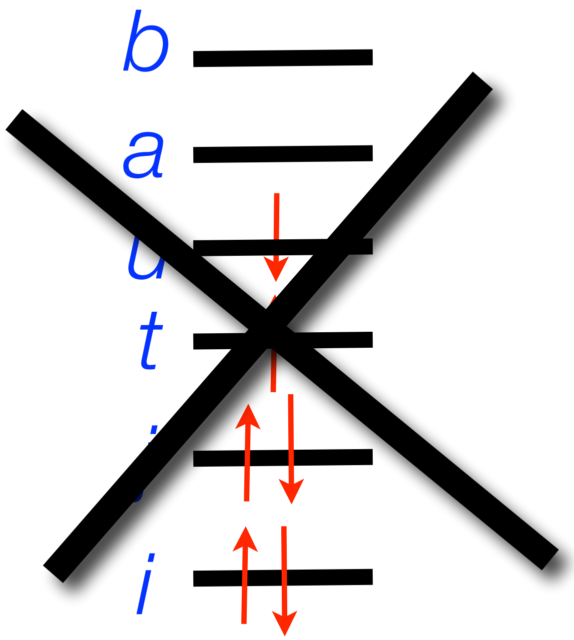
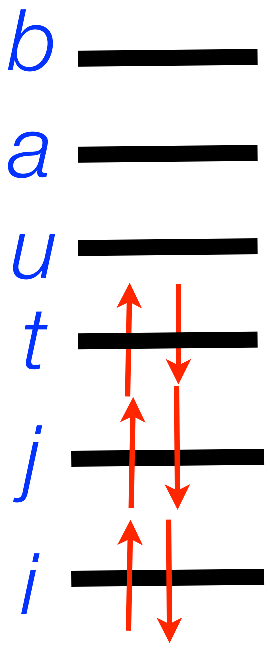


t→t



t→u

Translation to Modern QC: Linear Response

$$D_{kl}^{SOC-(0)} = -\frac{1}{4S^2}\sum_{\mu\nu}\frac{\partial P_{\mu\nu}^{(0)}}{\partial S_l^{(0)}}\left\langle \varphi_\mu \middle| h_k^{SOC} \middle| \varphi_\mu \right\rangle \equiv -\frac{1}{4S^2}\left\langle\left\langle h_k^{SOC}; h_l^{SOC}\right\rangle\right\rangle^{(0)}$$

$$D_{kl}^{SOC-(+1)} = \frac{1}{2(S+1)(2S+1)}\sum_{\mu\nu}\frac{\partial P_{\mu\nu}^{(-1)}}{\partial S_l^{(+1)}}\left\langle \varphi_\mu \middle| h_k^{SOC} \middle| \varphi_\mu \right\rangle \equiv -\frac{1}{2(S+1)(2S+1)}\left\langle\left\langle h_k^{SOC}; h_l^{SOC}\right\rangle\right\rangle^{(+1)}$$

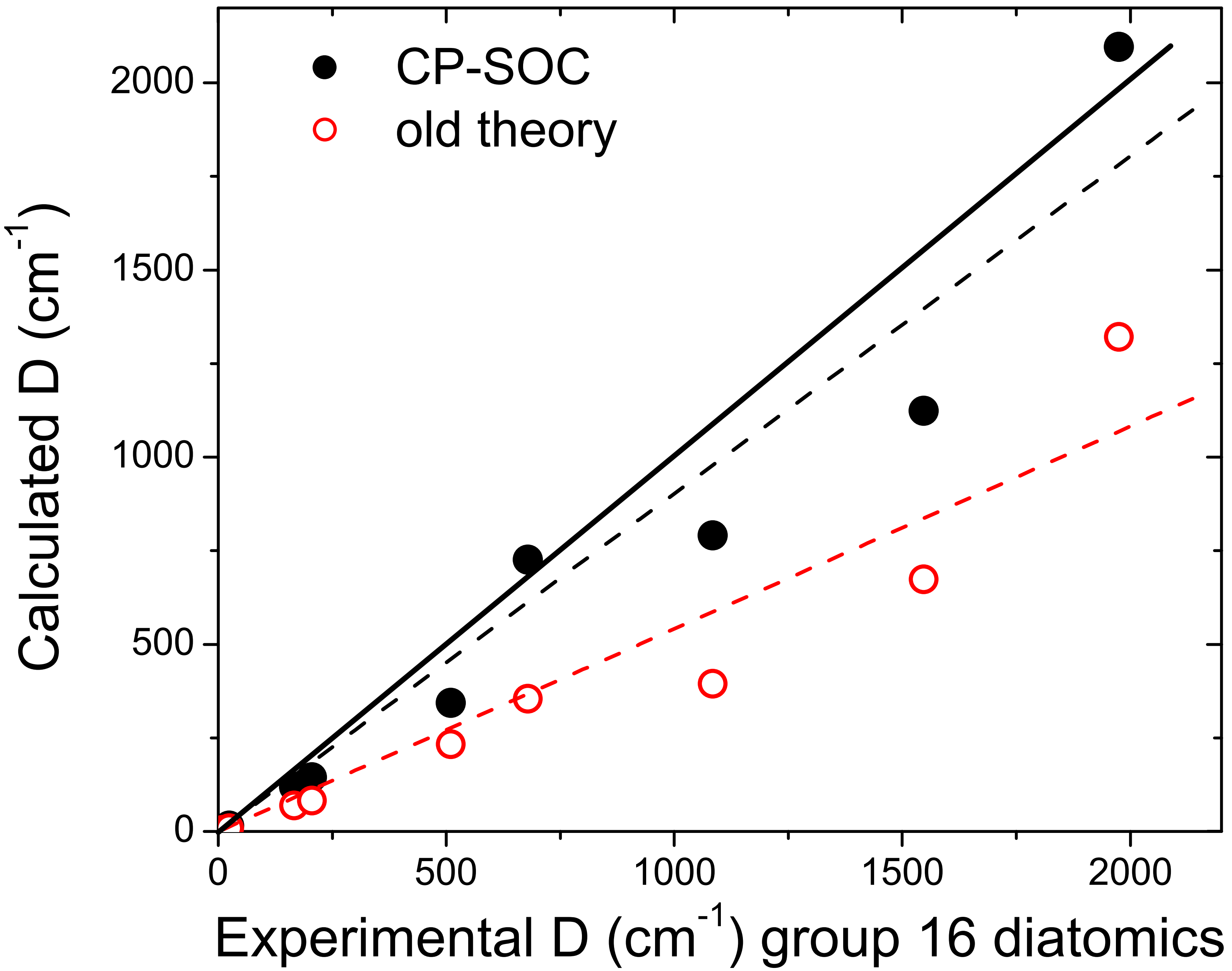
$$D_{kl}^{SOC-(-1)} = \frac{1}{2S(2S-1)}\sum_{\mu\nu}\frac{\partial P_{\mu\nu}^{(+1)}}{\partial S_l^{(-1)}}\left\langle \varphi_\mu \middle| h_k^{SOC} \middle| \varphi_\mu \right\rangle \equiv -\frac{1}{2S(2S-1)}\left\langle\left\langle h_k^{SOC}; h_l^{SOC}\right\rangle\right\rangle^{(-1)}$$

- ✓ General linear response equations valid for any approximate theory
- ✓ Exactly equivalent to the exact sum over states theory

FN *J. Chem. Phys.*, **2007**, 164112

Implementation and Validation

The linear response equations were implemented for HF and DFT theory. Validation study for $^3\Sigma$ molecules.



FN *J. Chem. Phys.*, **2007**, 164112

The Spin-Spin Contribution to the ZFS

Direct magnetic dipole-dipole interaction between unpaired electrons:

(McWeeny 1961,Petrenko 2002)

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Spin-Density

2-Electron Dipole-Dipole integrals

FN (**2009**) *Mag. Res. Biol.,* (Ed. G. Hanson) Vol. 28, p 175-232

S Sinnecker, FN (**2006**) *J. Phys. Chem. A*, 110, 12267-12275

The Spin-Spin Contribution to the ZFS

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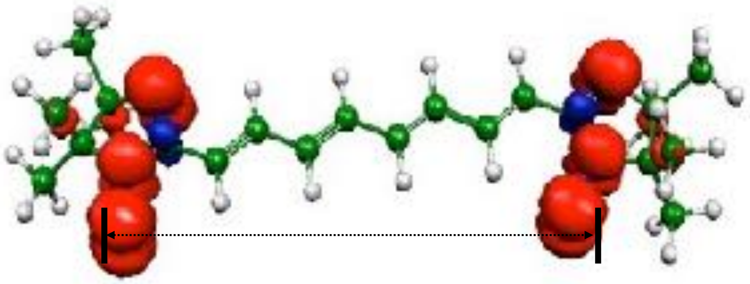
Spin-Density **2-Electron Dipole-Dipole integrals**

Physical interpretation:

(1) Coulomb type Interaction:

Long-Range; For well-separated spin densities goes into „quasi-classical“ point dipole.

$$D_{kl}^{SS} \approx -\frac{g_e^2}{16}\frac{\alpha^2}{S(2S-1)}\sum_{A,B}P_A^{\alpha-\beta}P_B^{\alpha-\beta}R_{AB}^{-5}\left\{3\mathbf{R}_{AB,k}\mathbf{R}_{AB,l} - \delta_{kl}R_{AB}^2\right\}$$



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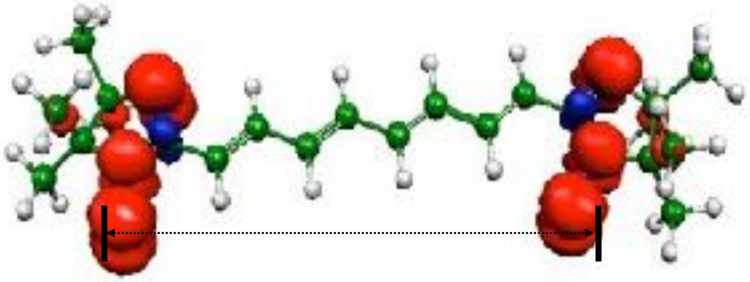

(2) Exchange type Interaction:

Short-Range; QM correction; has nothing to do with „*genuine exchange*“!

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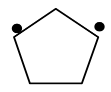
S Sinnecker, FN (**2006**) *J. Phys. Chem. A*, 110, 12267-12275

Benchmarks for Spin-Spin



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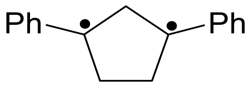

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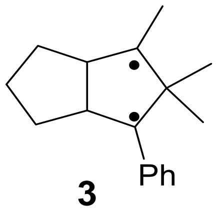

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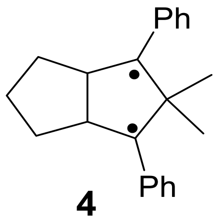

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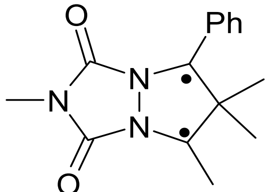

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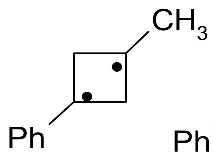

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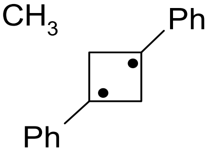

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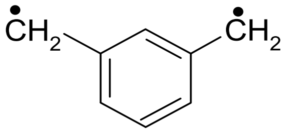

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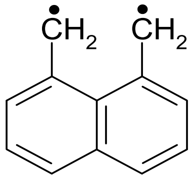

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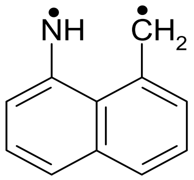

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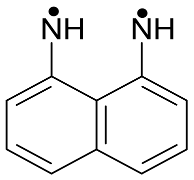

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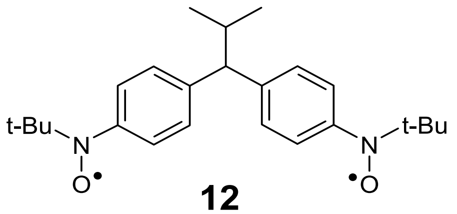

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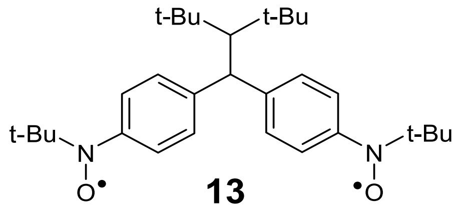

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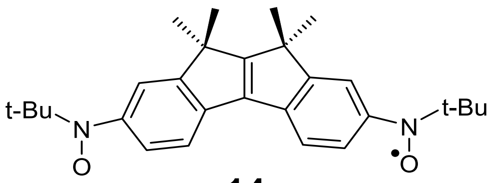

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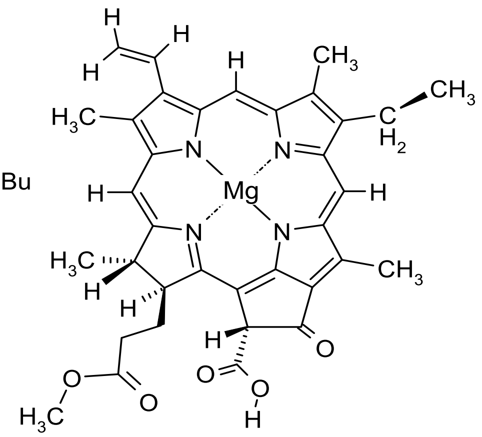
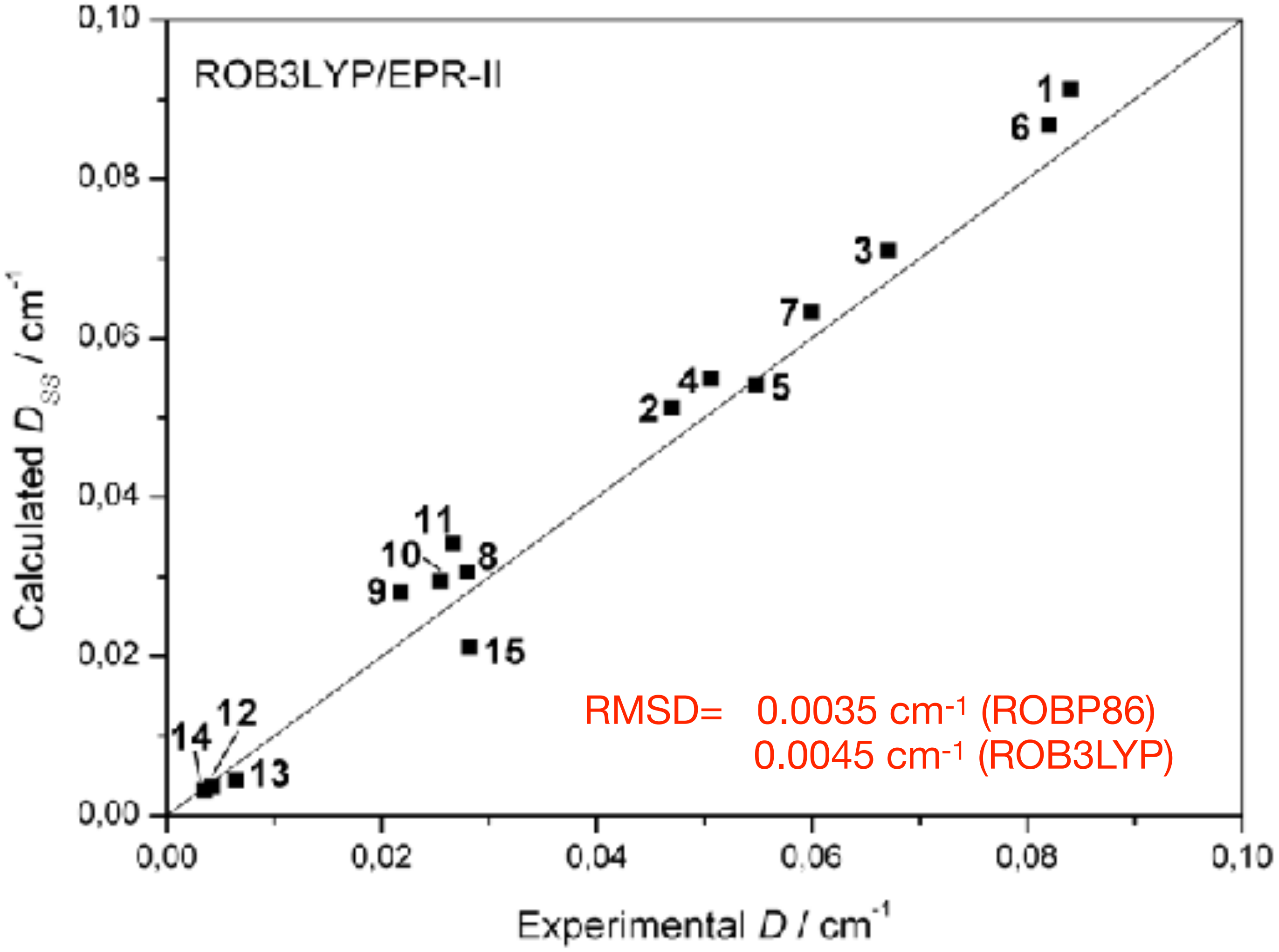


15

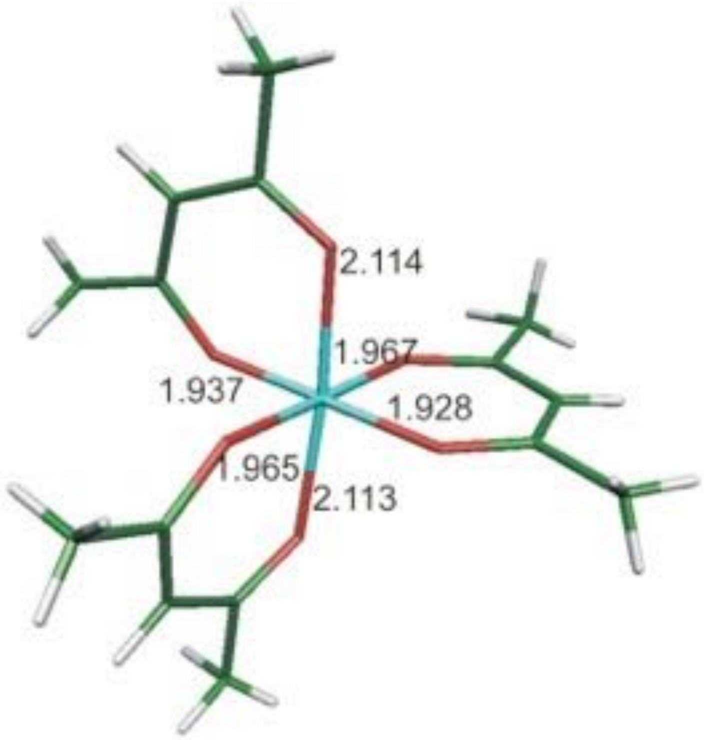
→ *D* is Dominated by Spin-Spin Part



RMSD= 0.0035 cm^{-1} (ROBP86)
0.0045 cm^{-1} (ROB3LYP)

S Sinnecker, FN (**2006**) *J. Phys. Chem. A*, 110, 12267-12275

A Case Study: Mn(acac)$_3$



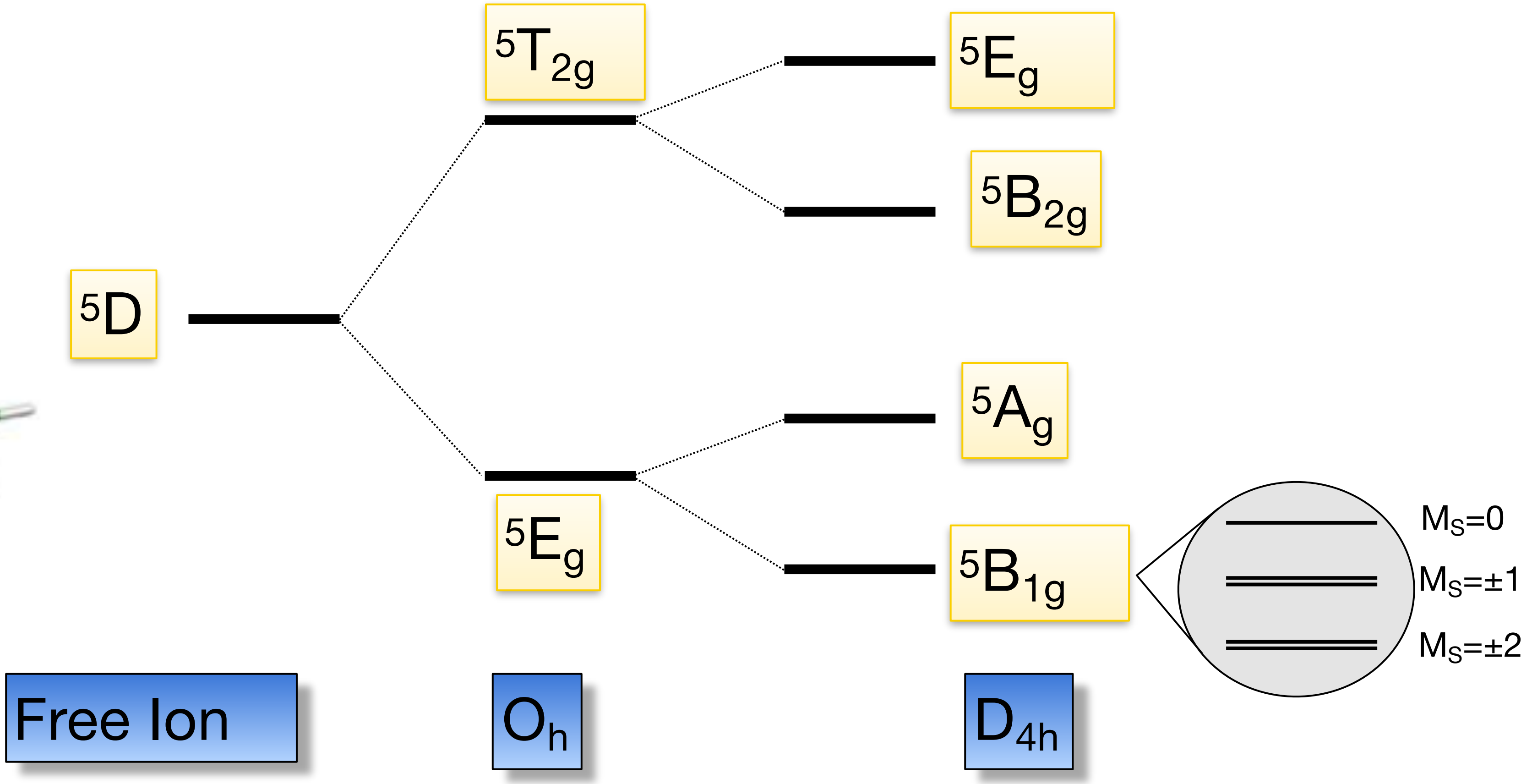
[Mn(acac)$_3$]

(elongated octahedron)

D_{exp}=-4.52 cm^{-1}

Krzystek, J.; Yeagle, G. J.; Park, J.-H.; Britt, R. D.; Meisel, M. W.; Brunel, L.-C.; Telser, J. *Inorg. Chem.* 2003, *42*, 4610

Conventional Ligand Field Arguments



^5D

$^5T_{2g}$

^5E_g

^5E_g

$^5B_{2g}$

^5A_g

$^5B_{1g}$

M_S=0

M_S=±1

M_S=±2

Free Ion

O_h

D_{4h}

Ground State Zero-Field Splitting

$$D = -\frac{\zeta^2}{16}\left[\frac{4}{E(^5B_{2g})} - \frac{4}{E(^5E_g)}\right] < 0$$

(Frequently used in analysis and fitting LF parameters)

FN (**2006**) *J. Am. Chem. Soc.*, 128, 10213-10222

Importance of Spin-Flip and Spin-Spin Terms ?

BUT: In order to calculate *D* from first principles we have to take into account:

a) Excited states of triplet spin-multiplicity
b) The direct spin-spin contribution

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SPIN-FLIP CONTRIBUTIONS (cm^{-1}):

	DFT	**CASSCF**	**SORCI**
ΔS=0	-0.42	-1.38	-1.57
ΔS=-1	-1.07	-2.28	-2.56

a) Spin-Flips Dominate
b) DFT underestimates *D*

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”The value of ρ in transition metal ions is uncertain, but at least it is probably not greater than 0.1 cm^{-1} in the ground terms of divalent or trivalent ions of the first transition series„

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”The value of ρ in transition metal ions is uncertain, but at least it is probably not greater than 0.1 cm⁻¹ in the ground terms of divalent or trivalent ions of the first transition series„

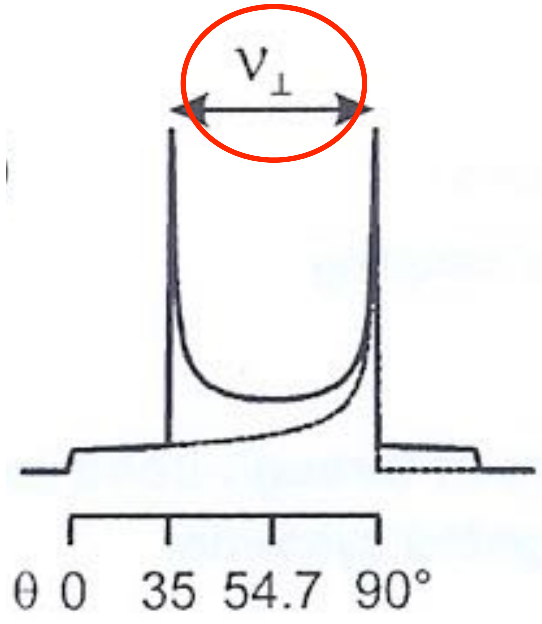
DFT : ***D*(SS)= -1.0 cm^{-1}**

CASSCF : ***D*(SS)= -1.6 cm^{-1}**

FN (**2006**) *J. Am. Chem. Soc.*, 128, 10213-10222

Measuring Distances with EPR

Sandra and Gareth Eaton
(Denver)

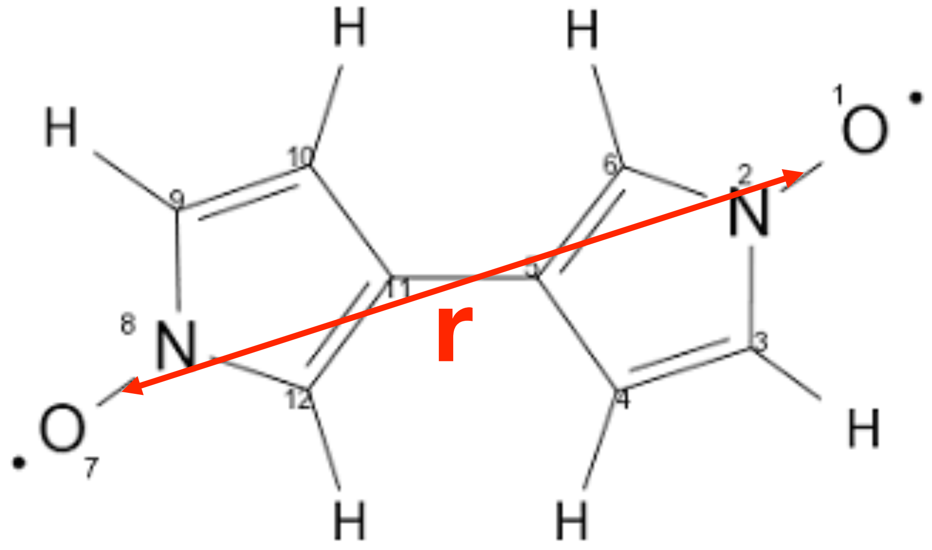


$$\nu_\perp \propto |D| \propto r^{-3}$$

$$\boxed{r = \sqrt[3]{\frac{52.16\ \text{MHz}}{\nu_\perp}}}$$

at *g*=2.0069
(nitroxide)

But sometimes it doesn‘t work?!



Dinitroxide System:

- r-measured = **7.0 Å**
- r-predicted = **5.1 Å**

- D-measured = **0.02** cm^{-1}
- D-(point dipole) = **0.008** cm^{-1}
- D^{SS}(DFT) = **0.02** cm^{-1}

➡ Huge error of the point dipole approximation but quantum chemistry gets it right

➡ Analyze the origin of the discrepancy in detail!

➡ Which conclusions should we draw for distance measurements by EPR?

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, ASAP

But sometimes it doesn‘t work?!

Dinitroxide System:

J|A|C|S
ARTICLES

Interaction of Radical Pairs Through-Bond and Through-Space: Scope and Limitations of the Point−Dipole Approximation in Electron Paramagnetic Resonance Spectroscopy

Christoph Riplinger,[†] Joseph P. Y. Kao,[‡] Gerald M. Rosen,[‡,§] Velavan Kathirvelu,[||]
Gareth R. Eaton,*[,||] Sandra S. Eaton,[||] Andrei Kutateladze,[||] and Frank Neese*[,†]

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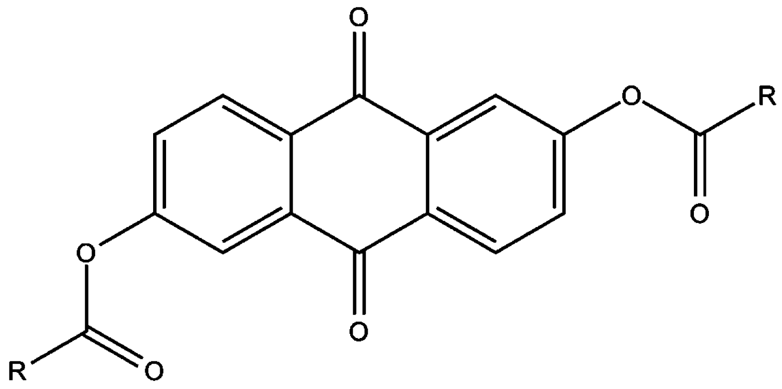
Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, ASAP

Is the Good Agreement with Experiment just Luck?

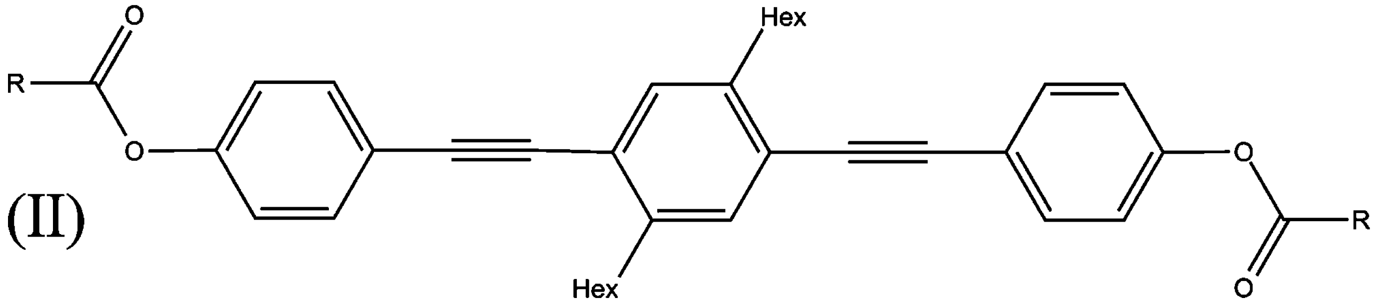
(I)



D^{exp}=-0.000341 cm^{-1}

D^{calc}=-0.000335 cm^{-1}

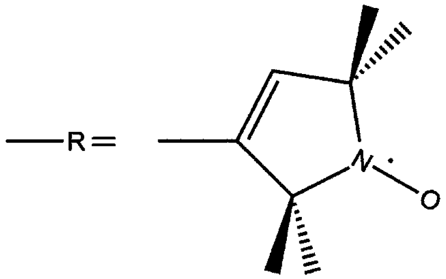
(II)



D^{exp}=-0.000115 cm^{-1}

D^{calc}=-0.000109 cm^{-1}

a)



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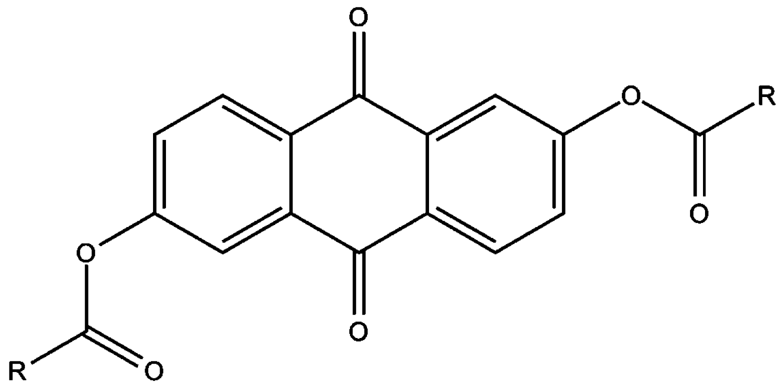

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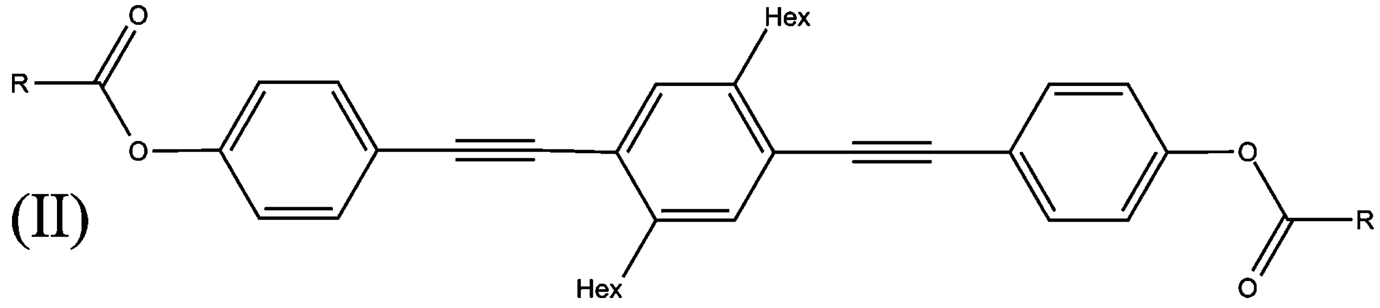

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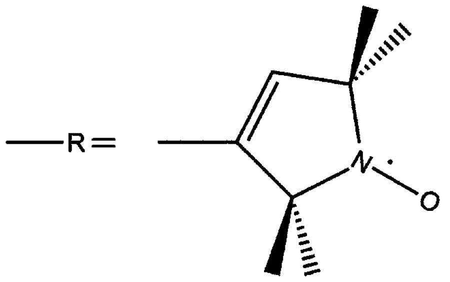
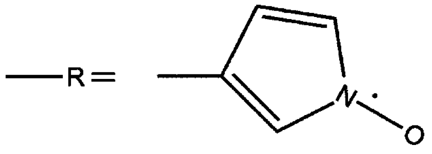


b)

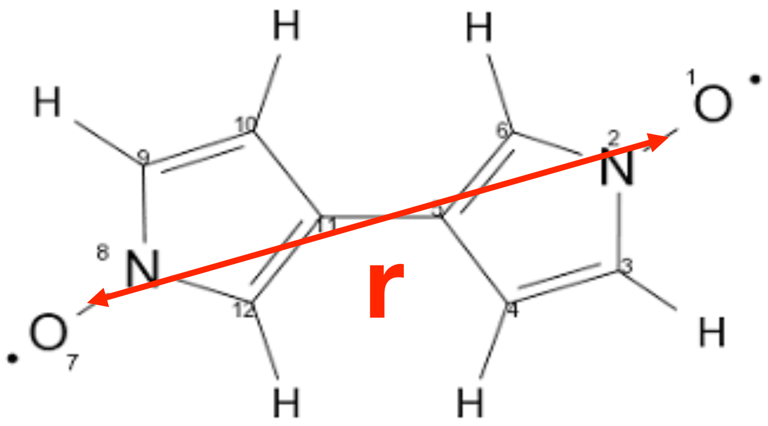


	biradical **7**			biradical **8**		
system	*D* [cm^{-1}]	interspin distance [Å]	N—N distance [Å]	*D* [cm^{-1}]	interspin distance [Å]	N—N distance [Å]
experimental results[a]	−0.000341 ± 0.000005	19.73 ± 0.14	–	−0.000115 ± 0.000006	28.3 ± 0.5	27.84 ± 0.01[b]
DFT model (a)	−0.000335	19.8	19.11[b]	−0.000109	28.8	28.46[c]
DFT model (b)	−0.000455	17.9	18.93[b]	−0.000357	19.4	28.29[c]

... so why did the point dipole „measurement“ not work? ...

Variants of Point Dipole Approximations

1. „Generic" Point Dipole



Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

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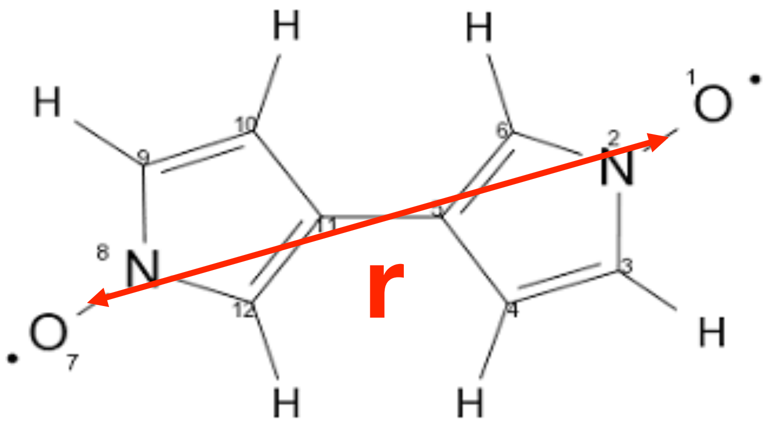
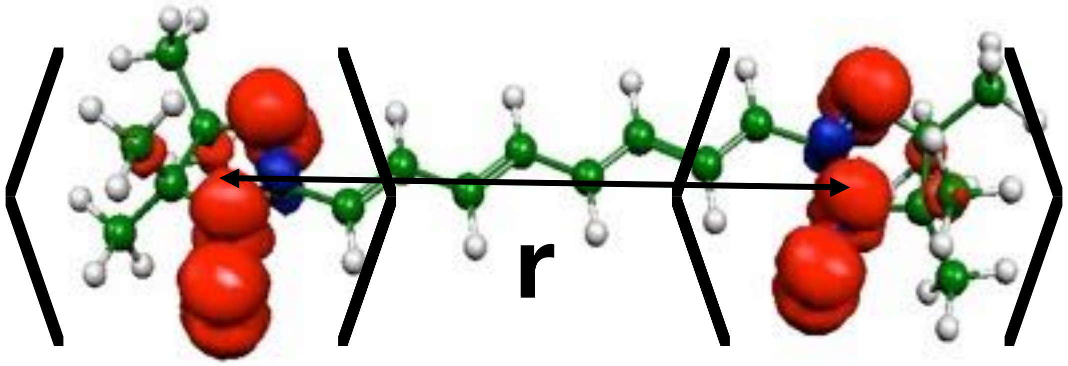


2. „Center of Gravity“ Point Dipole

Take the first moment of the spin distribution in each fragment (in real space)



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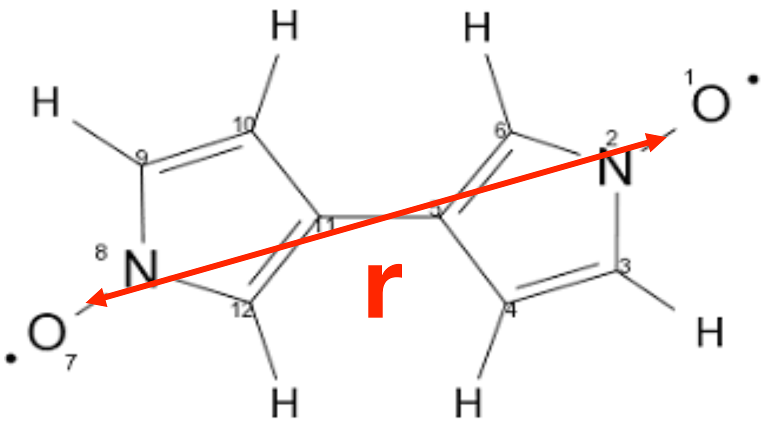

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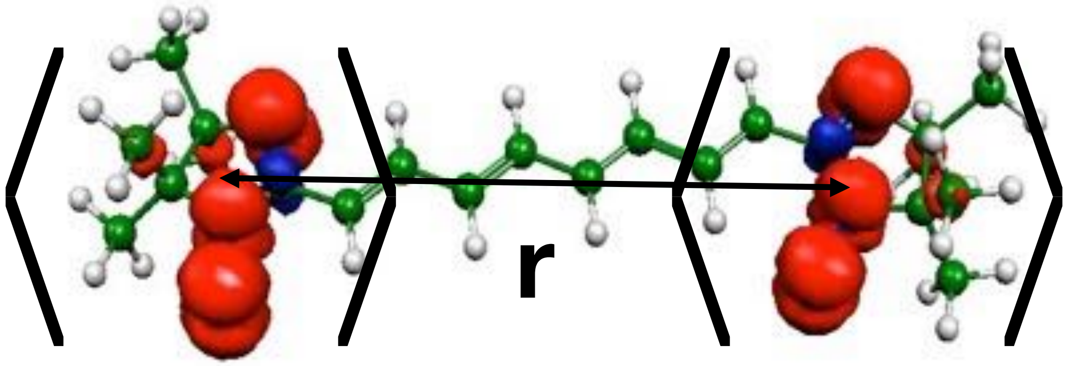
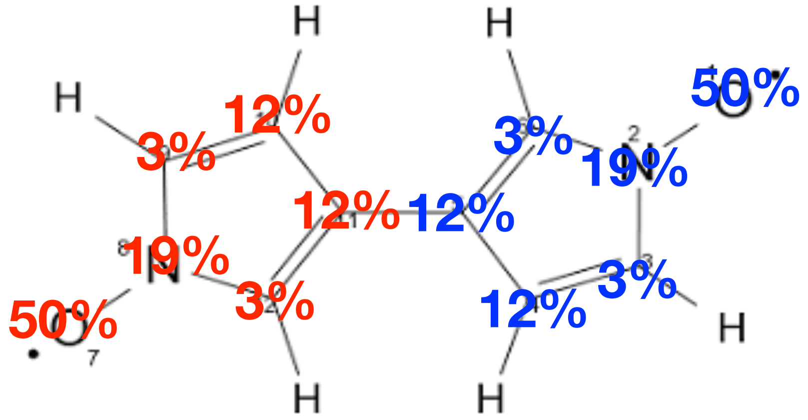


3. „Distributed“ Point Dipole

„Contract“ all the basis functions to δ-functions:

$$D_{kl}^{(2-center)} = -\frac{g_e^2}{8}\frac{\alpha^2}{S(2S-1)}\sum_{AB} P_A^{\alpha-\beta} P_B^{\alpha-\beta} R_{AB}^{-5}\left[3\mathbf{R}_{AB,k}\mathbf{R}_{AB,l} - \delta_{kl}R_{AB}^2\right]$$



R^A = Position of nucleus A

P^A = (Gross) Spin-population at atom A (NOT Mulliken)

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

Partitioning of Quantum Chemical Calculations

1. Coulomb versus Exchange (SOMO‘s *i*,*j*)

$$D_{kl}^{SS} = -\frac{g_e^2}{8}\frac{\alpha^2}{S(2S-1)}\left\{\left\langle ii\middle|g_{kl}\middle|jj\right\rangle - \left\langle ij\middle|g_{kl}\middle|ij\right\rangle\right\} \qquad g_{kl} = 3r_{12,k}r_{12,l} - \delta_{kl}r_{12}^2$$

Coulomb

Exchange
(not present in the point dipole model)

2. Multicenter contributions

$$D_{kl}^{SS} = -\frac{g_e^2}{16}\frac{\alpha^2}{S(2S-1)}\sum_{\mu_A\nu_B}\sum_{\kappa_C\tau_D}\left\{P_{\mu\nu}^{\alpha-\beta}P_{\kappa\tau}^{\alpha-\beta} - P_{\mu\kappa}^{\alpha-\beta}P_{\nu\tau}^{\alpha-\beta}\right\}\left\langle \varphi_\mu^A\varphi_\nu^B\middle|g_{kl}\middle|\varphi_\kappa^C\varphi_\tau^D\right\rangle$$

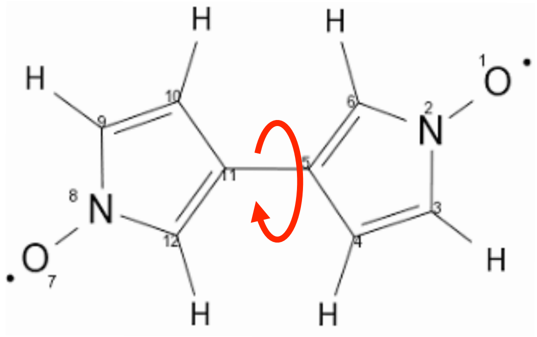
Up to 4-center contributions

Any point dipole model only treats the two-center Coulomb part approximately:

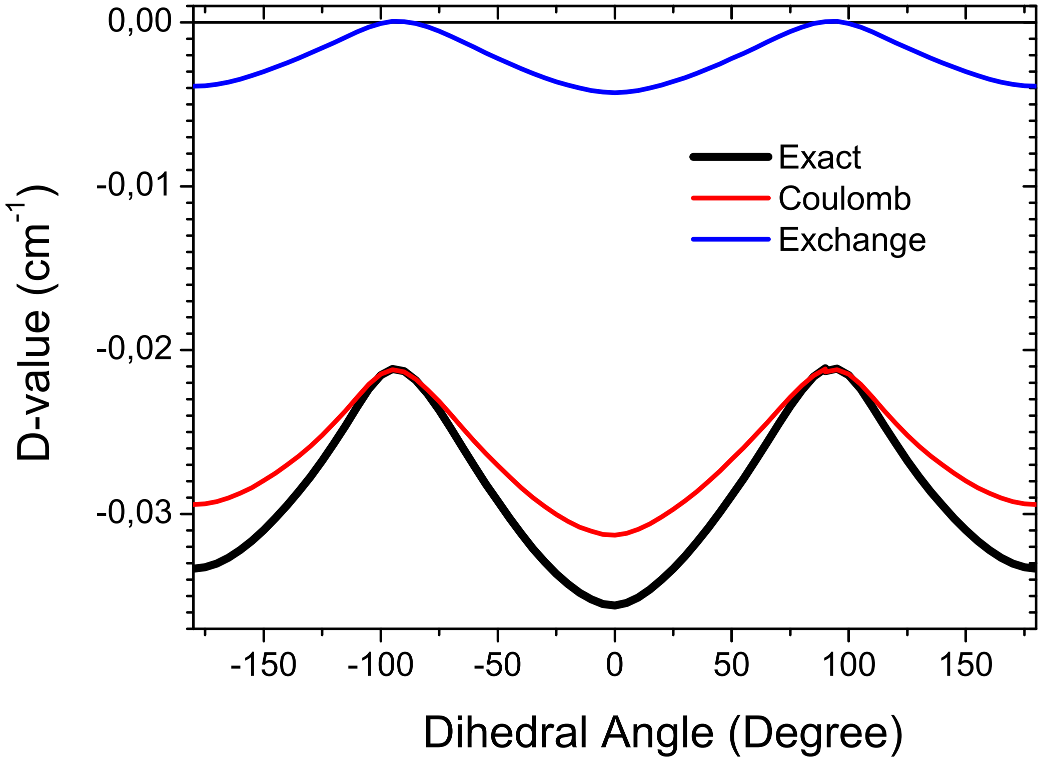
$$D_{kl}^{(2-center)} = -\frac{g_e^2}{16}\frac{\alpha^2}{S(2S-1)}\sum_{\mu_A\nu_A}\sum_{\kappa_B\tau_B}P_{\mu\nu}^{\alpha-\beta}P_{\kappa\tau}^{\alpha-\beta}\left\langle \varphi_\mu^A\varphi_\nu^A\middle|g_{kl}\middle|\varphi_\kappa^B\varphi_\tau^B\right\rangle$$

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

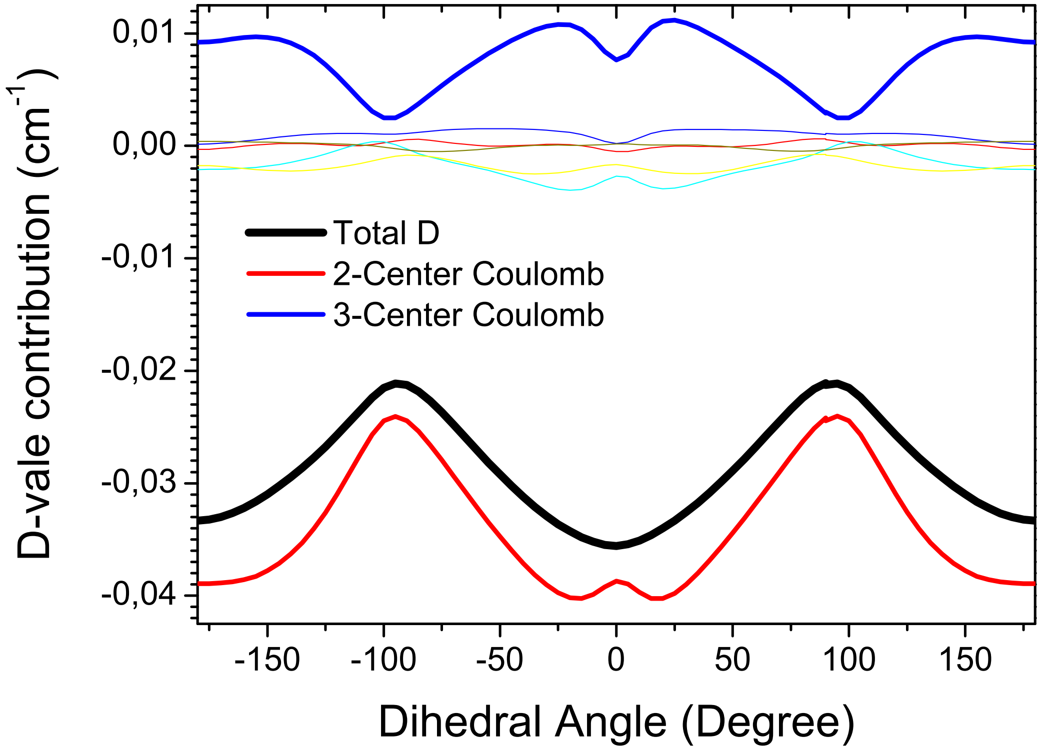
Rotation Curve



Coulomb vs Exchange



Multicenter

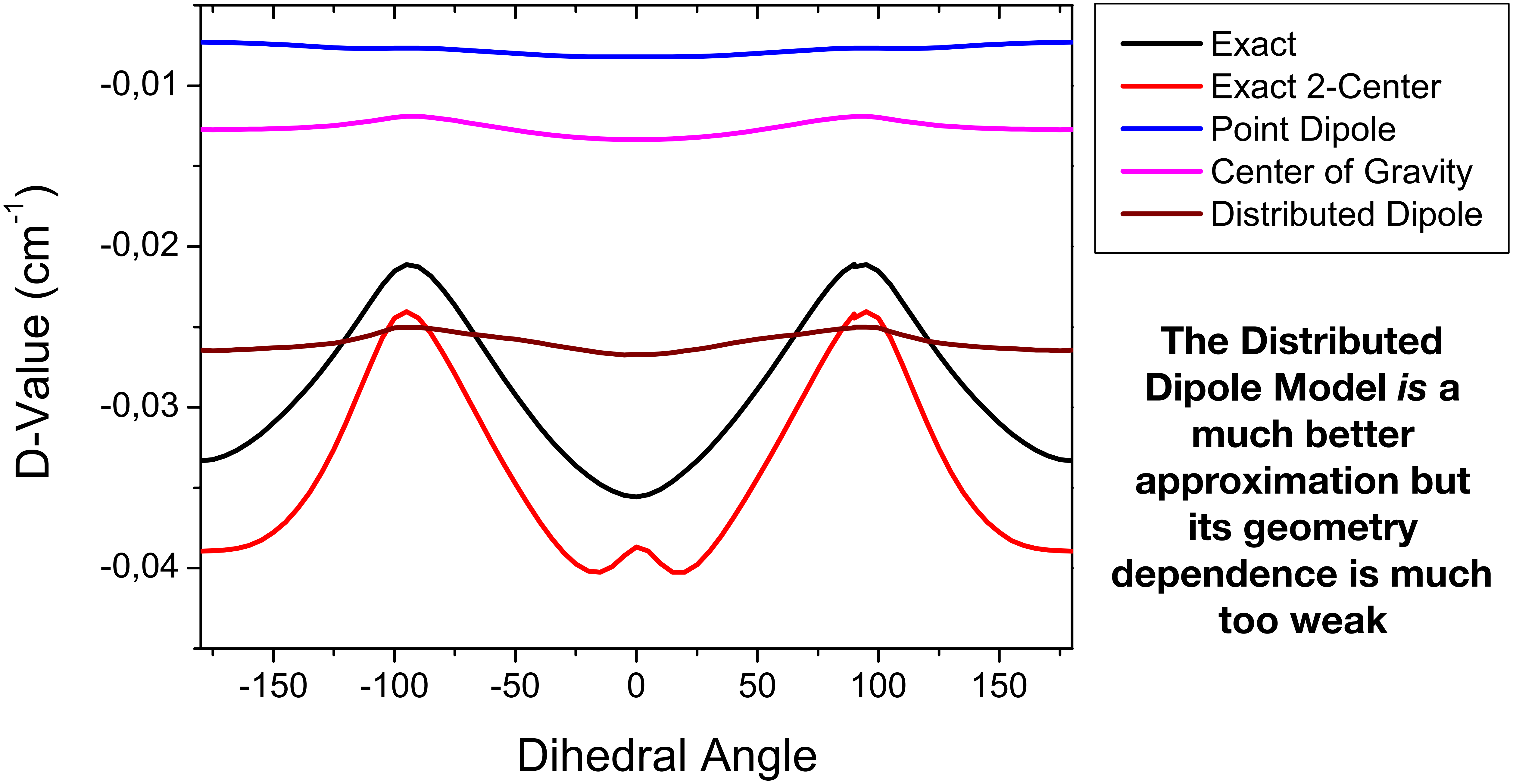


- Exchange part can make up to 15-20% contribution
- Not the major error source

- 3-center terms are the 2nd most important contribution (~30%)
- Not the major error source

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

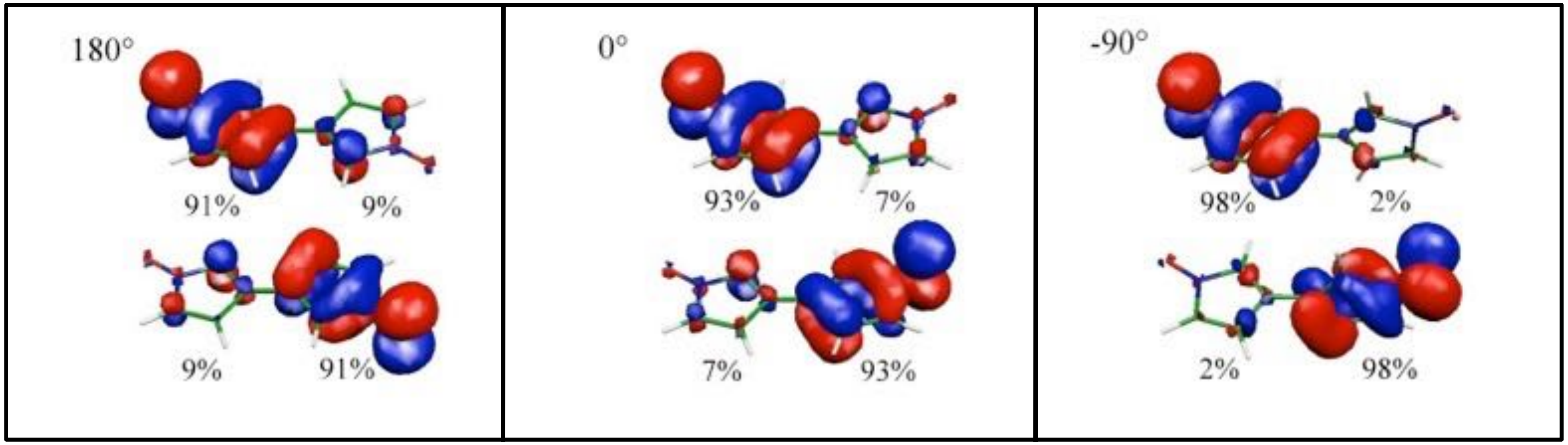
Comparison of Point Dipole Models



The Distributed Dipole Model *is* a much better approximation but its geometry dependence is much too weak

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

Electronic Structure Origin of the PD Failure



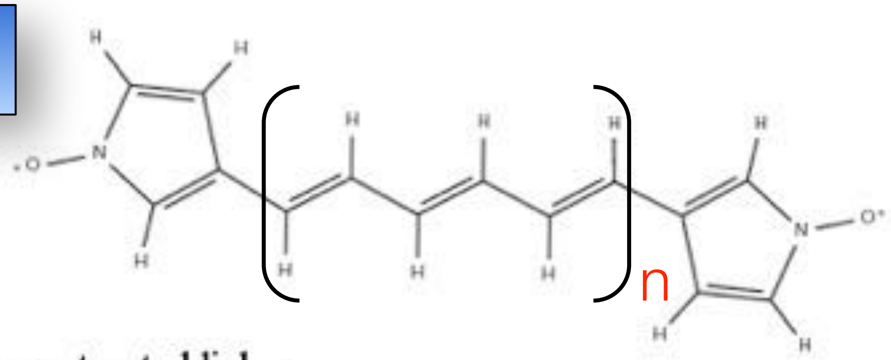
Conformation dependent delocalization of the SOMOs accounts for the main deviations between the point-dipole model and the precise calculation

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

„Through-Bond“ versus „Through-Space“

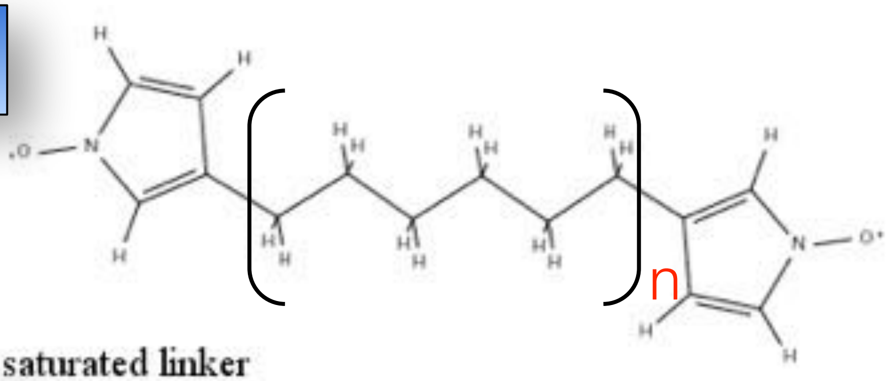
Study the distance dependence of the ZFS *in-silico* via model systems:

1



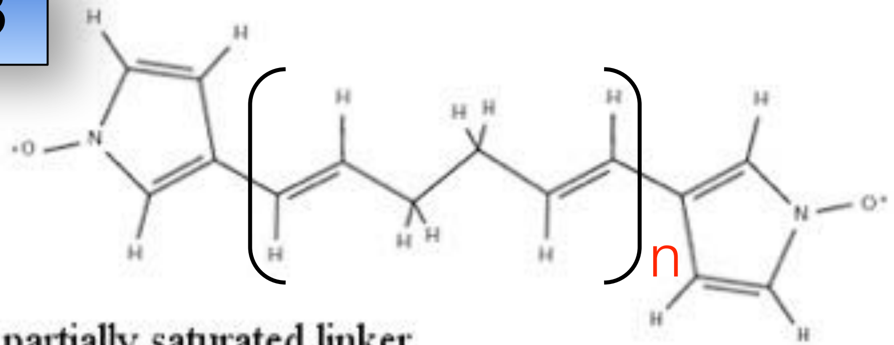
unsaturated linker

2



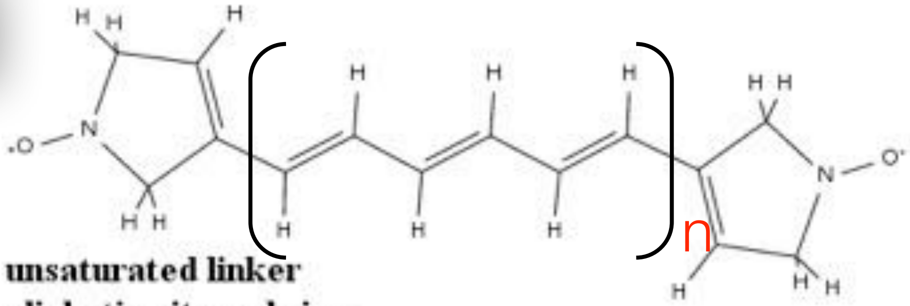
saturated linker

3



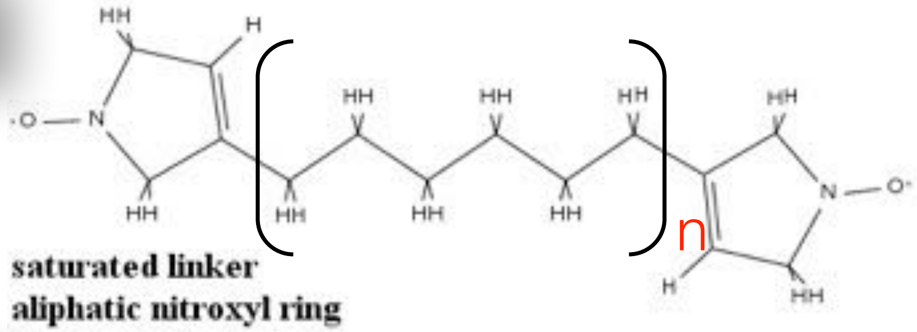
partially saturated linker

4



unsaturated linker
aliphatic nitroxyl ring

5



saturated linker
aliphatic nitroxyl ring

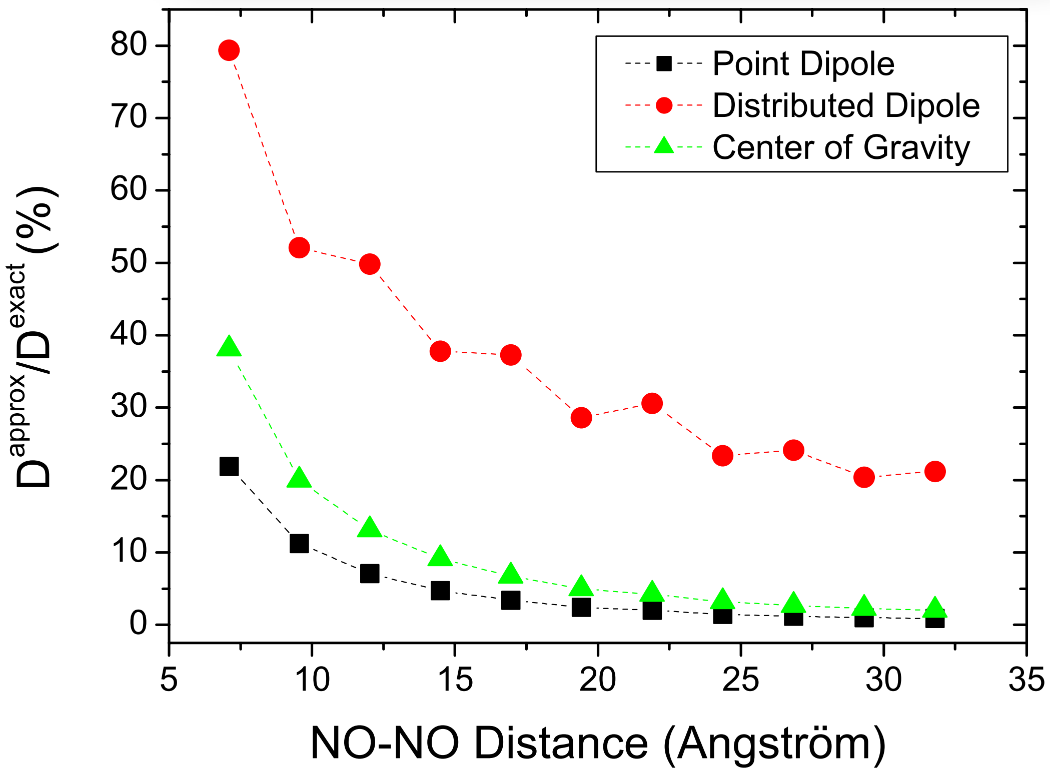
6

No linker, e.g. vacuum

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

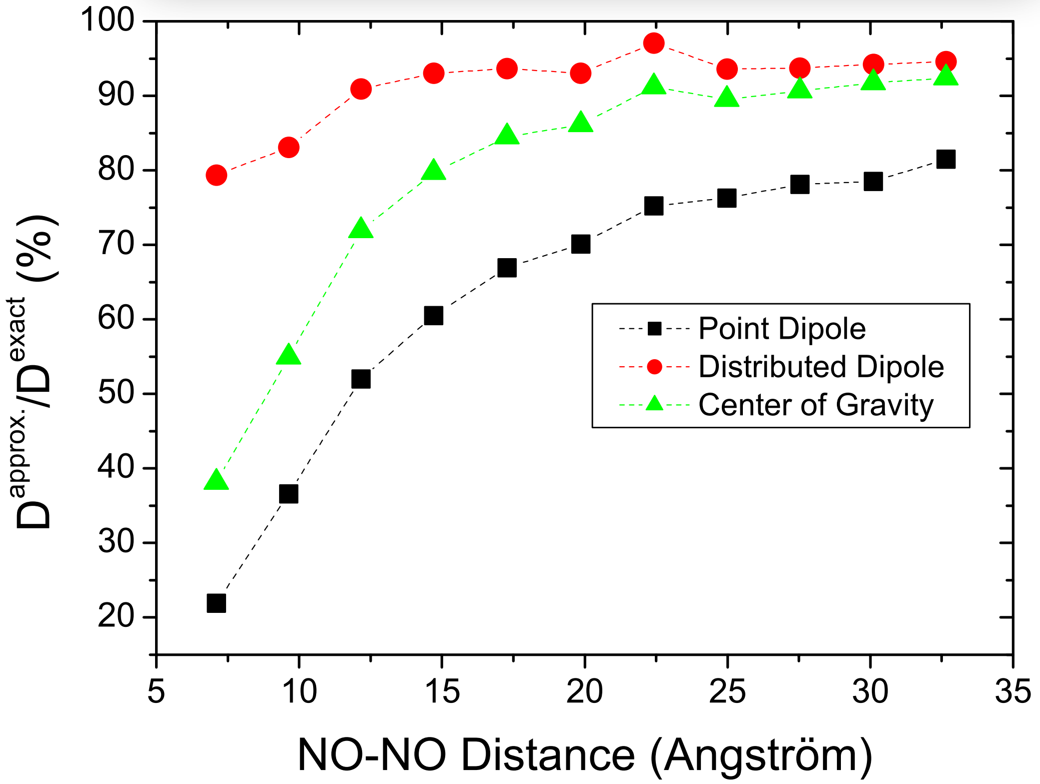
„Observed“ Distance Dependence

Unsaturated Linker



- All PDMs fail miserably for all distances
- ZFS Decay is $\mathbf{R^{-1.6}}$ rather than R^{-3}

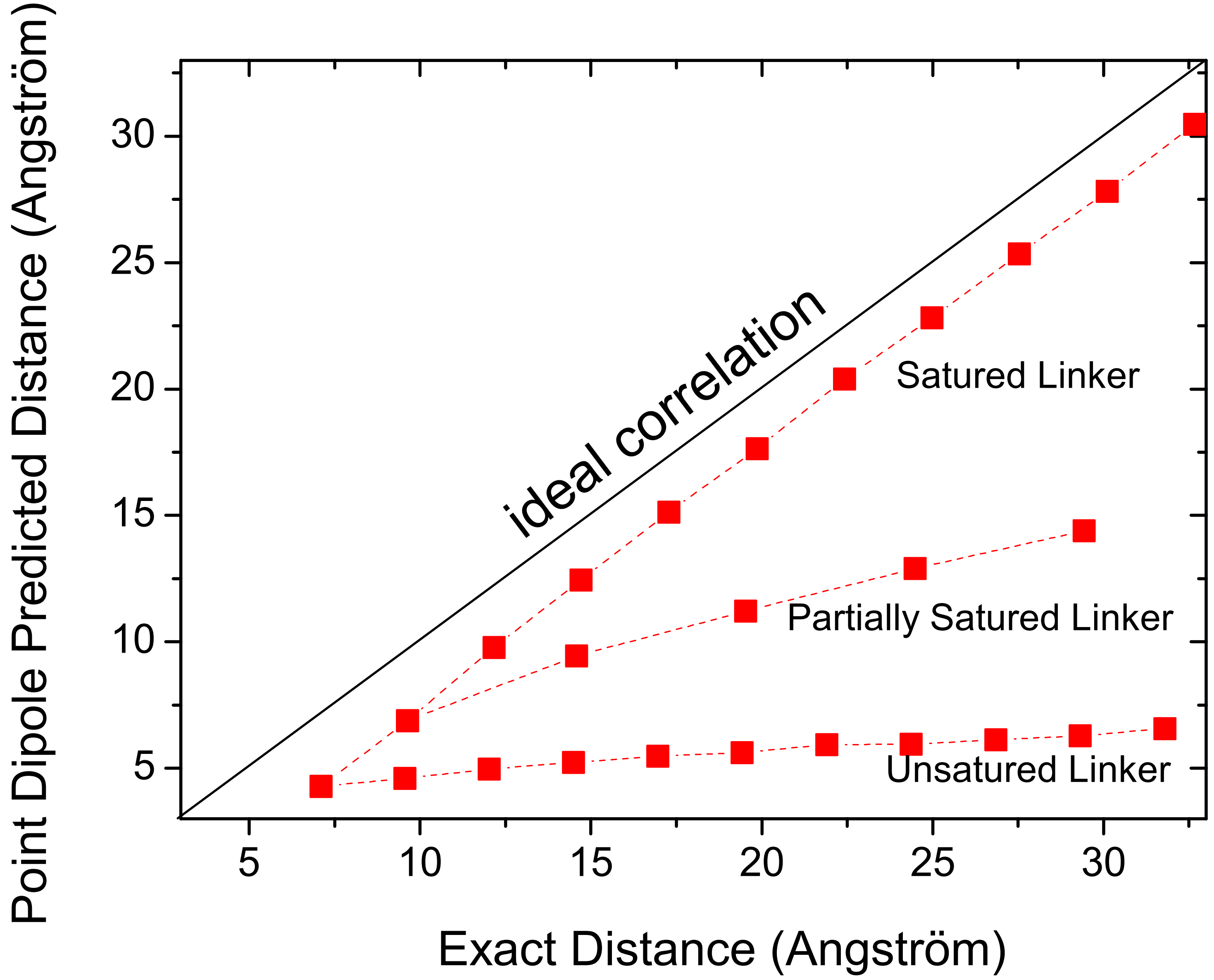
Saturated Linker



- Distributed Dipole becomes ok ~ 12-15 Å
- The ‚naive‘ PDM becomes ok (90%) only ~22-25Å
- ZFS decay is ~$\mathbf{R^{-3}}$

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

Errors in predicted Distances



For unsaturated linkers the predictions of the genuine PDM are absurd

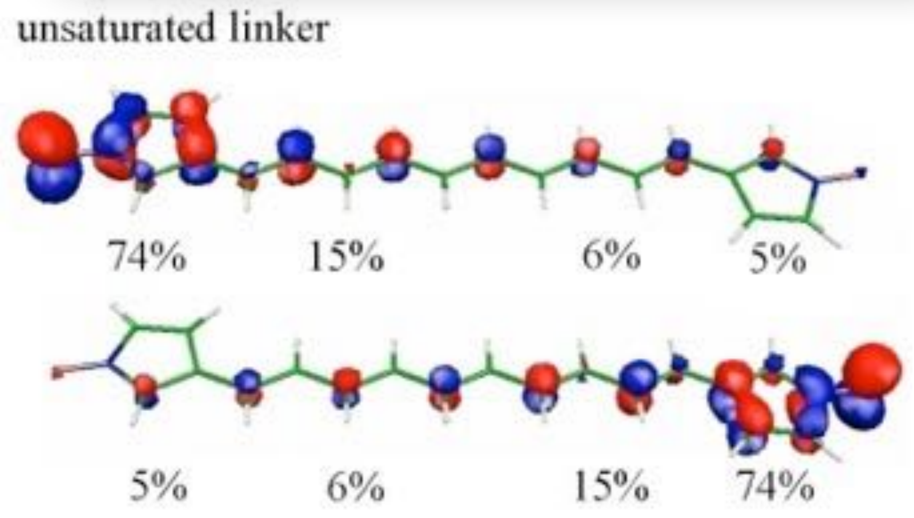
Even for saturated linkers the error is ~2-3 Å!

This error only vanishes at longer distances >15 Angström if a **non-aromatic** nitroxide is used

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

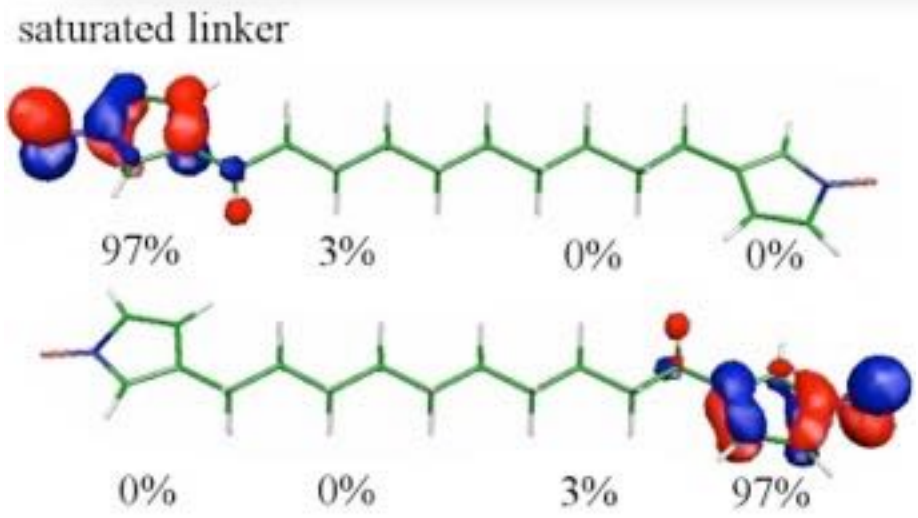
Electronic Structure Origin of the PDM Failures

Unsaturated Linker



- „Magnetically conducting“
- Long range spin-delocalization
- ZFS is dominated by the small tails on the bridge (r_{12}^{-3})

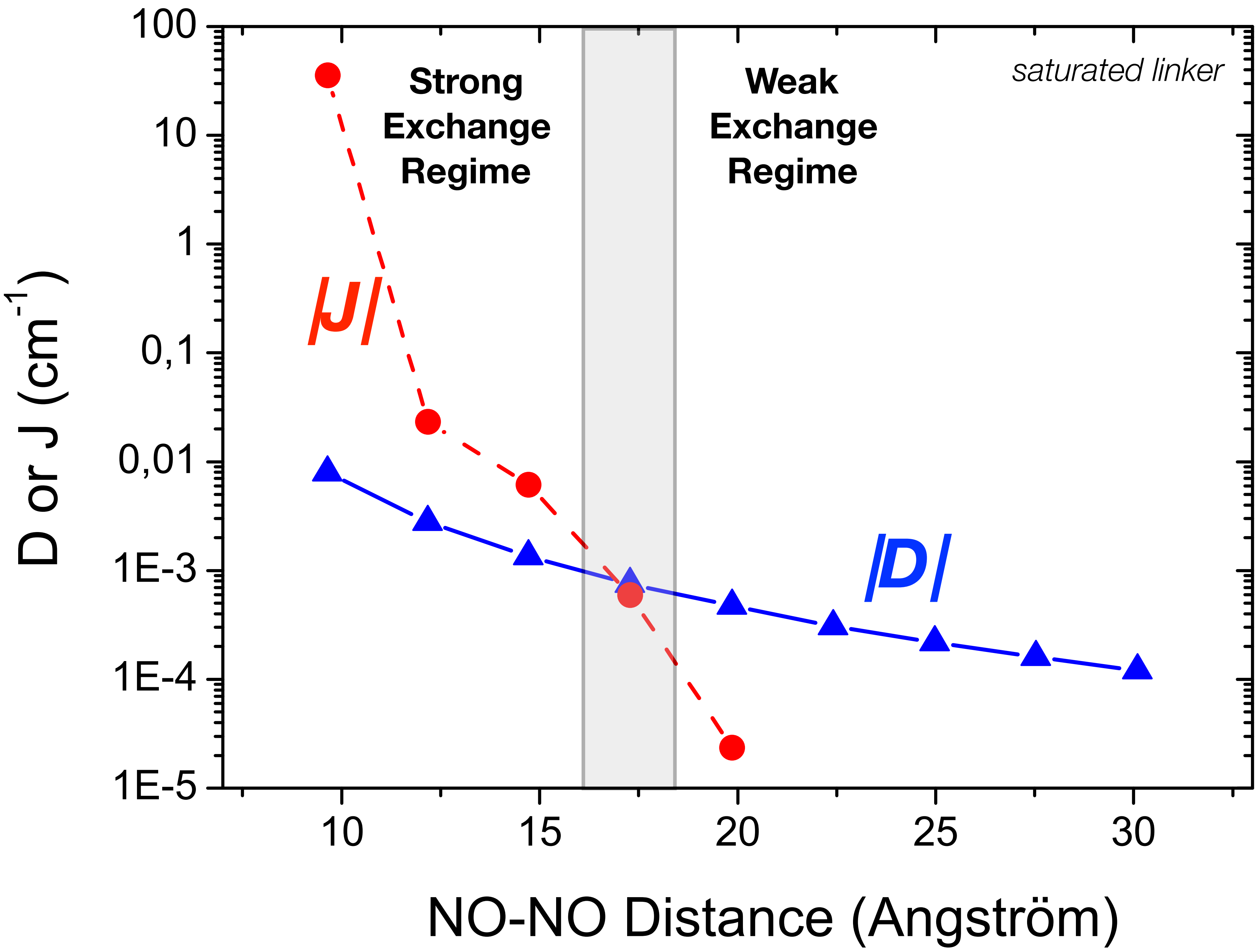
Saturated Linker



- Small „leakage“
- Only delocalization inside the monomers becomes important

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

Spin-Spin Interaction versus Heisenberg Exchange



The isotropic exchange decays exponentially with a decay constant of

0.9-1 Å^{-1}

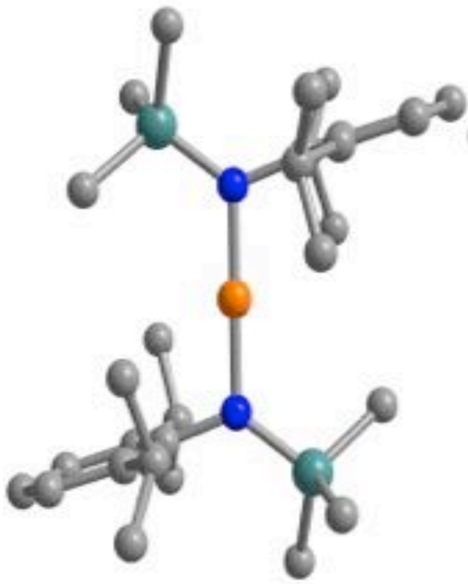
(Compare: Electron transfer matrix element ~0.7 Å^{-1})

Riplinger, C.; Kao, J.P.Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G.R.; Eaton, S.S.; Kutateladze, A.; FN, **2009**, 131, 10092

Limitations of the Spin-Hamiltonian Approach

Currents, Spin-Orbit Coupling and Multireference

Linear Fe(II) Complexes

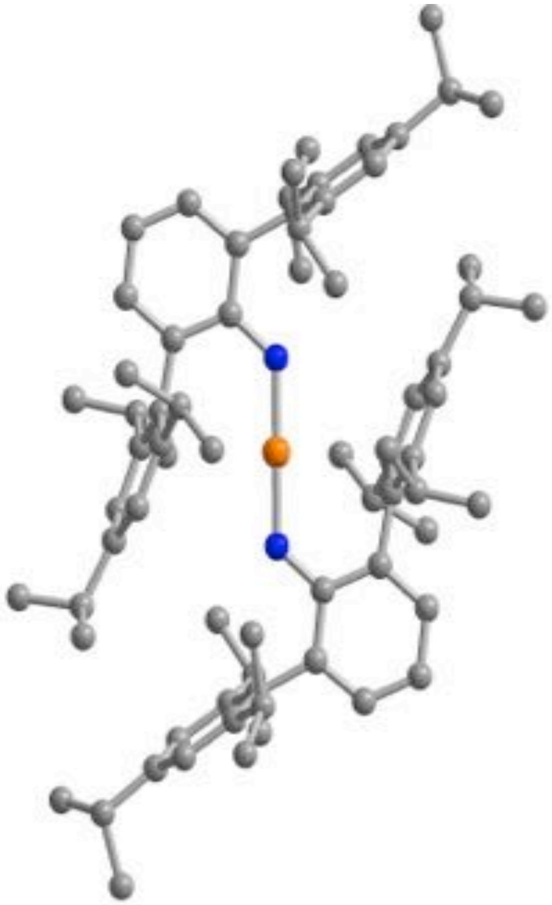


1

FeN_2

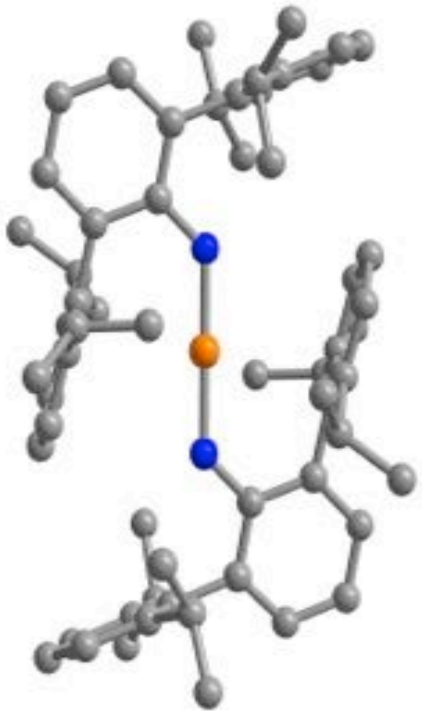
2

FeC_2



3

FeN_2

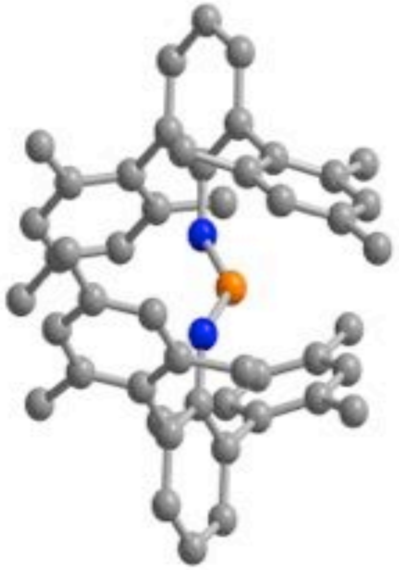


4

FeN_2

5

FeO_2

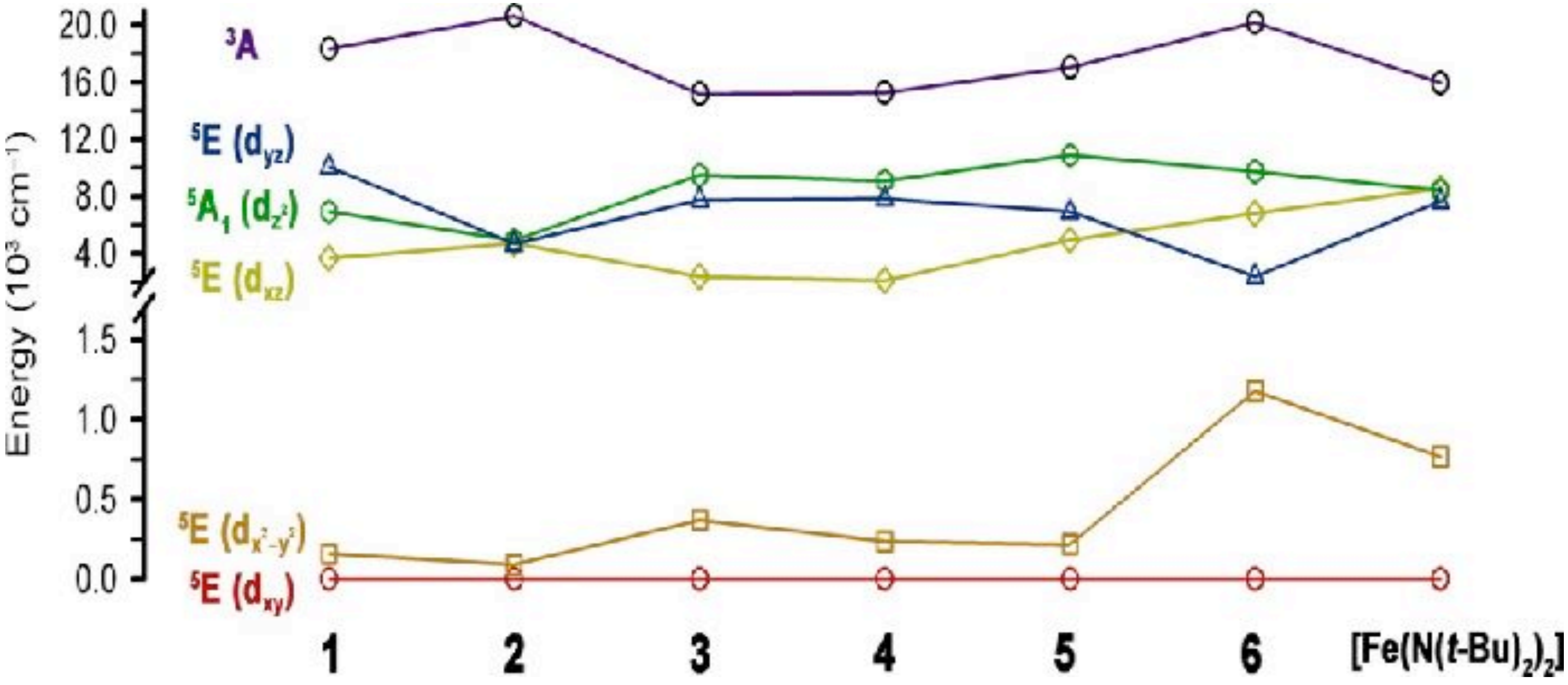


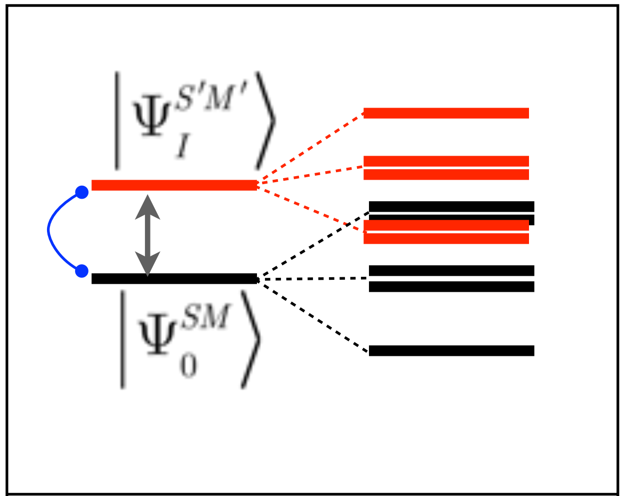
6

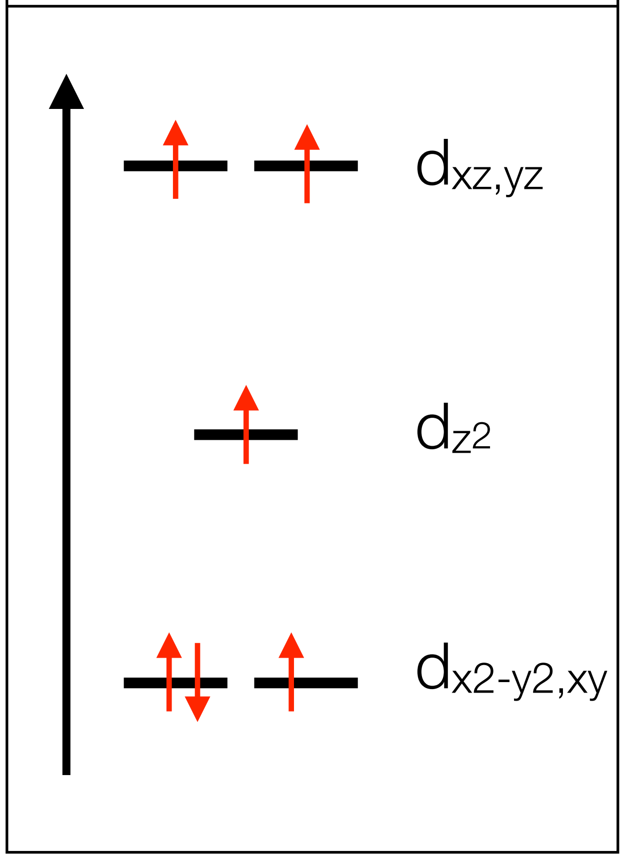
FeN_2

Chem.Science, **2013,4**, 125-138 (exp.); *Chem. Sci.* **2013**, 139-156 (theory and modeling)

Currents, Spin-Orbit Coupling and Multireference



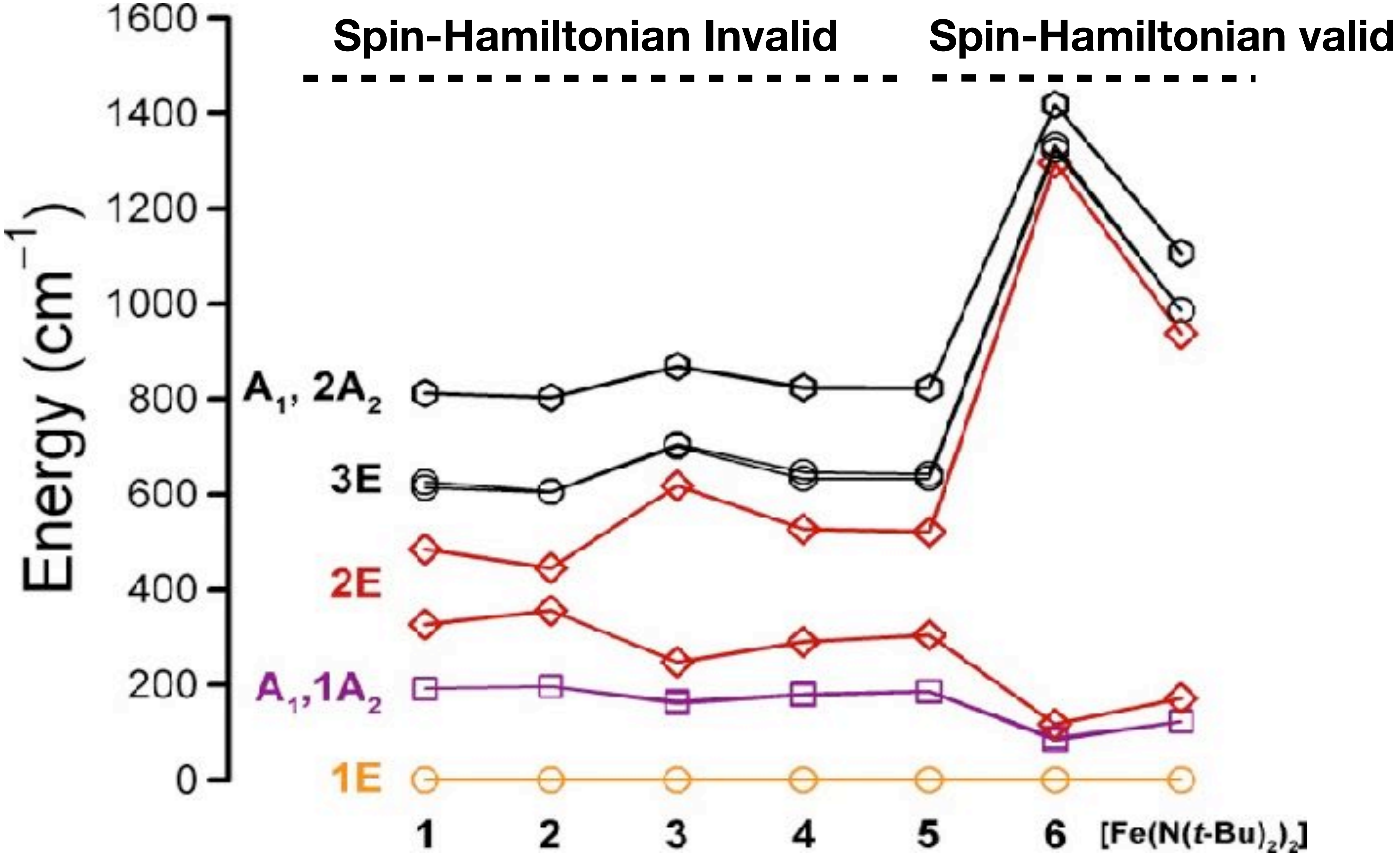




- ➡ Orbitally almost degenerate ground states (as in introduction)
- ➡ „Crazy magnetism“

Zadrozny, J. M.; Atanasov, M.; Bryan, A. M.; Lin, C. Y.; Rekken, B. D.; Power, P. P.; FN; Long, J. R. *Chem. Sci.* **2013**, *4*, 125.

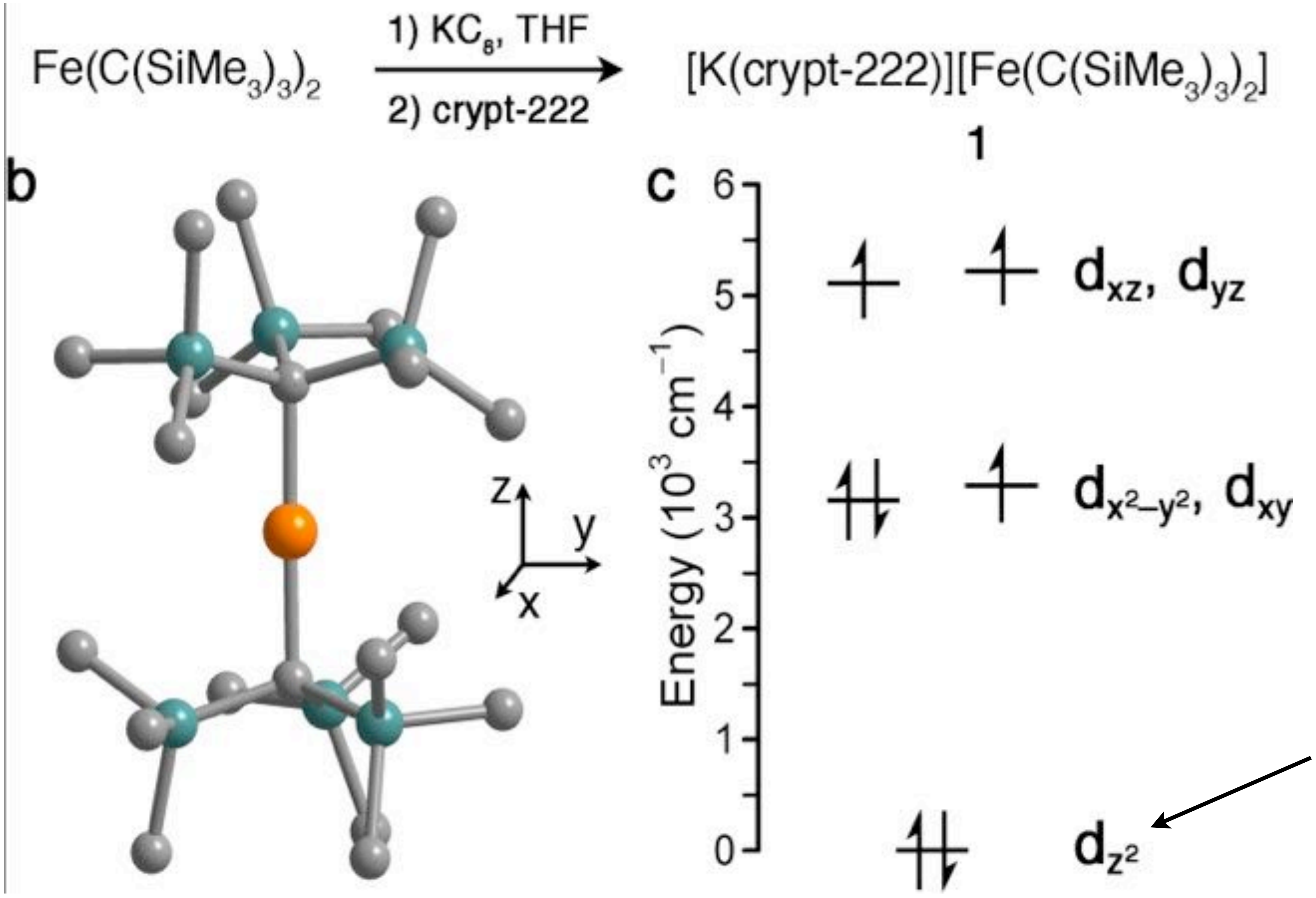
Currents, Spin-Orbit Coupling and Multireference


Spin-Hamiltonian Invalid

Spin-Hamiltonian valid

Zadrozny, J. M.; Atanasov, M.; Bryan, A. M.; Lin, C. Y.; Rekken, B. D.; Power, P. P.; FN; Long, J. R. *Chem. Sci.* **2013**, *4*, 125.

Currents, Spin-Orbit Coupling and Multireference

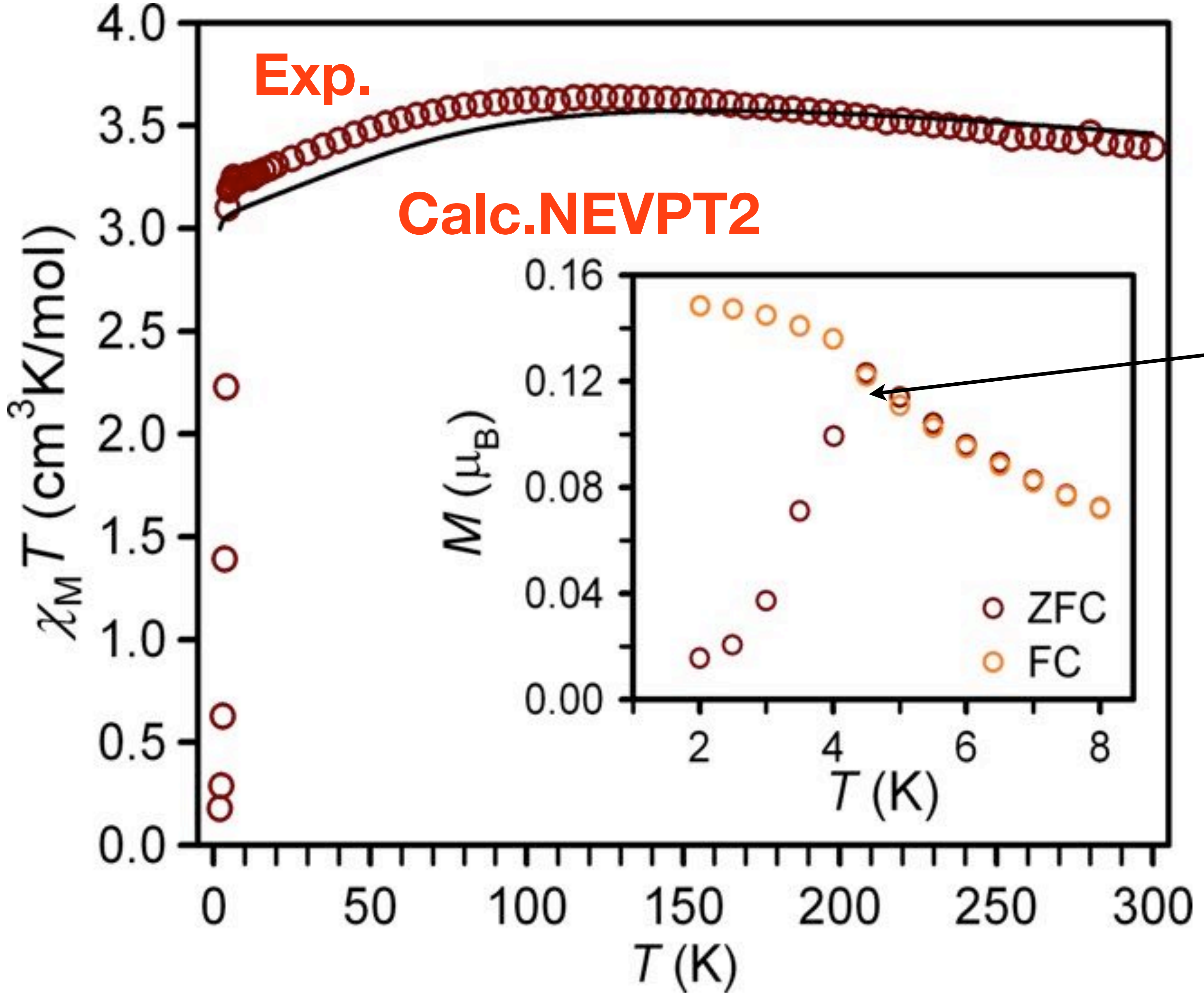


very special:
4s-3d mixing
makes d_{z2} the
lowest energy
orbital (essentially
nonbonding)

The weaker ligand field in Fe^IC_2 (^4E) greatly ***quenches the Renner-Teller effect***
→ Opportunity for higher temperature magnetic blocking

Zadrozny, J. M.; Xiao, D. J.; Atanasov, M.; Long, G. J.; Grandjean, F.; FN; Long, J. R. *Nature Chem.* **2013**, *5*, 577.

Currents, Spin-Orbit Coupling and Multireference



Real
magnetic
blocking

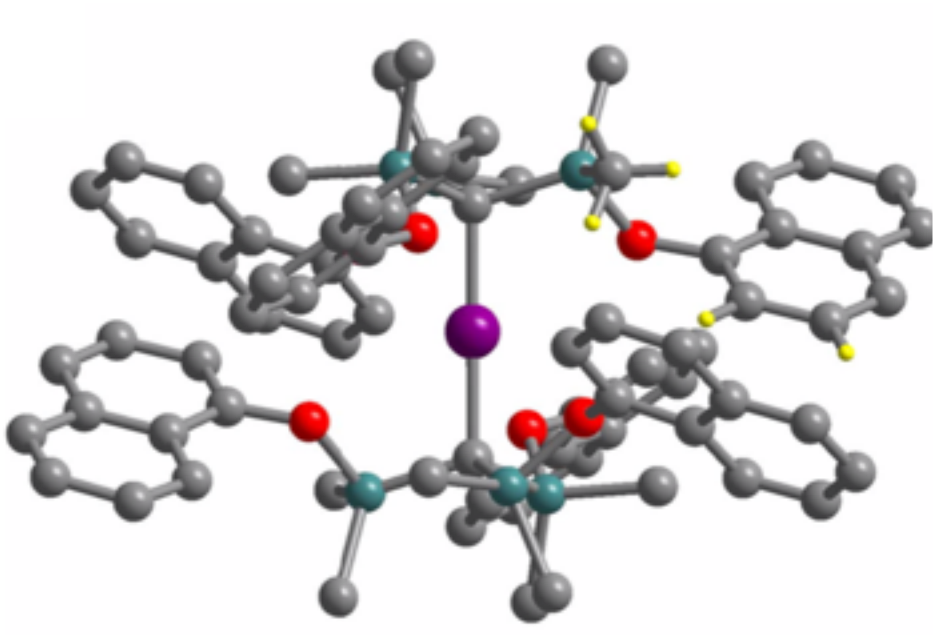
Zadrozny, J. M.; Xiao, D. J.; Atanasov, M.; Long, G. J.; Grandjean, F.; FN; Long, J. R. *Nature Chem.* **2013**, *5*, 577.

‚Non-Aufbau‘ States

- Prediction from theory: Linear Co(II) would be an even better SMM than Fe(I)

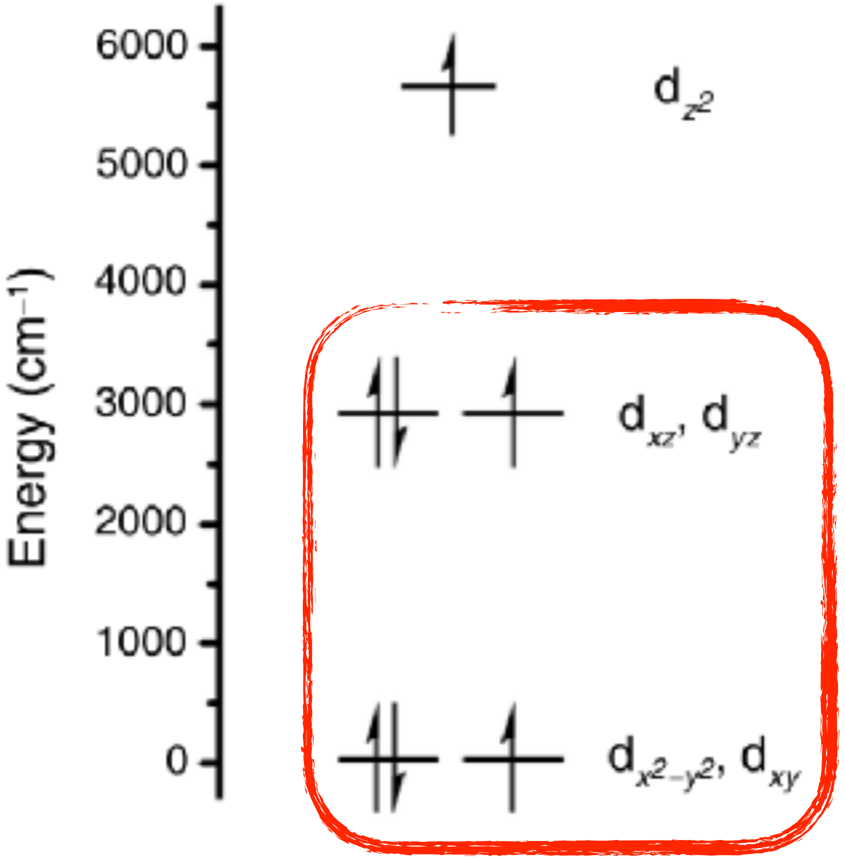
Atanasov, M.; Aravena, D.; Suturina, E.; Bill, E.; Maganas, D.; Neese, F. *Coord. Chem. Rev.* **2015**, *289*, 177.

- After 5 years of trying:



$Co(C(SiMe_2ONaph)_3)_2$

- MO diagram



Aufbau:

$(x_2\text{-}y_2,xy)^4(xz,yz)^2(z^2)^1$

S=3/2 ‚L'=2

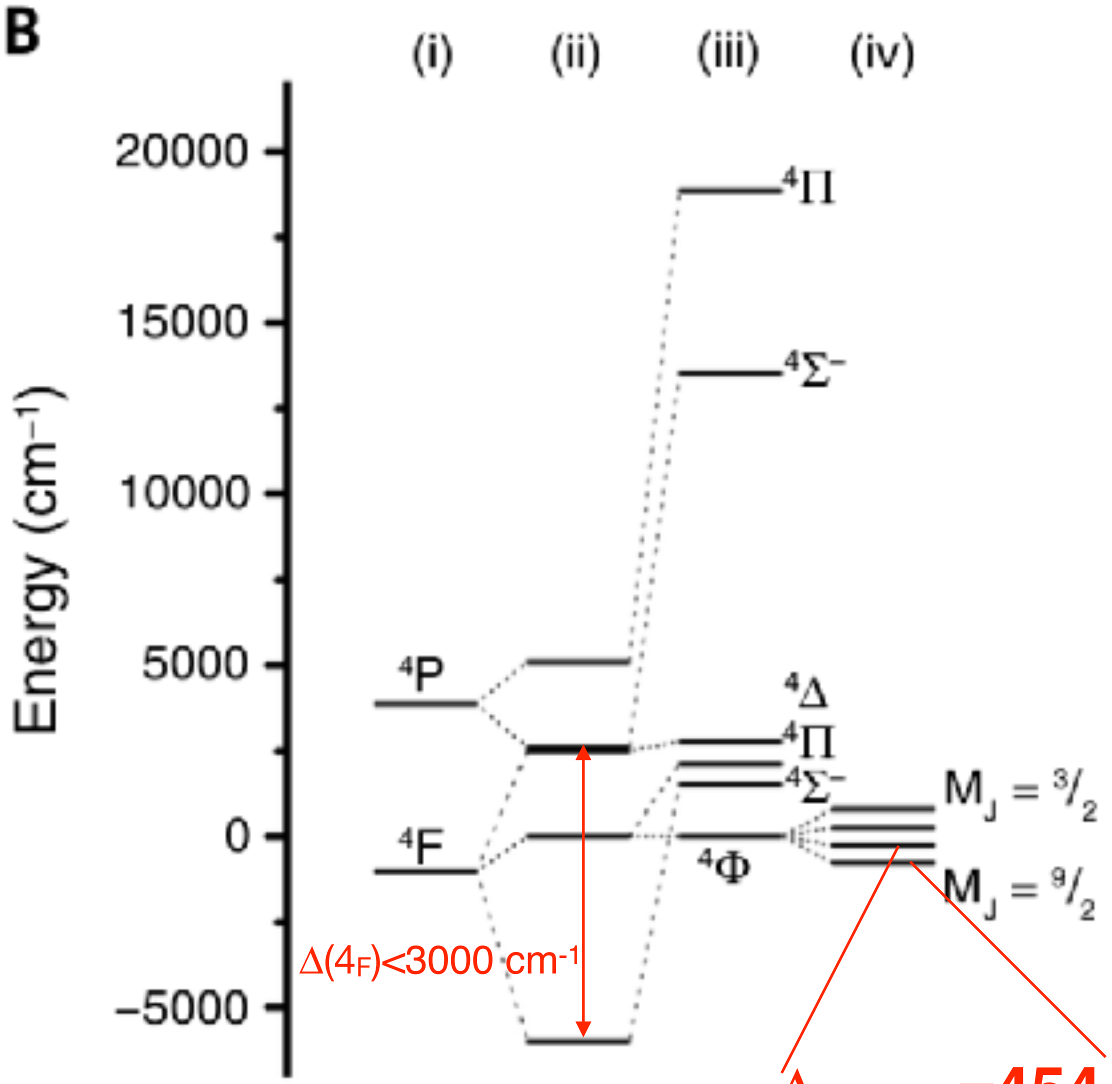
Non-Aufbau:

$(x_2\text{-}y_2,xy)^3(xz,yz)^3(z^2)^1$

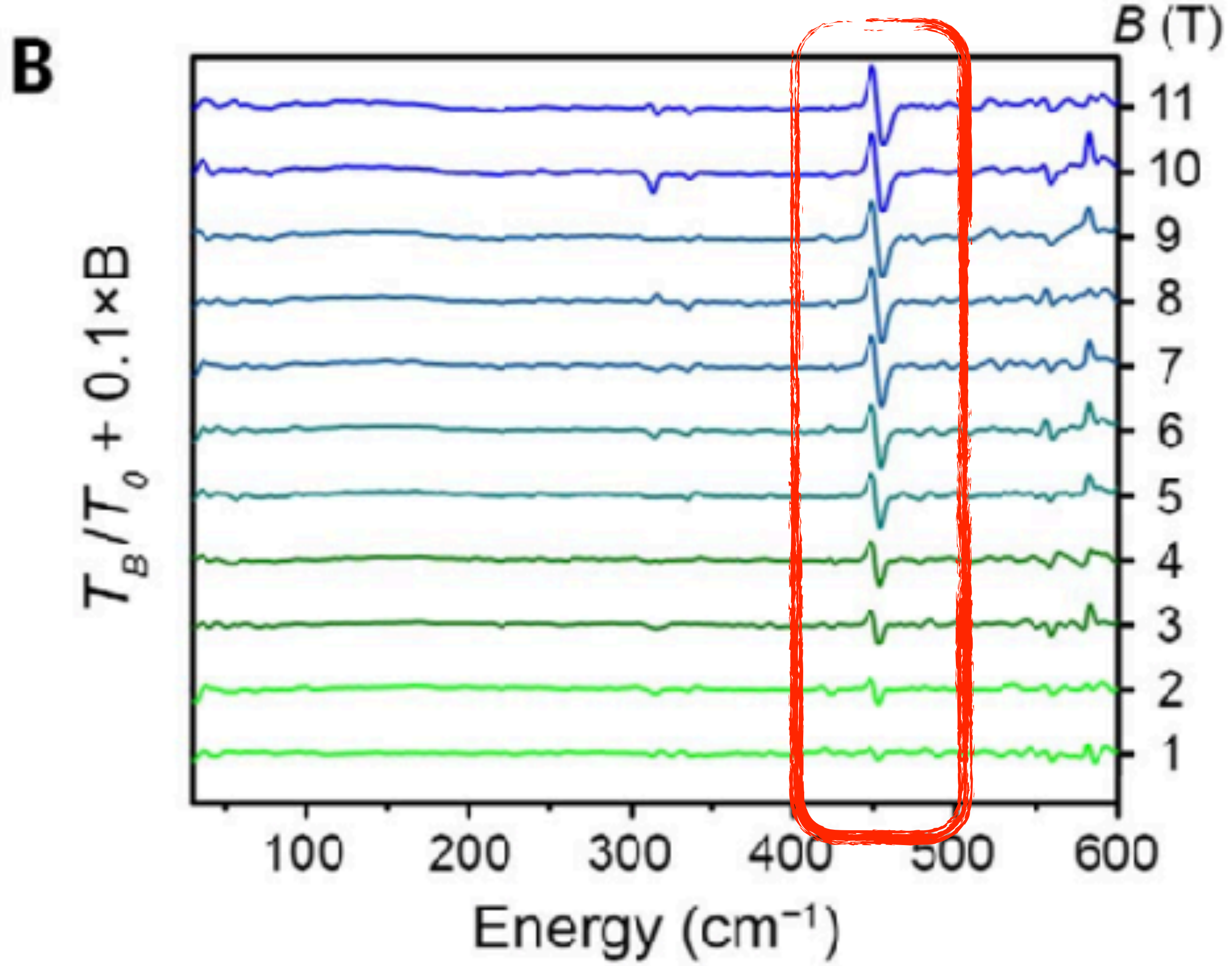
S=3/2 **‚L'=3**

Bunting, P. C.; Atanasov, M.; Damgaard-Moller, E.; Perfetti, M.; Crassee, I.; Orlita, M.; Overgaard, J.; van Slageren, J.; FN; Long, J. R. *Science* **2018**, *362*, 1378.

‚Non-Aufbau‘ States



$\Delta_{(9/2-7/2)}$**=454 cm^{-1}**

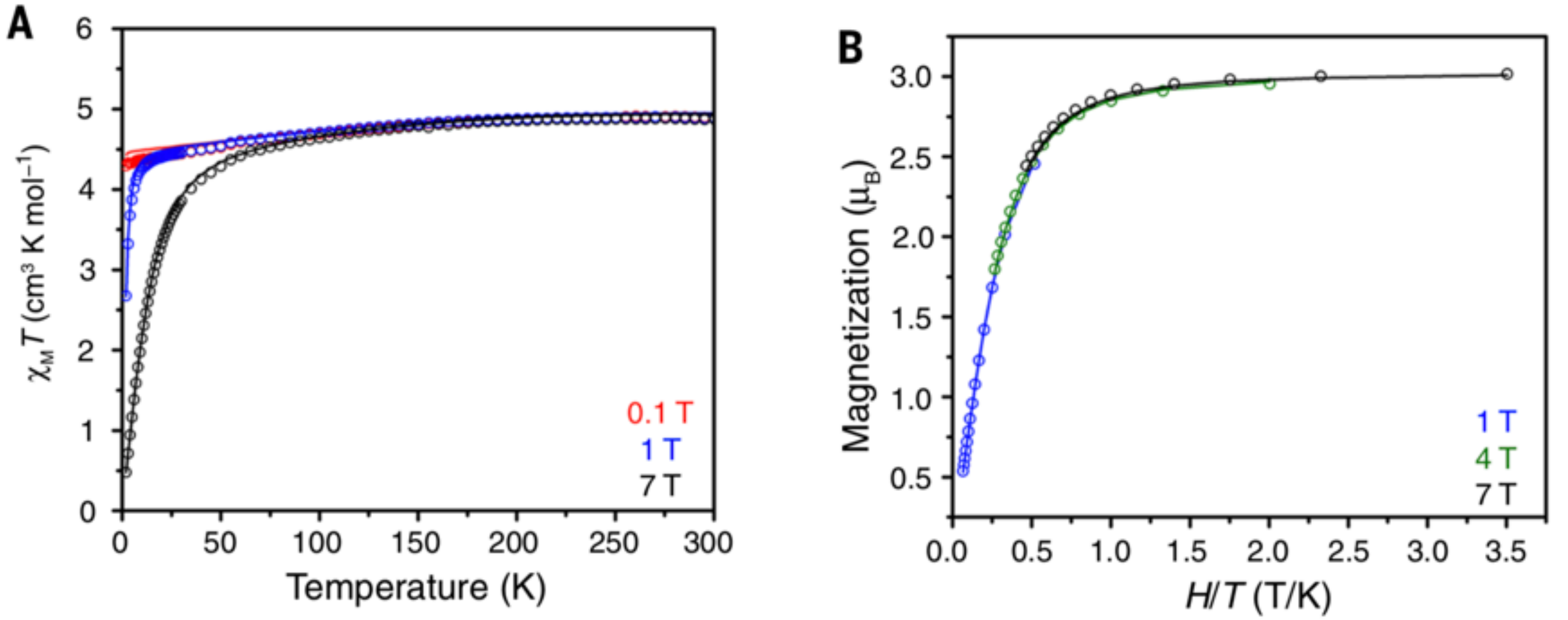


Largest ever measured
Effective barrier

Atanasov, M.; Aravena, D.; Suturina, E.; Bill, E.; Maganas, D.; Neese, F. *Coord. Chem. Rev.* **2015**, *289*, 177.

Bunting, P. C.; Atanasov, M.; Damgaard-Moller, E.; Perfetti, M.; Crassee, I.; Orlita, M.; Overgaard, J.; van Slageren, J.; FN; Long, J. R. *Science* **2018**, *362*, 1378.

‚Non-Aufbau‘ States



Solid lines = Quantum Chemical Prediction!

Bunting, P. C.; Atanasov, M.; Damgaard-Moller, E.; Perfetti, M.; Crassee, I.; Orlita, M.; Overgaard, J.; van Slageren, J.; FN; Long, J. R. *Science* **2018**, *362*, 1378.