FrenchBic METBIO summer school
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Lecture #3
Theoretical chemistry

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DE LA RECHERCHE À L'INDUSTRIE cea

INSTITUT NANOSCIENCES ET CRYOGÉNIE

SyMMES SYSTÈMES MOLÉCULAIRES ET NANOMATÉRIAUX POUR L'ÉNERGIE ET LA SANTÉ

Outline of the lecture

- ***Basic introduction to DFT***
  - ***Hartree-Fock* versus *DFT***
- ***Application : (mono-metal) g-tensors***
  - ***Relativistic origin***
  - ***Perturbative & self-consisten approaches***
  - ***When it does not work ...***
- ***Polymetallic complexes***
  - ***Spin-coupling***
  - ***g-tensor (dimer)***
  - ***Hyperfine couplings (dimer)***
    - ***More complex systems : hyperfine & Mössbauer***
- ***Conclusions***

DFT & (metal) spectroscopies :

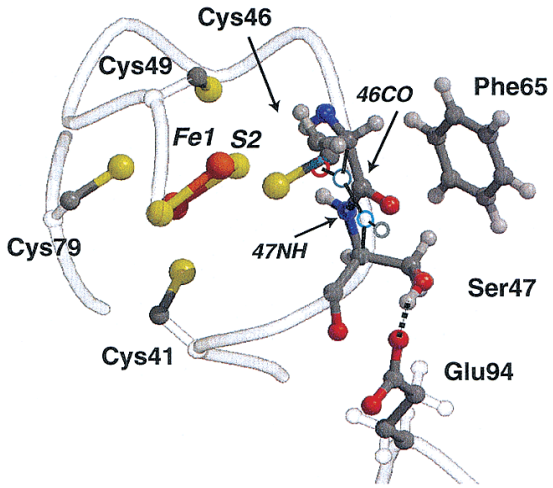
Molecular structure

φ-chemical properties

Crystallography
(X-rayx)
Solution NMR

Redox potentials
Electron transfer
Magnetism

Spectroscopic parameters



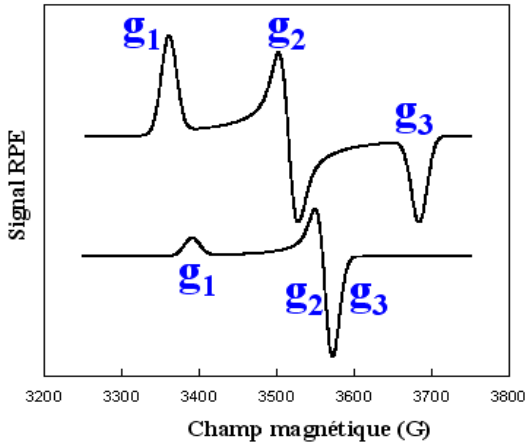
Chemical shifts : NMR

g-tensors : EPR

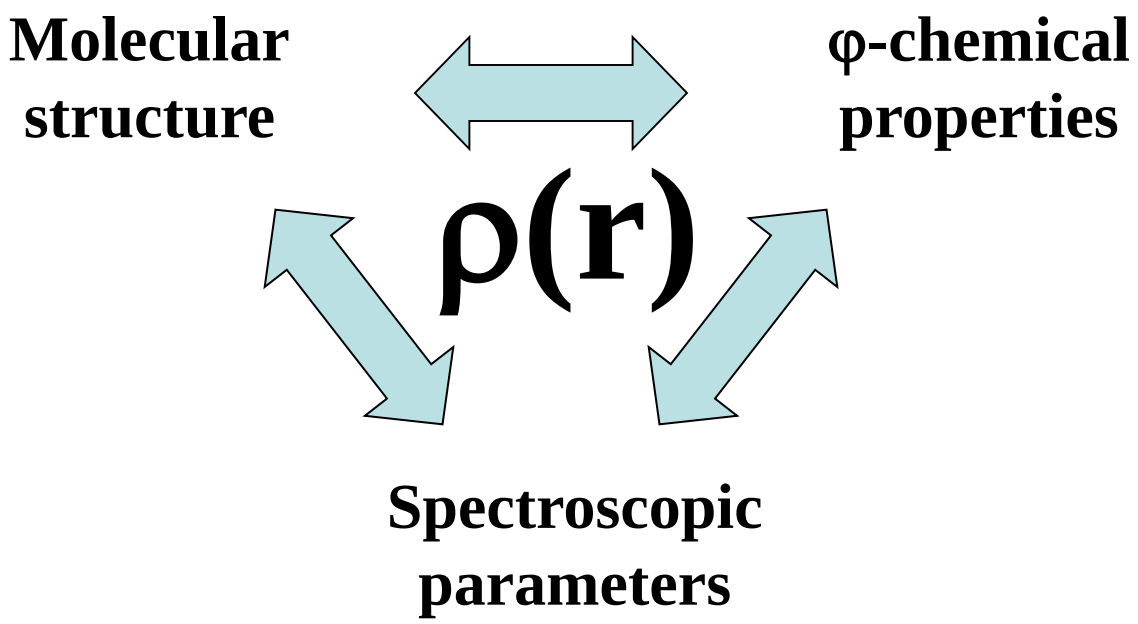
Hyperfine couplings: NMR/ EPR

But also

Mössbauer, etc



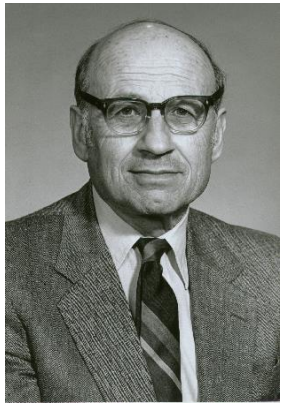
Density Functional Theory



Density function $\rho(r) = \Psi^2(r)$

- of charge : $\rho_e(r) = \rho_\alpha(r) + \rho_\beta(r)$
- of spin : $\rho_s(r) = \rho_\alpha(r) - \rho_\beta(r)$

α β



Walter Kohn

+ « home-made » codes (spectroscopies)

Density Functional Theory

What can we compute ?

Charge (diamagnetic) $\rho_e(r) = \rho_\alpha(r) + \rho_\beta(r)$		Spin (paramagnetic) $\rho_s(r) = \rho_\alpha(r) - \rho_\beta(r)$
diamag. NMR		param. NMR (hyperfine)
		EPR (g-tensors, hyperfine)
	UV-vis	
	IR spectra	
Mössbauer (δ, ΔE_Q)		Mössbauer (hyperfine)
		SQUID (exchange J)
	Redox potentials	
etc.	etc.	etc.

Practical implementations

SCM
Software for Chemistry & Materials

Spectroscopic properties

- IR spectra, (resonance) Raman, VROA, VCD
- Time-dependent DFT
- Excitation energies: UV/Vis, X-ray, CD, MCD

  Excited state (geometry) optimizations
- Vibrationally resolved electronic spectra
- (Hyper-)Polarizabilities, ORD, magnetizabilities, Verdet constants

- Ligand Field and Density Functional Theory (LFDFT)
- NMR
- ESR/EPR

  Nuclear Quadrupole Interaction (EFG)

  Mössbauer spectroscopy

ESR/EPR

ESR/EPR g-tensor and A-tensor

ESR/EPR Q-tensor

ESR/EPR Zero-field splitting (D-tensor)

NMR

- NMR Chemical Shifts

  Paramagnetic NMR Chemical Shifts
- NMR spin-spin coupling constants

Excitation energies: UV/Vis, X-ray, CD, MCD

- Excitation energies, UV/Vis spectra

  Excitation energies for open-shell systems

  Spin-flip excitation energies

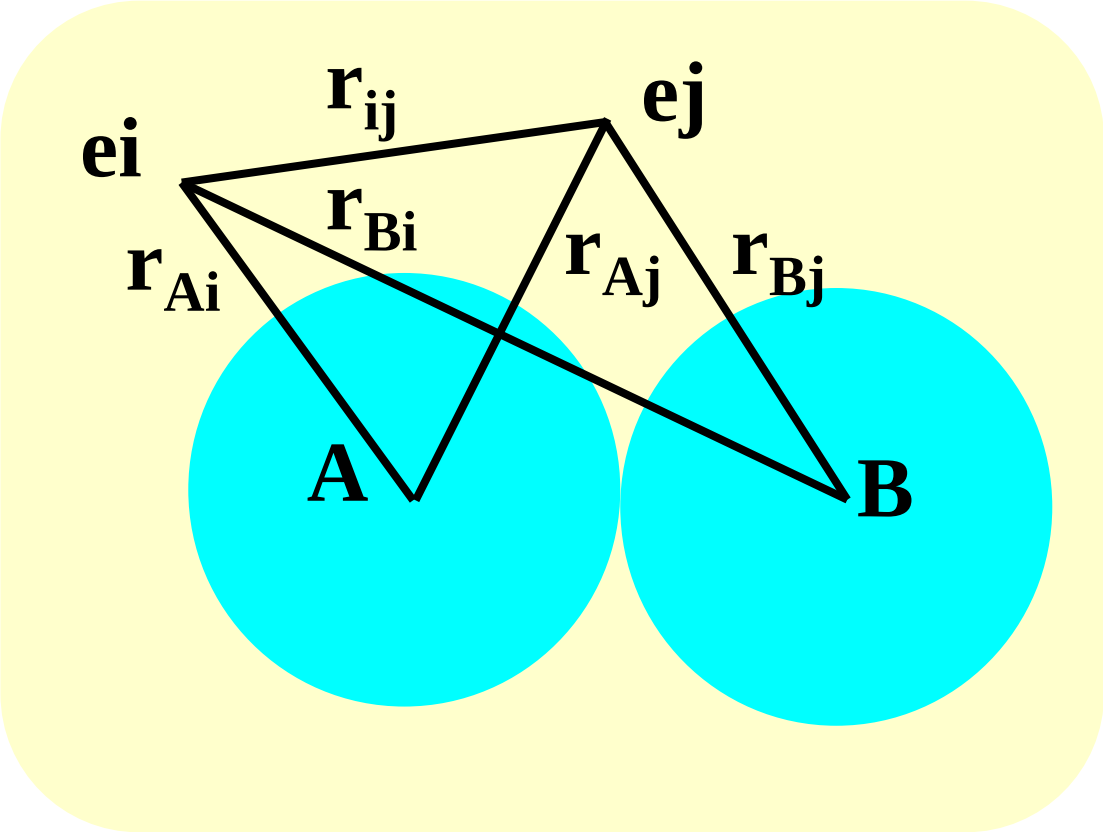
+ Solvent effects

Schrödinger equation

(classical & time-independant)

$$\mathbf{H_T \Psi = E\,\Psi}$$

$$H_T = -\sum_A \frac{\hbar^2}{2M_A}\nabla_A^2 - \sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 + \sum_A \sum_{B>A} \frac{Z_A Z_B e^2}{|R_A - R_B|} + \sum_i \sum_{j>i} \frac{e^2}{|r_i - r_j|} - \sum_A \sum_i \frac{Z_A e^2}{|R_A - r_i|}$$



$$\mathbf{H_{elec}\Psi_{elec} = E_{elec}\Psi_{elec}}$$

Schrödinger equation

(classical & time-independant)

$$\mathbf{H_T \Psi = E\,\Psi}$$

$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 + \sum_i \sum_{j>i} \frac{e^2}{|r_i - r_j|} - \sum_A \sum_i \frac{Z_A e^2}{|R_A - r_i|}$$

$$\mathbf{H_{elec}\Psi_{elec} = E_{elec}\Psi_{elec}}$$

$$\mathbf{E_{tot} = E_{elec} + E_{nuc}}$$

$$\mathbf{E_{test} \geq E_0 = \min_{\{\Psi\}} E[\Psi_{test}]}$$

$$\{N, Z_A, R_A\} \Rightarrow H \Rightarrow \Psi_0 \Rightarrow E_0$$

$$\mathbf{\Psi(x_i,x_j) = -\Psi(x_j,x_i)}$$

Hartree-Fock & Slater determinant

$$\Psi_{test} \approx \Psi_{Slater} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \varphi_2(x_1) & \dots & \varphi_N(x_1) \\ \varphi_1(x_2) & \varphi_2(x_2) & \dots & \varphi_N(x_2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(x_N) & \varphi_2(x_N) & \dots & \varphi_N(x_N) \end{vmatrix}$$

$$\sigma(\uparrow) = \alpha$$

$$\sigma(\downarrow) = \beta$$

$$\varphi_1(x_1) \equiv \varphi_1(r_1, s_1) \approx \varphi_1(r_1)\sigma_1(s_1)$$

$$\mathbf{E_{HF} = \min_{\{\Psi_{Slater}\}} E[\Psi_{Slater}]}$$

Hartree-Fock equations

$$\Psi_{test} \approx \Psi_{Slater} = \frac{1}{\sqrt{2!}} \begin{vmatrix} \varphi_1(r_1)\sigma_1(s_1) & \varphi_2(r_1)\sigma_2(s_1) \\ \varphi_1(r_2)\sigma_1(s_2) & \varphi_2(r_2)\sigma_2(s_2) \end{vmatrix}$$

$$E_{HF} = \langle \Psi_{Slater} | H_{elec} | \Psi_{Slater} \rangle =$$

$$\sum_{i=1}^{2} \langle \varphi_i(x_1) | \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_A \frac{Z_A e^2}{|R_A - r_i|} \right) | \varphi_i(x_1) \rangle$$

$$+ \langle \varphi_1(x_1)^2 | \frac{e^2}{|r_1 - r_2|} | \varphi_1(x_2)^2 \rangle + \langle \varphi_1(x_1)^2 | \frac{e^2}{|r_1 - r_2|} | \varphi_2(x_2)^2 \rangle$$

$$- \langle \varphi_1(x_1)^2 | \frac{e^2}{|r_1 - r_2|} | \varphi_1(x_2)^2 \rangle - \langle \varphi_1(x_1)\varphi_2(x_2) | \frac{e^2}{|r_1 - r_2|} | \varphi_2(x_1)\varphi_1(x_2) \rangle$$

K_{12}

J_{12}

Case of 2 electrons : triplet state (S=1)

$$\det_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(r_1)\alpha_1(s_1) & \varphi_2(r_1)\alpha_2(s_1) \\ \varphi_1(r_2)\alpha_1(s_2) & \varphi_2(r_2)\alpha_2(s_2) \end{vmatrix}$$

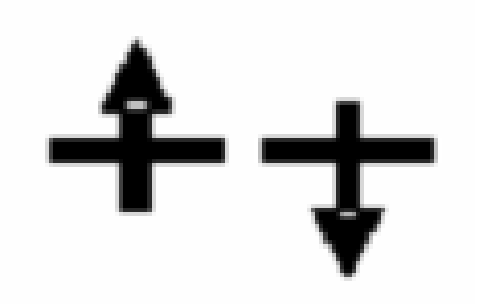
$$\left[\Phi_1(r_1)\Phi_2(r_2) - \Phi_2(r_1)\Phi_1(r_2)\right]\alpha(1)\alpha(2)$$

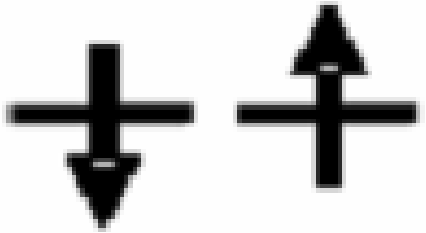
$$E_{HF}^{\alpha\alpha} = h_1 + h_2 + \boxed{K_{12} - J_{12}}$$

Case of 2 electrons : singlet state (S=0)

$$\det_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \Phi_1(r_1)\alpha(1) & \Phi_1(r_2)\alpha(2) \\ \Phi_2(r_1)\beta(1) & \Phi_2(r_2)\beta(2) \end{vmatrix}$$

$$\det_3 = \frac{1}{\sqrt{2}} \begin{vmatrix} \Phi_1(r_1)\beta(1) & \Phi_1(r_2)\beta(2) \\ \Phi_2(r_1)\alpha(1) & \Phi_2(r_2)\alpha(2) \end{vmatrix}$$

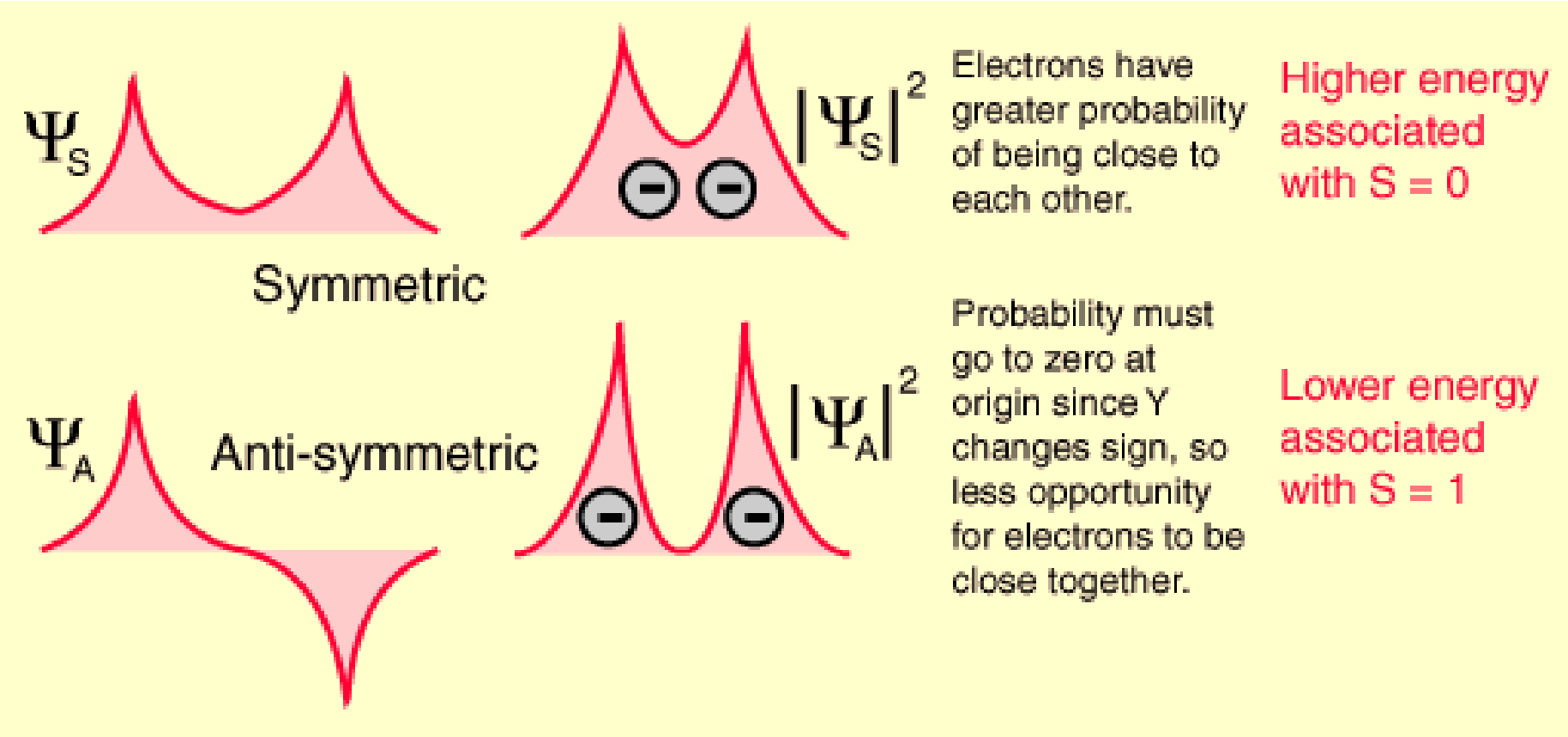




$$\left[\Phi_1(r_1)\Phi_2(r_2) + \Phi_2(r_1)\Phi_1(r_2)\right]\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

$$E_{HF}^{\alpha\beta} = h_1 + h_2 + \boxed{K_{12}}$$

Exchange term



Triplet state $\rightarrow$ $E_{HF}^{\alpha\alpha} = h_1 + h_2 + \boxed{K_{12} - J_{12}}$

Singlet state $\rightarrow$ $E_{HF}^{\alpha\beta} = h_1 + h_2 + \boxed{K_{12}}$

What about electronic correlation ?

$$E_{correlation} \equiv E_0 - E_{HF} < 0$$

$$\Psi_{test} = c_0 \Psi_0 + \sum_k c_k \Psi_k$$

Dynamic correlation :
Instantaneous repulsion

Static correlation :
Orbital degenerescence

$$(c_0)^2 >> (c_k)^2$$

$$\boxed{\rho_{CI} = \left(c_0 \Psi_0 + \sum_k c_k \Psi_k \right)^2}$$

$$(c_0)^2 \sim (c_k)^2$$

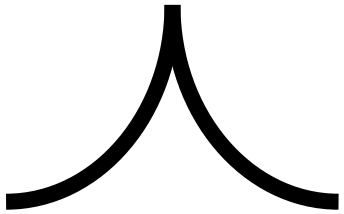
Basis of DFT

(Density Functional Theory)

$\Psi(r,s)$ not observable, in contrast to $\rho(r,s) = \Psi(r,s)^2$

$$\int \rho(r)dr = N$$

$$\rho(r) \text{ non differentiable in } R_A$$



$$\rho(r)\, en\, R_A \rightarrow Z_A$$

Basis of DFT

(Density Functional Theory)

Thomas-Fermi model (1927)

Kinetic energy:

$$\frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(r)dr$$

Electron-nucleus :

$$-Z\int \frac{\rho(r)}{r}dr$$

Electron-electron :

$$\frac{1}{2}\iint \frac{\rho(r_1)\rho(r_2)}{r_{12}}dr_1 dr_2$$

Basis of DFT

(Density Functional Theory)

Slater's model (1951) HFS (Xα)

Goal : simplify Hartree-Fock's exchange

$$\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle \varphi_j(x_1)\varphi_i(x_2)\left|\frac{e^2}{|r_1-r_2|}\right|\varphi_i(x_1)\varphi_j(x_2)\right\rangle$$

$$\Downarrow$$

$$E_{X\alpha}[\rho] = -\frac{9}{8}\left(\frac{3}{\pi}\right)^{1/3}\alpha\int\rho(r)^{4/3}dr$$

Basis of DFT

(Density Functional Theory)

Existence theorem : Hohenberg-Kohn (1964)

The external potential V_{ext} is a unique functional of the density $\rho(r)$. Since V_{ext} determines the hamiltonian H_{elec}, the fundamental state is a functional of the density.

$$H = T + V_{ee} + V_{ext}$$

$$\rho_0 \Rightarrow \{N, Z_A, R_A\} \Rightarrow H \Rightarrow \Psi_0 \Rightarrow E_0$$

Basis of DFT

$$H = T + V_{ee} + V_{ext}$$

$$E_0[\rho_0] = \underbrace{T[\rho_0] + E_{ee}[\rho_0]}_{F_{HK}[\rho_0]} + \int V_{ext}\rho_0(r)dr$$

Molecule

$$E_{ee}[\rho] = \underbrace{\frac{1}{2}\iint \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2}_{K[\rho]} + \boxed{E_{XC}[\rho]}$$

$$\rightarrow \begin{cases} \text{self} - \text{interaction} \\ \text{exchange} \\ \text{correlation} \end{cases}$$

Basis of DFT

(Density Functional Theory)

Kohn-Sham (1965)

Reference : non-interacting electrons (Slater determinant)

$$\hat{F}_{HF}\varphi_i^{HF} = \varepsilon_i^{HF}\varphi_i^{HF} \leftrightarrow \hat{F}_{KS}\varphi_i^{KS} = \varepsilon_i^{KS}\varphi_i^{KS}$$

$$F_{HK}[\rho] = T_{KS}[\rho] + K[\rho] + \int V_{ext}\rho(r)dr + \boxed{E_{XC}[\rho]}$$

Practical implementations

$$F_{HK}[\rho] = T_{KS}[\rho] + K[\rho] + \int V_{ext}\rho(r)dr + \boxed{E_{XC}[\rho]}$$

- **Density Functionals (XC)**
  - LDA
  - GGA
  - MetaGGA
  - Hartree-Fock
  - Hybrid
  - Meta-Hybrid
  - Range separated hybrids
  - Notes on Hartree-Fock and (meta-)hybrid functionals
  - Model Potentials

Available LDA functionals:

- **Xonly**: The pure-exchange electron gas formula. Technically this is identical to the Xalpha form (see next) with a value 2/3 for the X-alpha parameter.
- **Xalpha**: The scaled (parametrized) exchange-only formula. When this option is used you may (optionally) specify the X-alpha *parameter* by typing a numerical value after the string Xalpha (separated by a blank). If omitted this parameter takes the default value 0.7
- **VWN**: The parametrization of electron gas data given by Vosko, Wilk and Nusair (ref [20], formula version V). Among the available LDA options this is the more advanced one, including correlation effects to a fair extent.
- **PW92**: the parametrization of electron gas data given by Perdew and Wang (ref [288]).

Practical implementations

$$F_{HK}[\rho] = T_{KS}[\rho] + K[\rho] + \int V_{ext}\rho(r)dr + \boxed{E_{XC}[\rho]}$$

- **Density Functionals (XC)**
  - LDA
  - GGA
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For the **exchange** part the options are:

- **Becke**: Becke (1988) [22].
- **PW86x**: Perdew-Wang (1986) [23].
- **PW91x**: Perdew-Wang (1991) [24]
- **mPWx**: Modified PW91 by Adamo-Barone (1998) [25]
- **PBEx**: Perdew-Burke-Ernzerhof (1996) [26]
- **RPBEx**: revised PBE by Hammer-Hansen-Norskov (1999) [27]
- **revPBEx**: revised PBE by Zhang-Wang (1998) [28]
- **mPBEx**: Modified PBE by Adamo-Barone (2002) [174]
- **PBEsolx**: Perdew-Ruzsinszky-Csonka-Vydrov-Scuseria (2008) [285]
- **HTBSx**: [437]
- **OPTX**: Handy-Cohen (2001) [29]
- **BEEx**: Mortensen-Kaasbjerg-Frederiksen-Nørskov-Sethna-Jacobsen (2005) [284]

For the **correlation** part the options are:

- **Perdew**: Perdew (1986) [30].
- **PBEc**: Perdew-Burke-Ernzerhof (1996) [26] .
- **PBEsolc**: The PBEsol correlation correction by Perdew-Ruzsinszky-Csonka-Vydrov-Scuseria (2008) [285]
- **PW91c**: Perdew-Wang (1991), see [24].
- **LYP**: Lee-Yang-Parr (1988) correlation correction [31-33].

Practical implementations

$$F_{HK}[\rho] = T_{KS}[\rho] + K[\rho] + \int V_{ext}\rho(r)dr + \boxed{E_{XC}[\rho]}$$

- **Density Functionals (XC)**
  - LDA
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Available GGA functionals:

- **BP86**: Exchange: Becke, Correlation: Perdew
- **PW91**: Exchange: pw91x, Correlation: pw91c
- **mPW**: Exchange: mPWx, Correlation: pw91c
- **PBE**: Exchange: PBEx, Correlation: PBEc
- **RPBE**: Exchange: RPBEx, Correlation: PBEc
- **revPBE**: Exchange: revPBEx, Correlation: PBEc
- **mPBE**: Exchange: mPBEx, Correlation: PBEc
- **PBEsol**: Exchange: PBEsolx, Correlation: PBEsolc
- **HTBS**: Exchange: HTBSx, Correlation: PBEc
- **BLYP**: Exchange: Becke, Correlation: LYP
- **OLYP**: Exchange: OPTX, Correlation: LYP
- **OPBE**: Exchange: OPTX, Correlation: PBEc [175]
- **BEE**: Exchange: BEEx, Correlation: PBEc
- **XLYP**: Exchange: XLYPx [172] (exchange, not available separately from LYP) + LYP

Practical implementations

$$F_{HK}[\rho] = T_{KS}[\rho] + K[\rho] + \int V_{ext}\rho(r)dr + \boxed{E_{XC}[\rho]}$$

- **Density Functionals (XC)**
  - LDA
  - GGA
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  - Hybrid
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Available Hybrid functionals:

- **B3LYP**: ADF uses VWN5 in B3LYP. functional (20% HF exchange) by Stephens-Devlin-Chablowski-Frisch [176].
- **B3LYP***: Modified B3LYP functional (15% HF exchange) by Reiher-Salomon-Hess [177].
- **B1LYP**: Functional (25% HF exchange) by Adamo-Barone [178].
- **KMLYP**: Functional (55.7% HF exchange) by Kang-Musgrave [179].
- **O3LYP**: Functional (12% HF exchange) by Cohen-Handy [180].
- **X3LYP**: Functional (21.8% HF exchange) by Xu-Goddard [172].
- **BHandH**: 50% HF exchange, 50% LDA exchange, and 100% LYP correlation.
- **BHandHLYP**: 50% HF exchange, 50% LDA exchange, 50% Becke88 exchange, and 100% LYP correlation.
- **B1PW91**: Functional by (25% HF exchange) Adamo-Barone [178].
- **mPW1PW**: Functional (42.8% HF exchange) by Adamo-Barone [25].
- **mPW1K**: Functional (25% HF exchange) by Lynch-Fast-Harris-Truhlar [181].
- **PBE0**: Functional (25% HF exchange) by Ernzerhof-Scuseria [211] and by Adamo-Barone [212], hybrid form of PBE.
- **OPBE0**: Functional (25% HF exchange) by Swart-Ehlers-Lammertsma [175], hybrid form of OPBE.
- **S12H**: Dispersion corrected (Grimme-D3) functional (25% HF exchange) by Swart [367].

Comparaison between HF and DFT

$$\rho^{HF} = (\Psi^{HF})^2$$

$$\Psi_{\mathrm{CI}} = c_0 \Psi_0 + \sum_k c_k \Psi_k$$

→ Ψ^{HF} contains no correlation

→ ρ^{HF} is not the 'true' density ρ^{CI}

$$\Psi^{KS} \leftarrow \rho^{KS}$$

$$\rho_{\mathrm{CI}} = \left(c_0 \Psi_0 + \sum_k c_k \Psi_k \right)^2$$

→ Ψ^{KS} is not the wave function

→ ρ^{KS} close to the 'true' density ρ^{CI}

Case of 2 electrons : triplet state (S=1)

$$\Psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(r_1)\alpha_1(s_1) & \varphi_2(r_1)\alpha_2(s_1) \\ \varphi_1(r_2)\alpha_1(s_2) & \varphi_2(r_2)\alpha_2(s_2) \end{vmatrix}$$

$$\left[\Phi_1(r_1)\Phi_2(r_2) - \Phi_2(r_1)\Phi_1(r_2)\right]\alpha(1)\alpha(2)$$

$$\rho^{HF} \sim (\Psi_1)^2$$

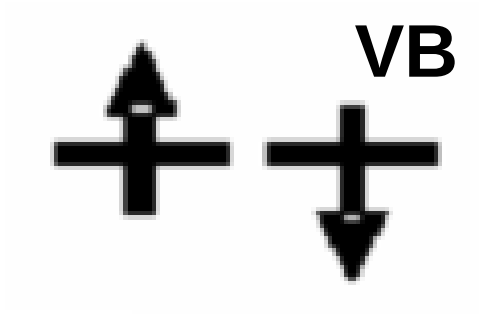
High-spin state :
~ one determinant

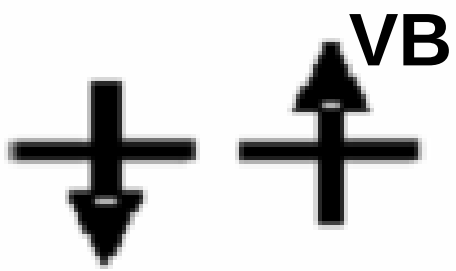
$$\rho^{KS} = \left(\Psi^{KS}\right)^2$$

Case of 2 electrons : singlet state (S=0)

$$\Psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \Phi_1(r_1)\alpha(1) & \Phi_1(r_2)\alpha(2) \\ \Phi_2(r_1)\beta(1) & \Phi_2(r_2)\beta(2) \end{vmatrix}$$

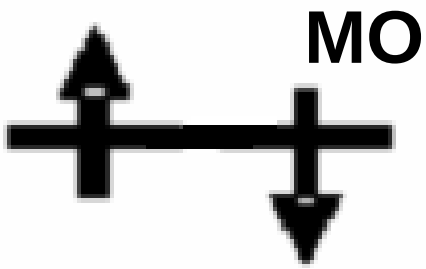
$$\Psi_3 = \frac{1}{\sqrt{2}} \begin{vmatrix} \Phi_1(r_1)\beta(1) & \Phi_1(r_2)\beta(2) \\ \Phi_2(r_1)\alpha(1) & \Phi_2(r_2)\alpha(2) \end{vmatrix}$$





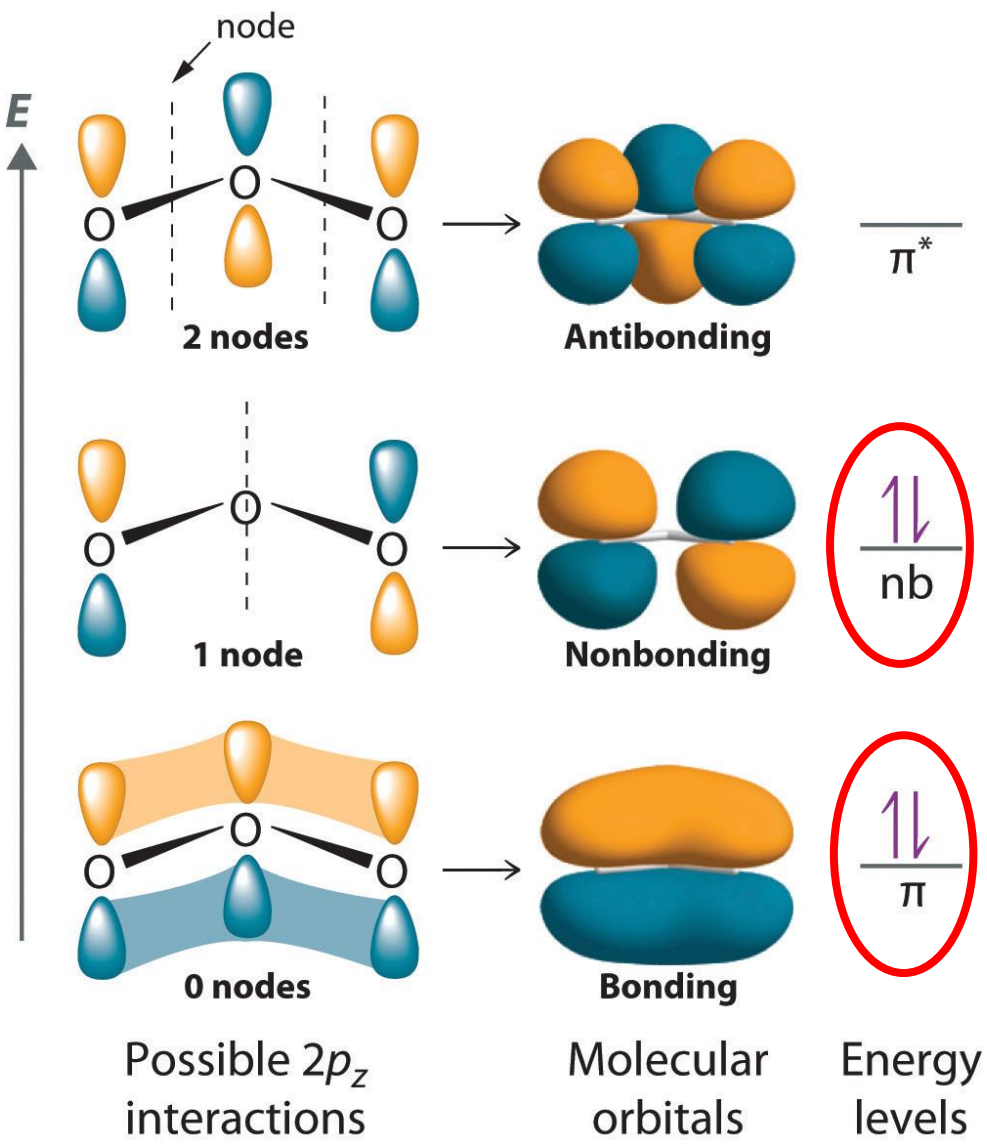
$$\left[\Phi_1(r_1)\Phi_2(r_2) + \Phi_2(r_1)\Phi_1(r_2)\right]\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

$$\rho^{HF} \sim (\Psi_2 - \Psi_3)^2$$

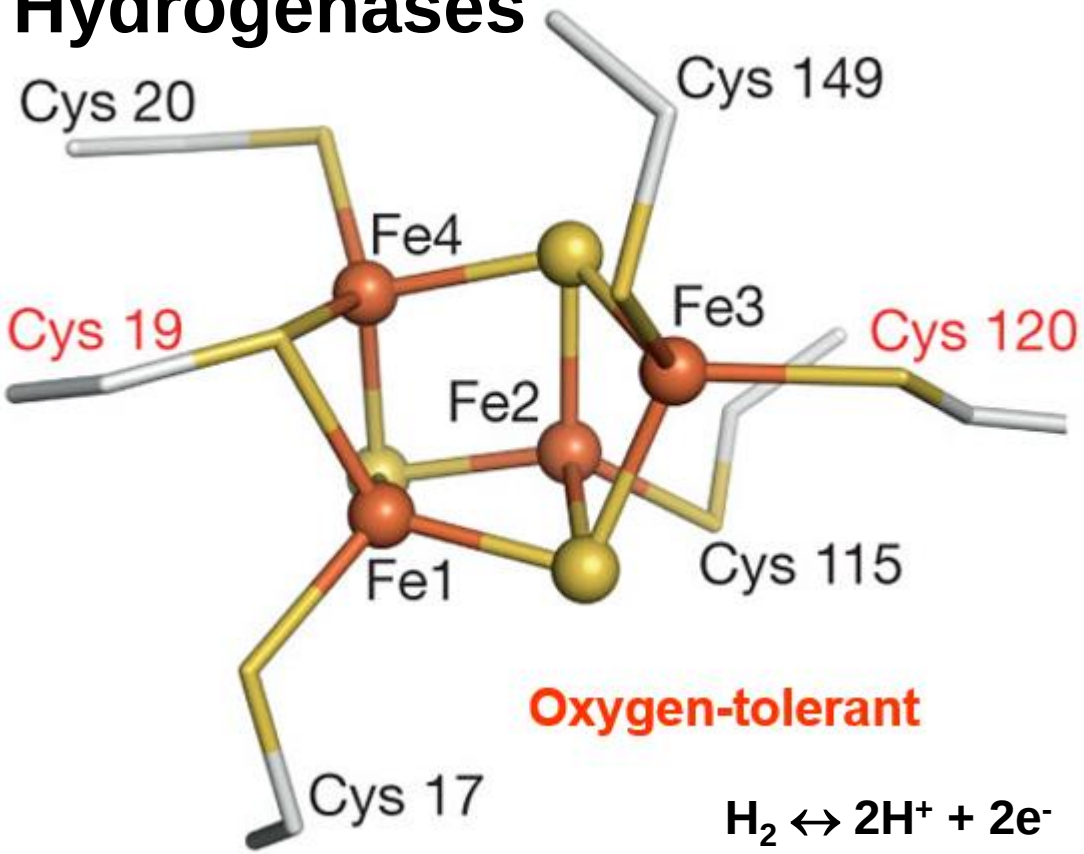


$$\rho^{KS} = \left(\Psi^{KS}\right)^2$$

Organic molecules *versus* (poly)metallic complexes



Hydrogenases



Oxygen-tolerant

$H_2 \leftrightarrow 2H^+ + 2e^-$

charge : $\rho_e(r) = \rho_\alpha(r) + \rho_\beta(r)$

spin : $\rho_s(r) = \rho_\alpha(r) - \rho_\beta(r)$

Outline of the lecture

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  - ***Hartree-Fock* versus *DFT***
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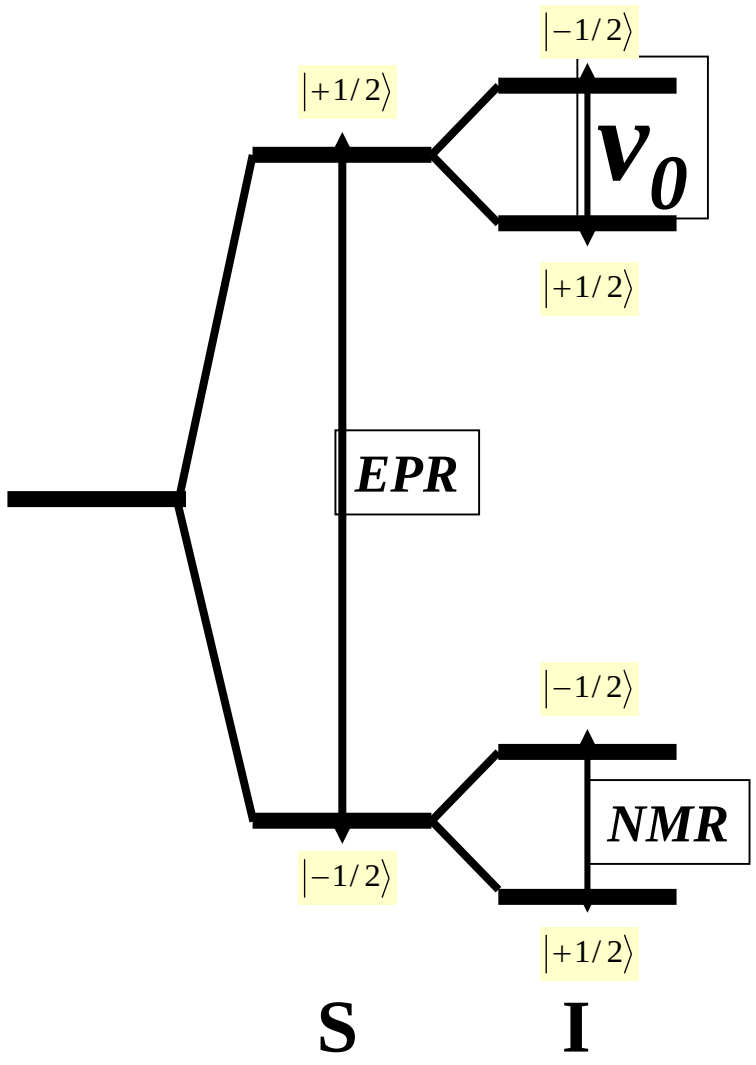
  - ***g-tensor (dimer)***
  - ***Hyperfine couplings (dimer)***
    - ***More complex systems : hyperfine & Mössbauer***
- ***Conclusions***

Zeeman interactions



Between nuclear spins {I} and the magnetic field H

→ ***NMR : chemical shifts***

$$g_I \beta_I \vec{B}.\vec{I}$$

Between electronic spins S and the magnetic field H

→ ***EPR : g tensors***

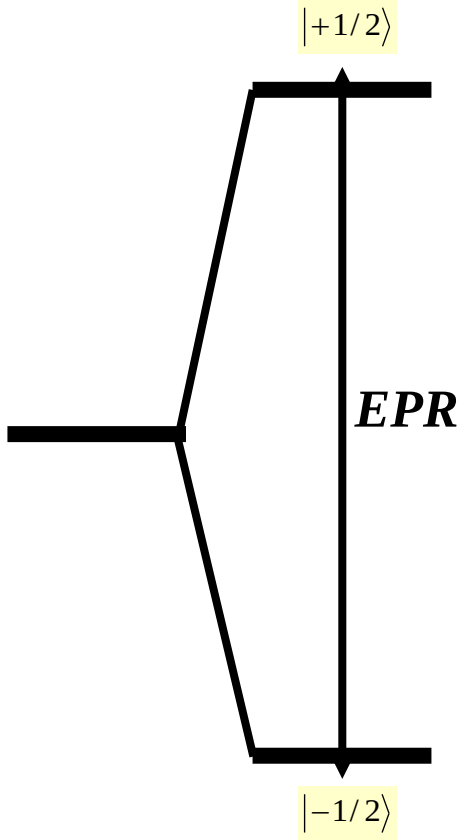
$$g_e \beta_e \vec{B}.\vec{s}$$

The « g » tensor

The origin of the signal is therefore the **electron**. In fact, since many students of chemistry are much more familiar with NMR, one way of describing EPR is as if it were NMR *with the electron as the* ***observe nucleus***. To extend this analogy a little further:

NMR property	EPR equivalent
• observe nucleus (e.g. ^{1}H, ^{77}Se)	• one or more unpaired electrons
• magnetic dipole vs. magnetic quadrupole	• $m_s = \pm ½$ (i.e. resembles spin-½ nuclei)
• chemical shift (i.e. field/frequency ratio)	• g-value (i.e. field/frequency ratio)
• homo-nuclear coupling	• *normally not seen - all electrons equivalent*
• hetero-nuclear coupling (*always* first-order)	• hyperfine splitting (*always* first-order)

Zeeman interactions



$$g_e \beta_e B$$

s

$$g_e \beta_e \vec{B}.\vec{s}$$

Electron $spin : \vec{s}$

orbital moment : $\vec{\ell}$

$$H_{Zeeman} = \beta_e (\vec{\ell} + g_e \vec{s}).\vec{B}$$

$$+ \zeta \vec{\ell}.\vec{s} \quad \text{(spin - orbit)}$$

$$\Rightarrow \beta_e \vec{B}.\tilde{g}.\vec{s}$$

$g_e \sim 2$

Introduction to the spin
(Dirac theory for one electron

Non linear $$\frac{E^2}{c^2} - p^2 = m^2c^2$$

$$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2})\phi = \frac{m^2c^2}{\hbar^2}\phi$$

Linear $$-\frac{\hbar^2}{2m}\nabla^2\phi = i\hbar\frac{\partial}{\partial t}\phi$$

Linearized $$\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} = (A\partial_x + B\partial_y + C\partial_z + \frac{i}{c}D\partial_t)(A\partial_x + B\partial_y + C\partial_z + \frac{i}{c}D\partial_t)$$

Pauli

$$\sigma_k = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\left(\beta mc^2 + \sum_{k=1}^{3}\alpha_k p_k c\right)\psi(\mathbf{x},t) = i\hbar\frac{\partial\psi}{\partial t}(\mathbf{x},t)$$

$2s_Y$	$\lvert\alpha\rangle$	$+i\lvert\beta\rangle$
$\langle\alpha\rvert$	0	1
$-i\langle\beta\rvert$	1	0

$2s_X$	$\lvert\alpha\rangle$	$+i\lvert\beta\rangle$
$\langle\alpha\rvert$	0	$+i$
$-i\langle\beta\rvert$	$-i$	0

$2s_Z$	$\lvert\alpha\rangle$	$+i\lvert\beta\rangle$
$\langle\alpha\rvert$	1	0
$-i\langle\beta\rvert$	0	-1

Introduction to the spin (approximated Dirac's theory : Breit equation)

$$H_e = \sum_i \frac{p_i^2}{2m_i} + \sum_i \sum_{j>i} \frac{e^2}{|r_i - r_j|} - \sum_A \sum_i \frac{Z_A e^2}{|R_A - r_i|}$$

$$H_1^e = \sum_i \pi^2(i)/2m$$

$$H_7^e = (e^2/2) \sum_{i,j}{}' (1/r_{ij})$$

$$H_1^{en} = -e^2 \sum_{i,n} Z_n/r_{ni}$$

McWeeny & Sutcliffe
Methods of Molecular QM
Academic Press (1969)

Electronic terms

Introduction to the spin (approximated Dirac's theory : Breit equation)

$$H_3^e = g\beta \sum_i \mathbf{S}(i).\mathbf{B}(i)$$

$$\sim g_e \beta_e \vec{B}.\vec{s}$$

$$H_2^n = -\beta_p \sum_n g_n \mathbf{I}(n).\mathbf{B}(n)$$

$$\sim g_I \beta_I \vec{B}.\vec{I}$$

Zeeman terms

$$H_{11}^e = -(g^2\beta^2/2) \sum_{i,j}{}' r_{ij}^{-5}[3(\mathbf{S}(j).\mathbf{r}_{ij})(\mathbf{S}(i).\mathbf{r}_{ij}) - r_{ij}^2 \mathbf{S}(i).\mathbf{S}(j)]$$

$$H_{12}^e = -(4\pi g^2\beta^2/3) \sum_{i,j}{}' \mathbf{S}(i).\mathbf{S}(j)\delta(\mathbf{r}_i - \mathbf{r}_j).$$

Spin-spin term $\vec{S}.\tilde{D}.\vec{S}$

$$H_9^e = -(g\beta^2/\hbar) \sum_{i,j}{}' r_{ij}^{-3}[2\mathbf{S}(i).\mathbf{r}_{ij} \times \boldsymbol{\pi}(j) + \mathbf{S}(j).\mathbf{r}_{ij} \times \boldsymbol{\pi}(j)]$$

$$+ \zeta \vec{\ell}.\vec{s}$$

$$H_5^{en} = (\beta^2/\hbar) \sum_{i,n} Z_n r_{ni}^{-3}[\mathbf{S}(i).\mathbf{r}_{ni} \times \boldsymbol{\pi}(i)]$$

Spin-orbit coupling

Spin-orbit coupling

$$H_9^e = -(g\beta^2/\hbar)\sum_{i,j}{}' r_{ij}^{-3}[2\mathbf{S}(i).\mathbf{r}_{ij}\times\boldsymbol{\pi}(j)+\mathbf{S}(j).\mathbf{r}_{ij}\times\boldsymbol{\pi}(j)]$$

$$H_5^{en} = (\beta^2/\hbar)\sum_{i,n} Z_n r_{ni}^{-3}[\mathbf{S}(i).\mathbf{r}_{ni}\times\boldsymbol{\pi}(i)]$$

$$H_{SO} = \sum_{\mathrm{i}} \zeta_i(r_i)\vec{\ell}_i.\vec{s}_i$$

$$\vec{L} = \sum_i \vec{\ell}_i$$

$$\vec{S} = \sum_i \vec{s}_i$$

$$H_{SO} \rightarrow \lambda\vec{L}.\vec{S}$$

$$\lambda \equiv \pm\frac{\zeta(r)}{2S} \sim \left\langle \frac{1}{r_{Ai}^3} \right\rangle$$

Russel-Saunders' scheme

$$H_{Zeeman} = \beta_e(\vec{\ell} + \mathrm{g_e}\vec{\mathrm{s}}).\vec{\mathrm{B}}$$

$$+\ \zeta\vec{\ell}.\vec{S} \quad \text{(spin - orbit)}$$

$$\Rightarrow \beta_e\vec{\mathrm{B}}.\tilde{\mathrm{g}}.\vec{\mathrm{s}}$$

$$+\vec{S}.\tilde{D}.\vec{S}$$

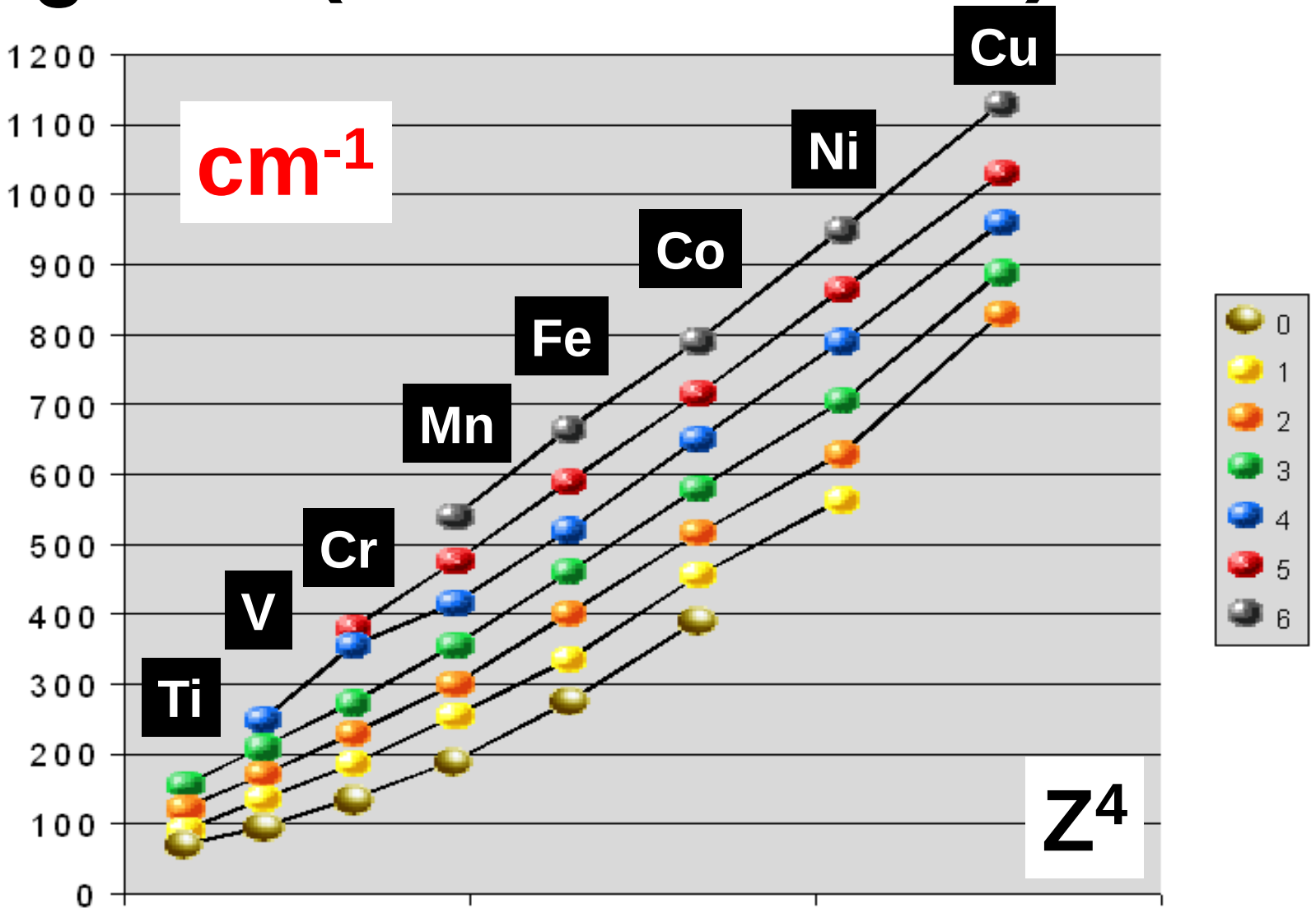
$$\Rightarrow \beta_e\vec{\mathrm{B}}.\tilde{\mathrm{g}}_{\mathrm{eff}}.\vec{\mathrm{s}}$$

SKIP !

Spin-orbit coupling (*mono-electronic*)

$$\lambda = \pm \frac{\zeta_{3d}}{2S}$$

n=3



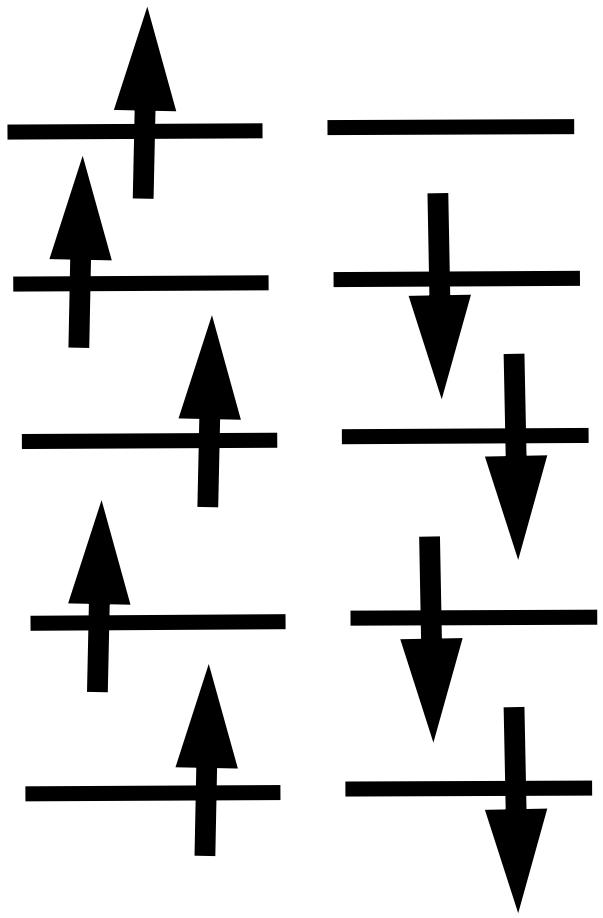
Spin-orbit coupling (*mono-electronic*)

$$\lambda = \pm \frac{\zeta_{3d}}{2S}$$

n=3

Métal	0	+1	+2	+3	+4	+5	+6
Ti	0.009	0.011	0.015	0.019			
V	0.012	0.017	0.021	0.026	0.031		
Cr	0.017	0.023	0.029	0.034	0.044	0.047	
Mn	0.024	0.032	0.037	0.044	0.051	0.059	0.067
Fe	0.034	0.042	0.050	0.057	0.064	0.073	0.082
Co	0.048	0.056	0.064	0.072	0.081	0.089	0.098
Ni		0.070	0.078	0.087	0.098	0.107	0.118
Cu			0.103	0.110	0.119	0.128	0.128

eV



Orbitals

Practical implementations

SCM
Software for Chemistry & Materials

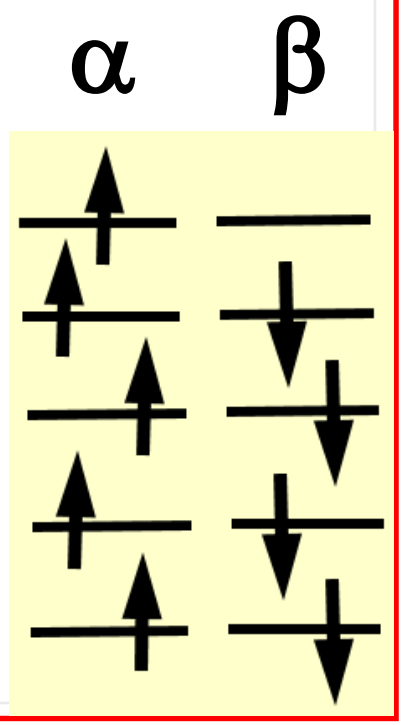
- ESR/EPR
  - ESR/EPR g-tensor and A-tensor
  - ESR/EPR Q-tensor
  - ESR/EPR Zero-field splitting (D-tensor)

Treatment of Spin-orbit coupling

$$H_{SO} \rightarrow \lambda \vec{L}.\vec{S}$$

g-tensor, perturbative inclusion spin-orbit coupling

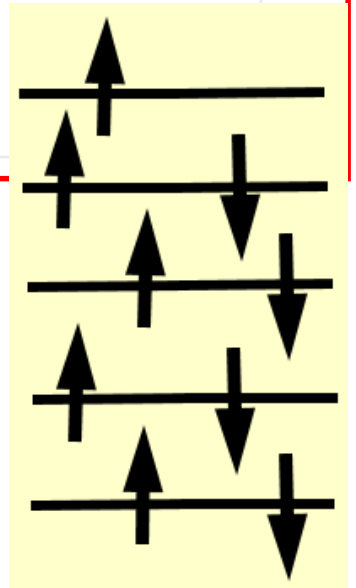
```
$ADFBIN/adf << eor
CHARGE charge spinpolarization
unrestricted
Relativistic scalar ZORA
Symmetry NOSYM
...
eor

$ADFBIN/nmr << eor
nmr
 gfactors
 u1k best
 calc all
 out iso tens
end
end input
eor
```



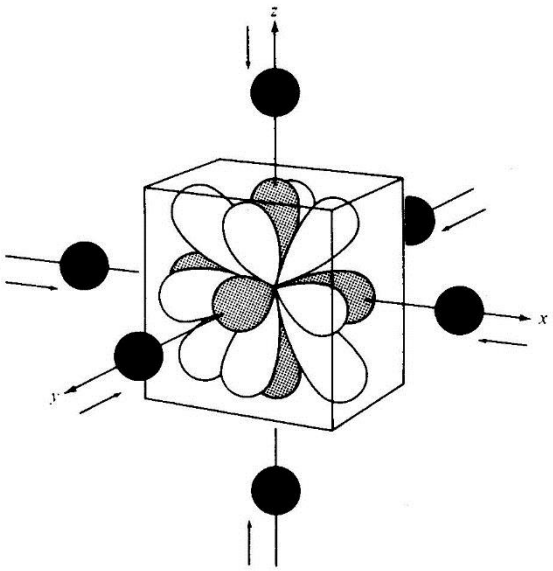
g-tensor and A-tensor, self consistent spin-orbit coupling

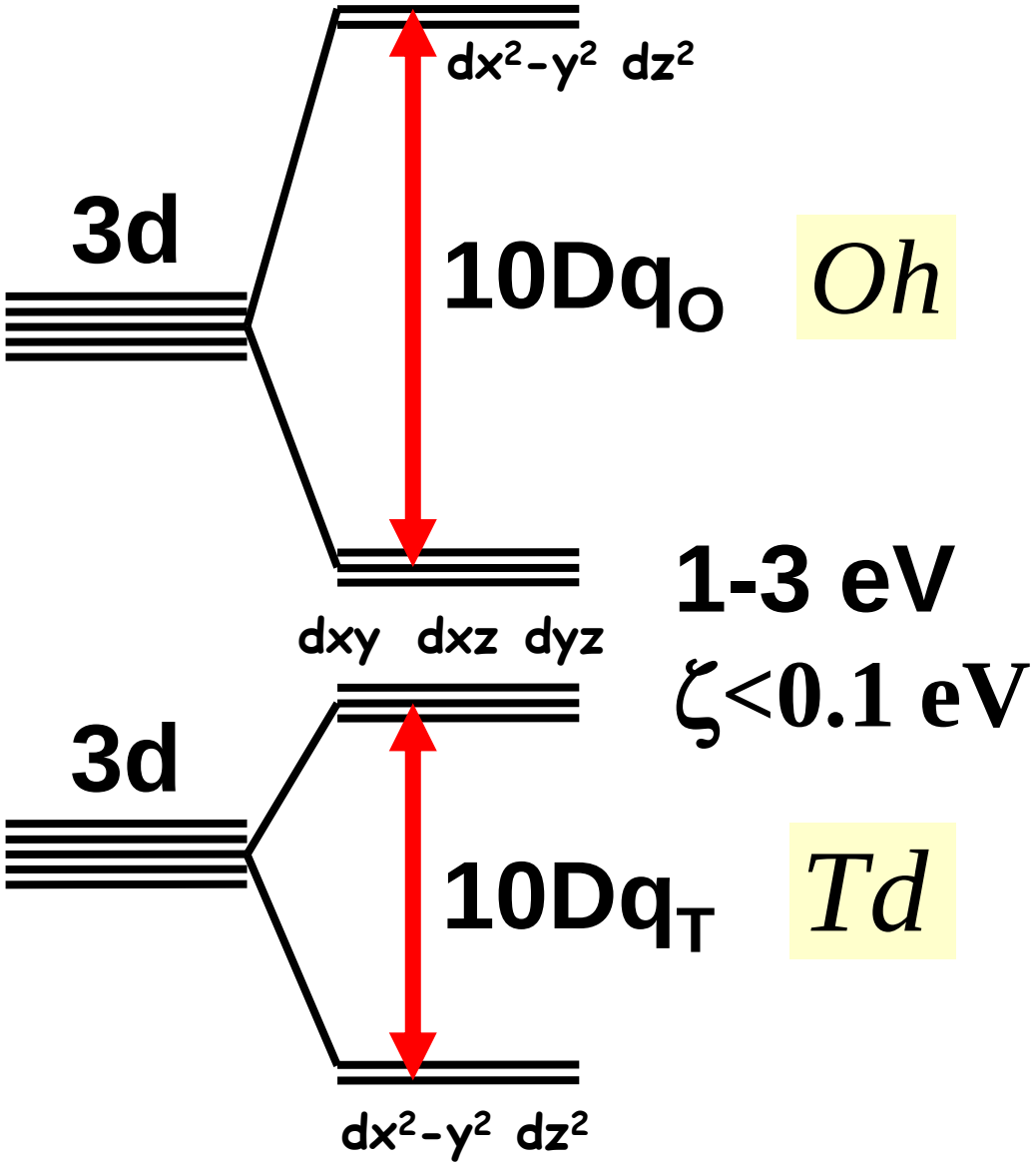
```
$ADFBIN/adf << eor
ESR
END
CHARGE charge
unrestricted
Relativistic spinorbit ZORA
Collinear
Symmetry NOSYM
eor
```

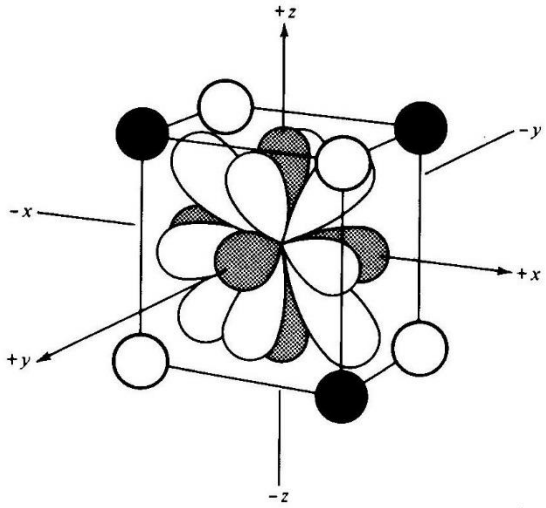
Spin-orbitals



Ligand field theory

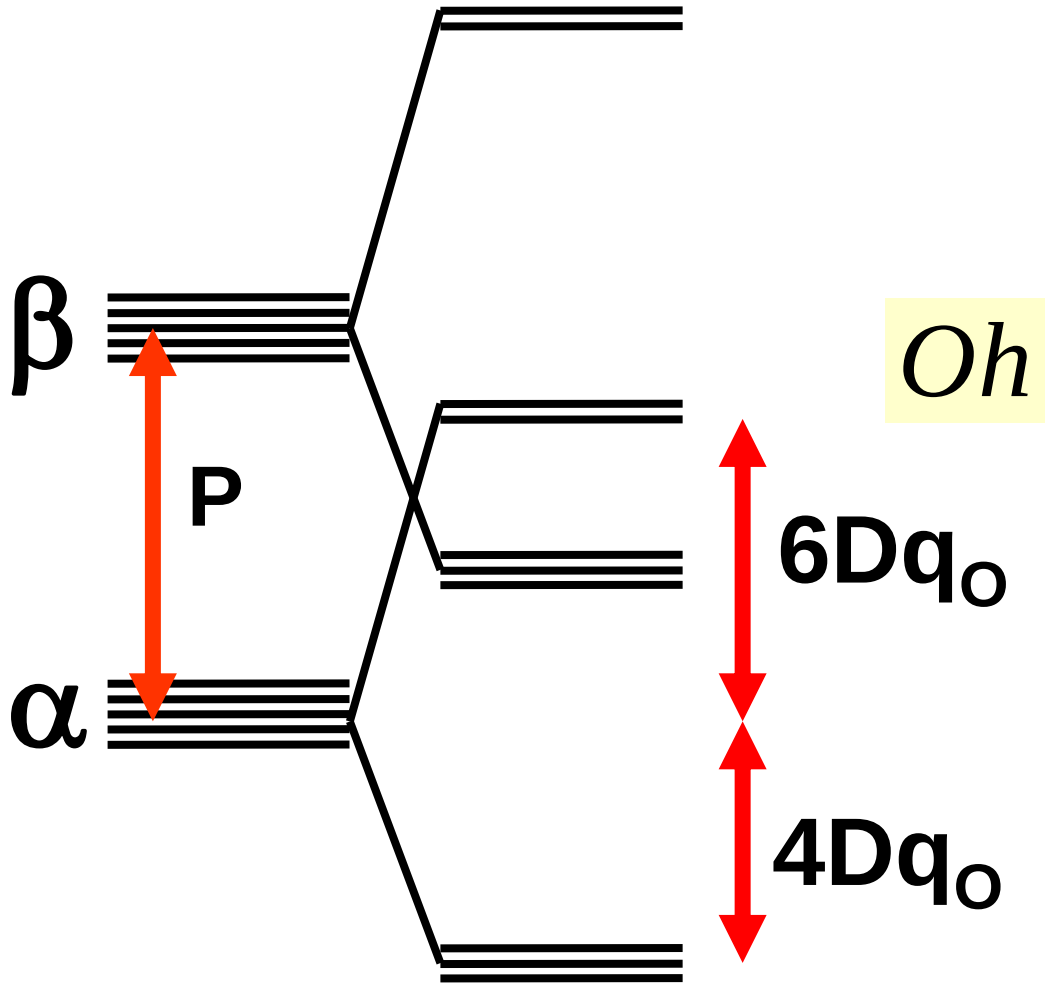






SKIP !

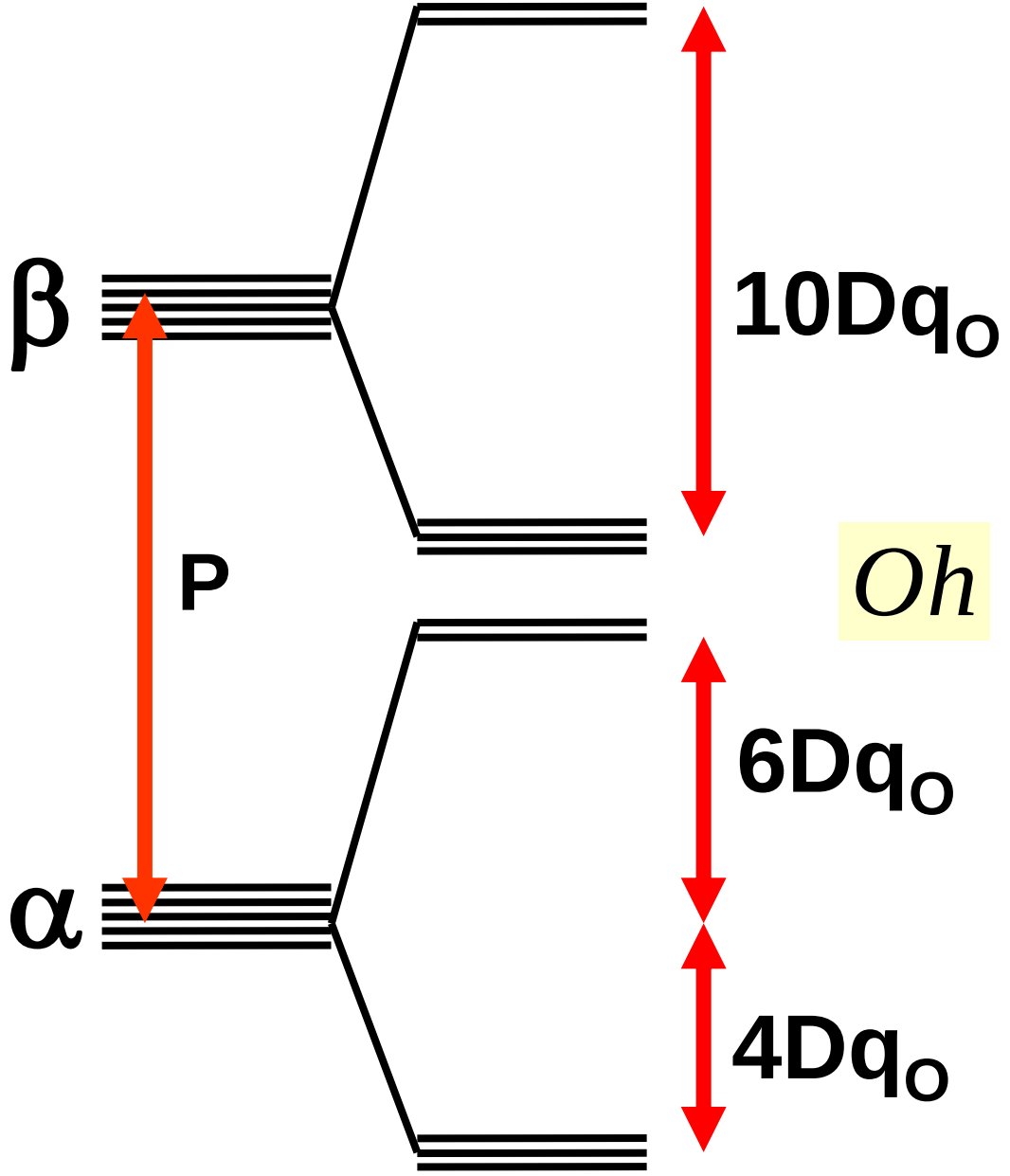
Strong ligand field



d^n	$CFSE$	$nb.$	$Spin$
d^1	$-4Dq$	1	$1/2$
d^2	$-8Dq$	2	1
d^3	$-12Dq$	3	$3/2$
d^4	$-16Dq+P$	2	1
d^5	$-20Dq+2P$	1	$1/2$
d^6	$-24Dq+2P$	0	0
d^7	$-18Dq+P$	1	$1/2$
d^8	$-12Dq$	2	1
d^9	$-6Dq$	1	$1/2$
d^{10}	$0Dq$	0	0

SKIP !

Weak ligand field

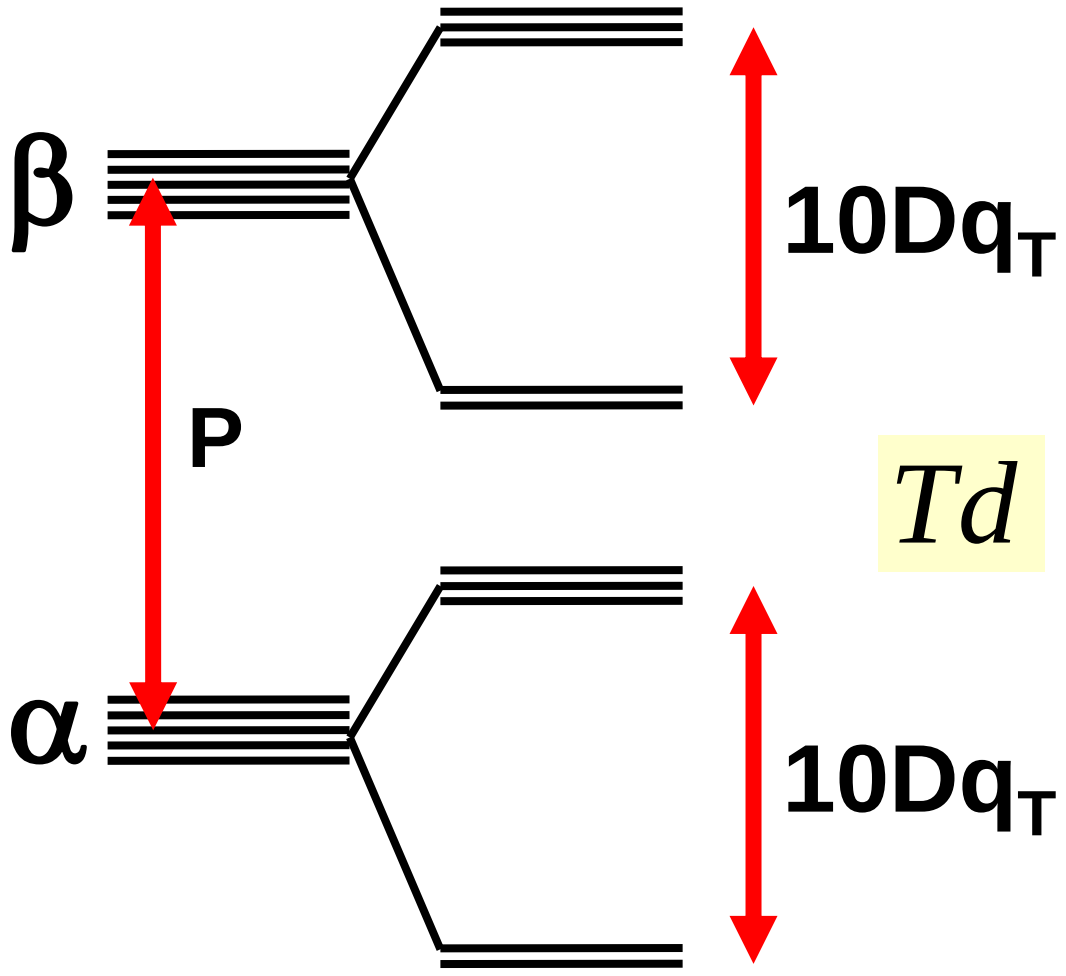


Oh

d^n	*CFSE*	*nb.*	*Spin*
d^1	$-4Dq$	1	1/2
d^2	$-8Dq$	2	1
d^3	$-12Dq$	3	3/2
d^4	$-6Dq$	4	2
d^5	$0Dq$	5	5/2
d^6	$-4Dq$	4	2
d^7	$-8Dq$	3	3/2
d^8	$-12Dq$	2	1
d^9	$-6Dq$	1	1/2
d^{10}	$0Dq$	0	0

SKIP !

Weak ligand field

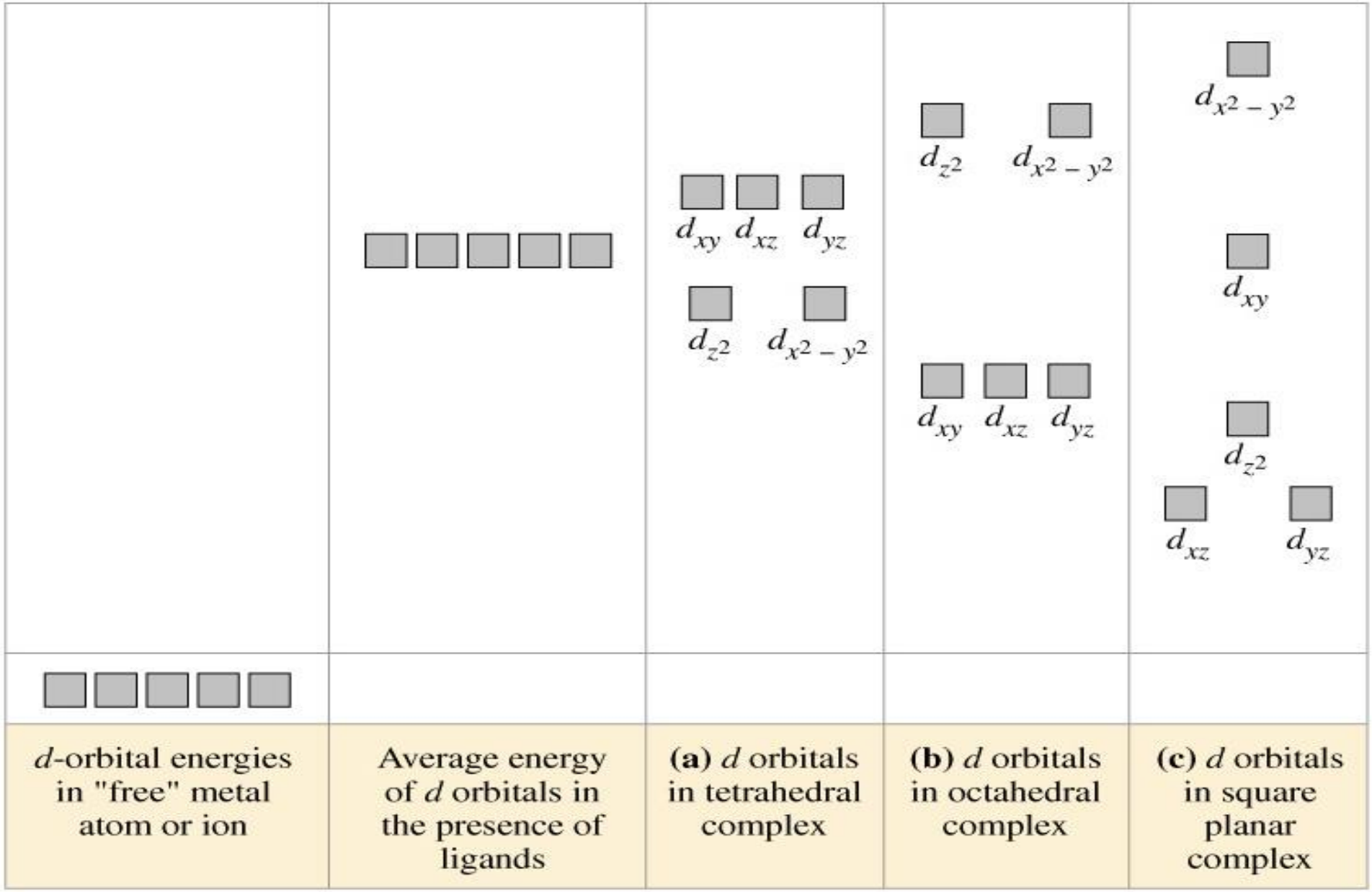


Td

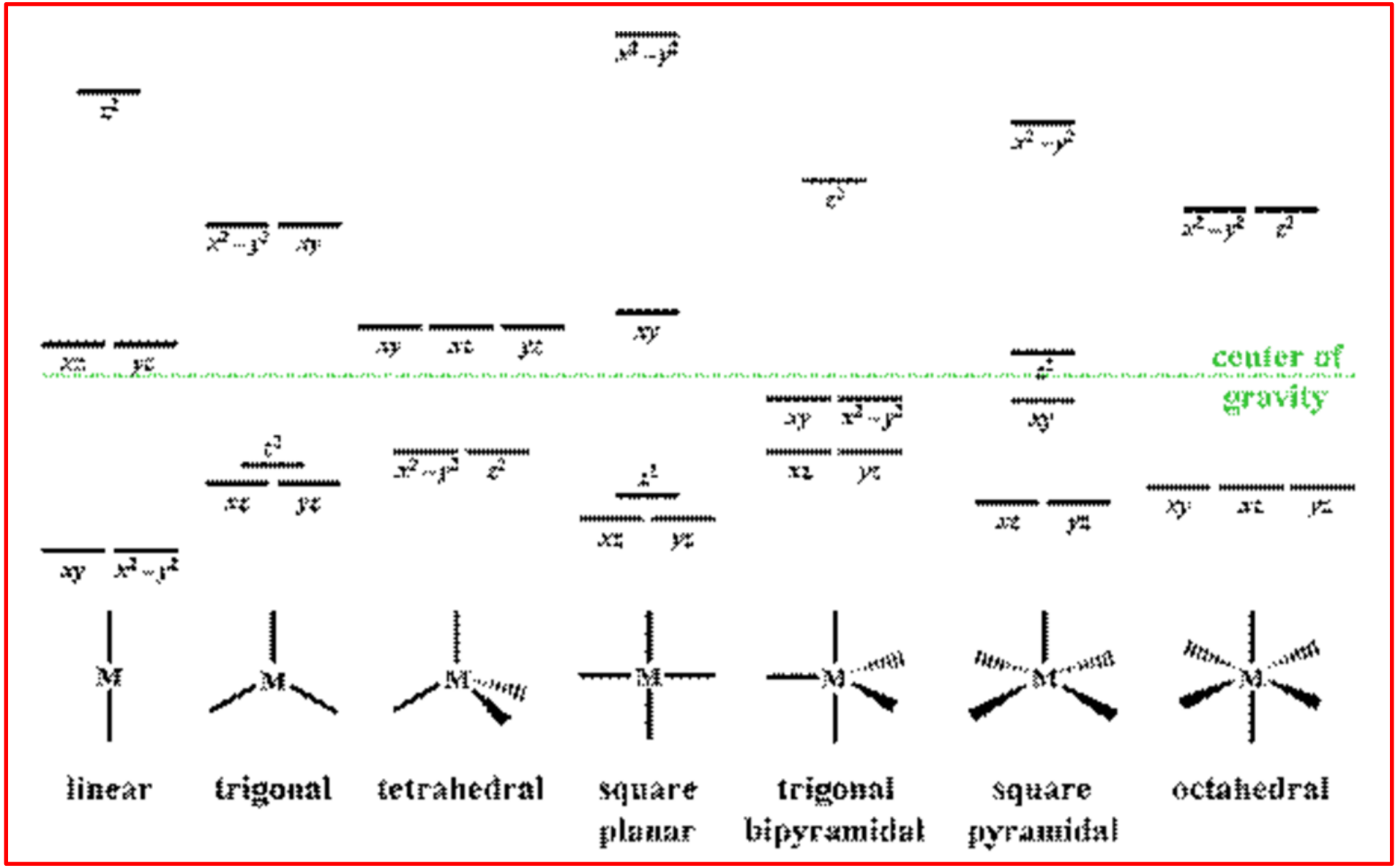
d^n	$CFSE$	$nb.$	$Spin$
d^1	$-6Dq$	1	$1/2$
d^2	$-12Dq$	2	1
d^3	$-8Dq$	3	$3/2$
d^4	$-4Dq$	4	2
d^5	$0Dq$	5	$5/2$
d^6	$-6Dq$	4	2
d^7	$-12Dq$	3	$3/2$
d^8	$-8Dq$	2	1
d^9	$-4Dq$	1	$1/2$
d^{10}	$0Dq$	0	0

SKIP !

Ligand field

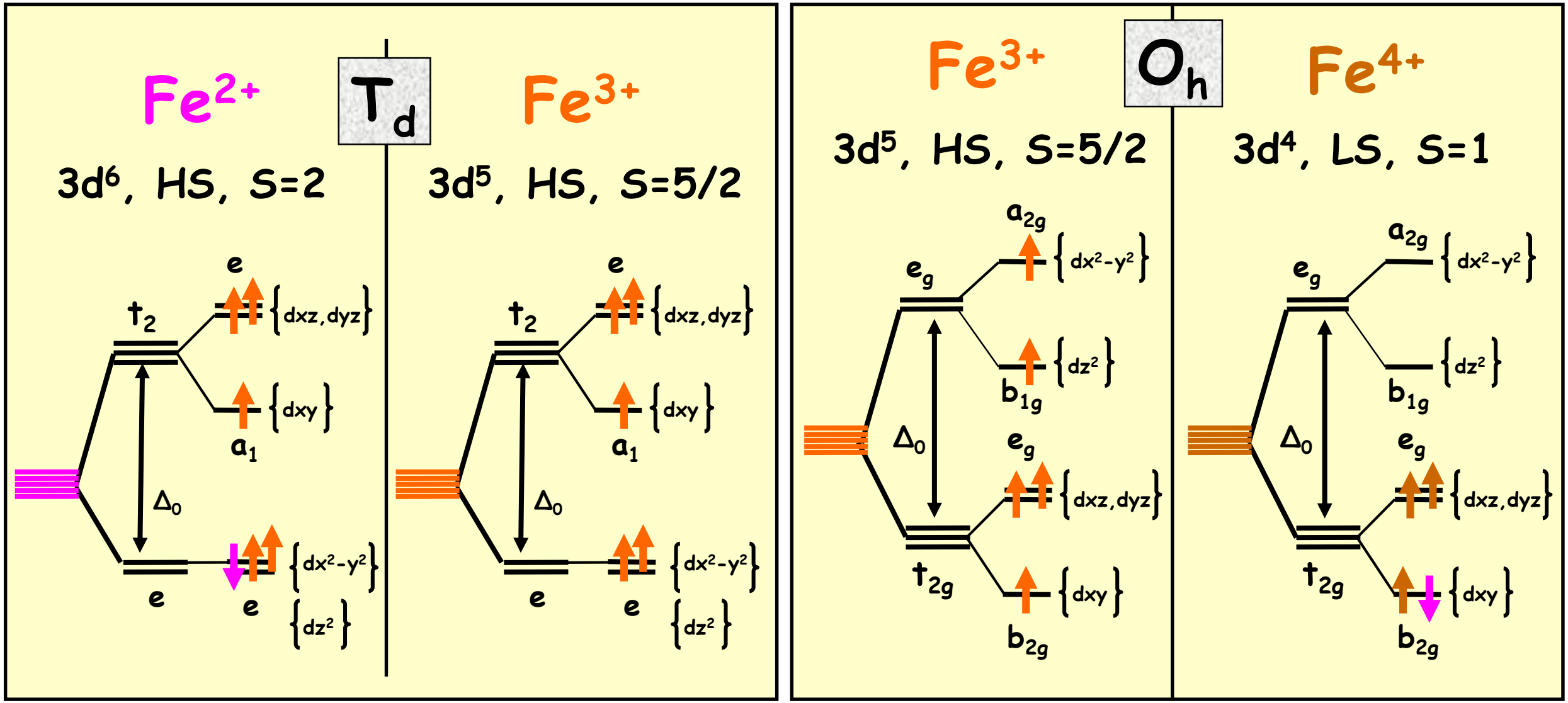


Ligand field

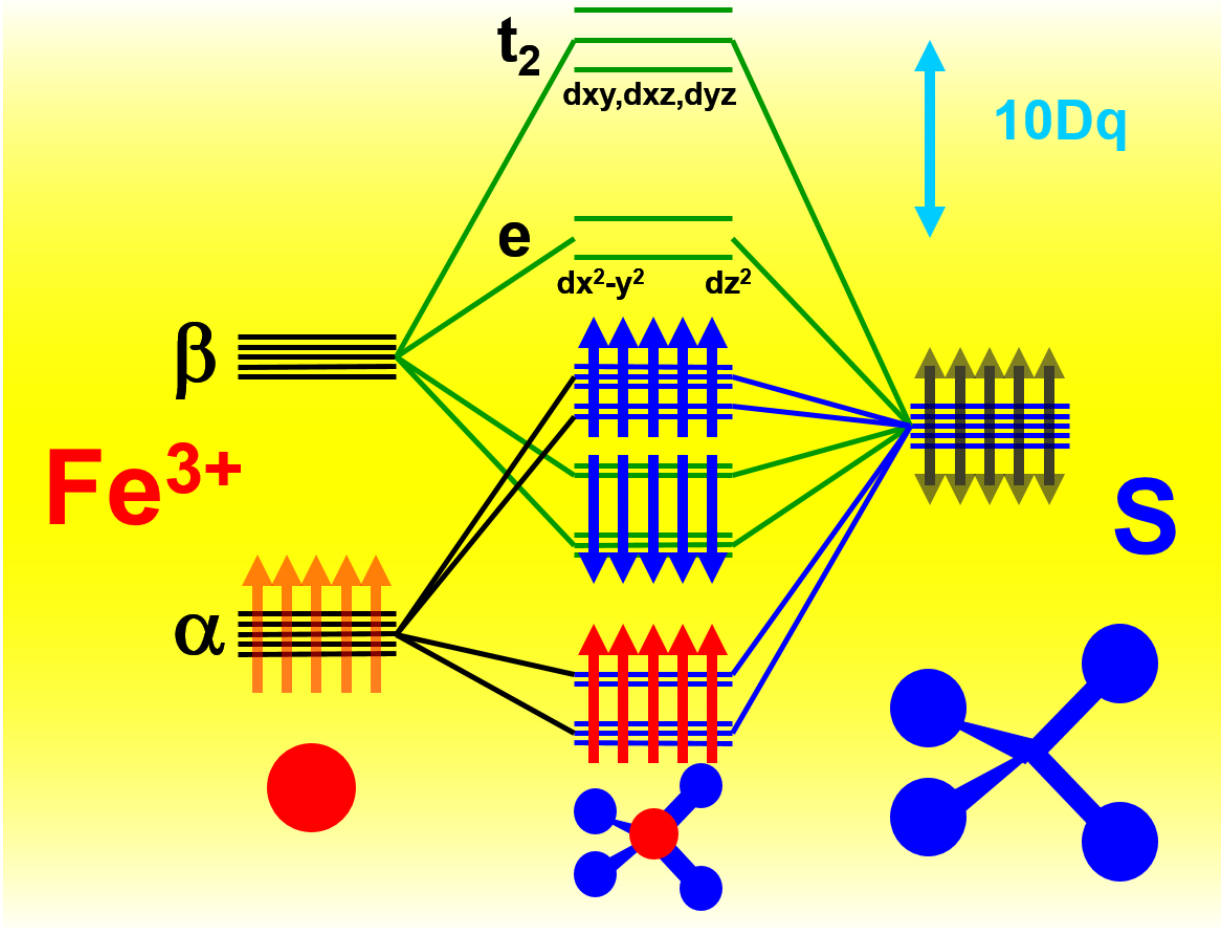


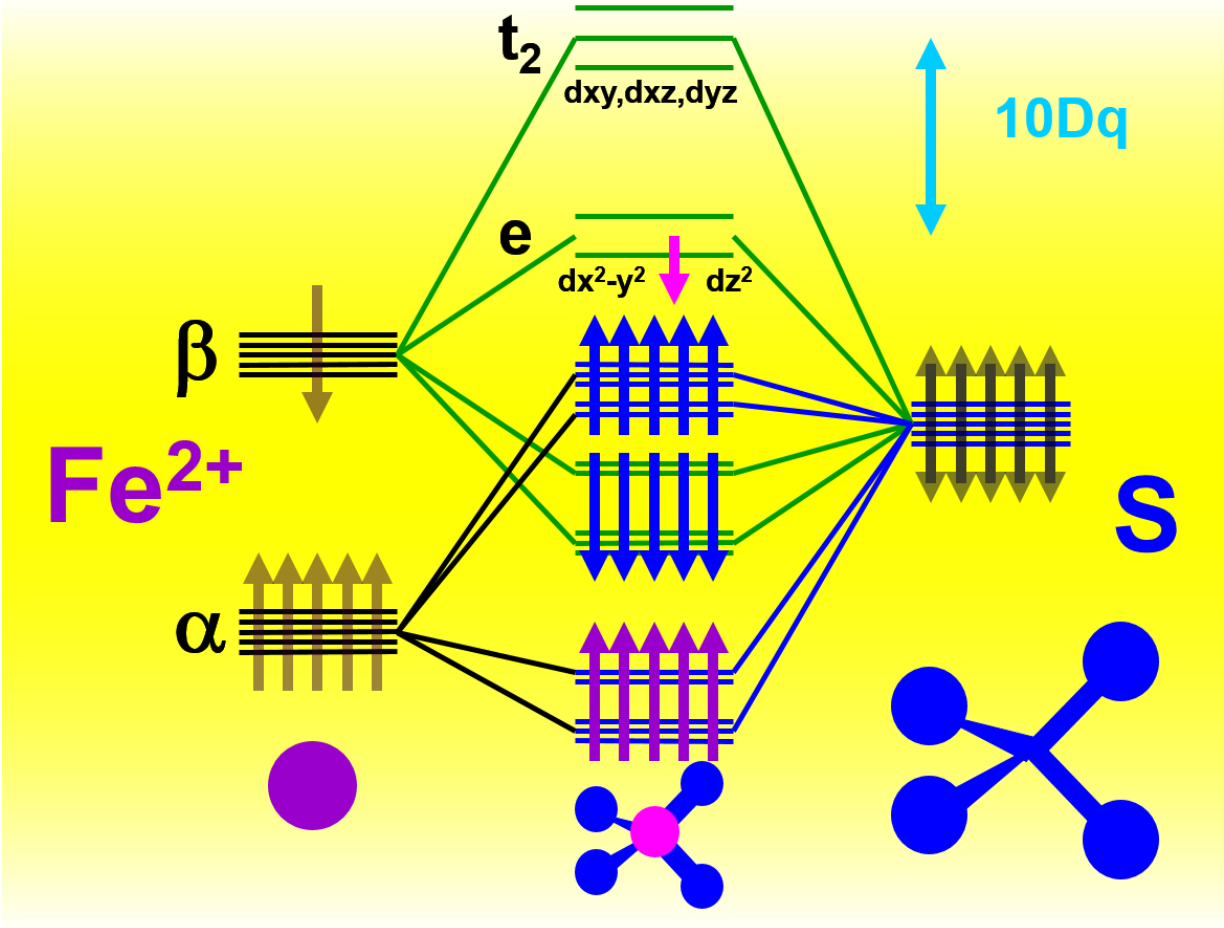
Source : plato.mercyhurst.edu/chemistry/kjircitano/InorgStudysheets/InorgStudyExamIII.htm

Ligand field



Ligand field in DFT :
Anti-bonding set of molecular orbitals





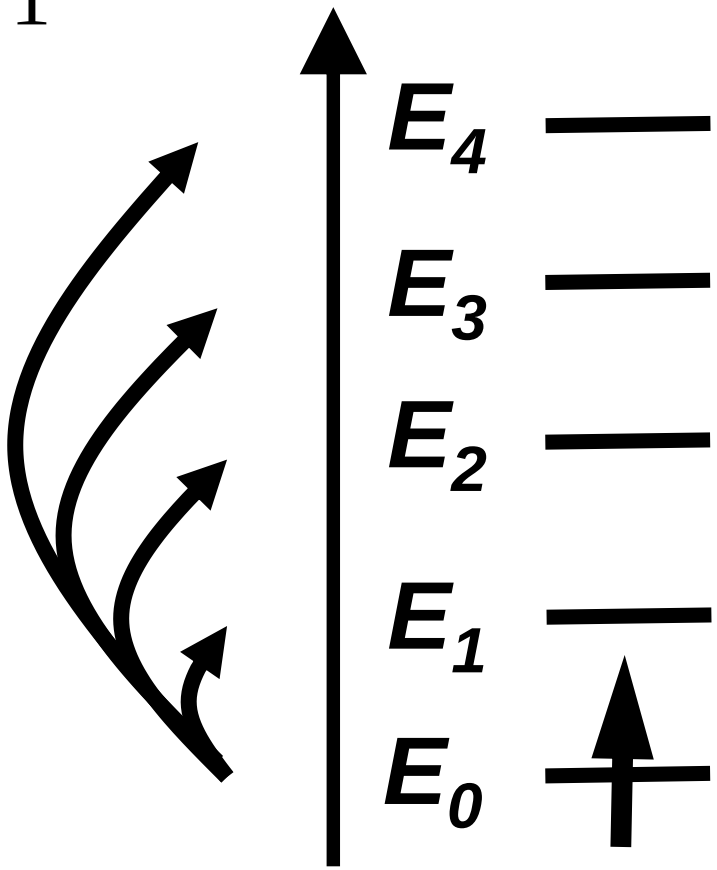
b_{2g} b_{2g}

(Perturbative) calculation of the g-tensor

$$H_{SO} = \lambda \vec{L}.\vec{S}$$

$$H_{Ze} = \beta_e \vec{\mathrm{B}}.(\vec{\mathrm{L}} + \mathrm{g_e}\vec{S})$$

d^1



$$H = \boxed{\beta \vec{B}.\tilde{g}.\vec{S}} + \vec{S}.\tilde{D}.\vec{S}$$

$$\boxed{g_{ij} \approx g_e \delta_{ij} - 2\lambda \sum_n \frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n - E_0}}$$

$$D_{ij} \approx \lambda^2 \sum_n \frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n - E_0}$$

g_e~2

(Perturbative) calculation of the g-tensor

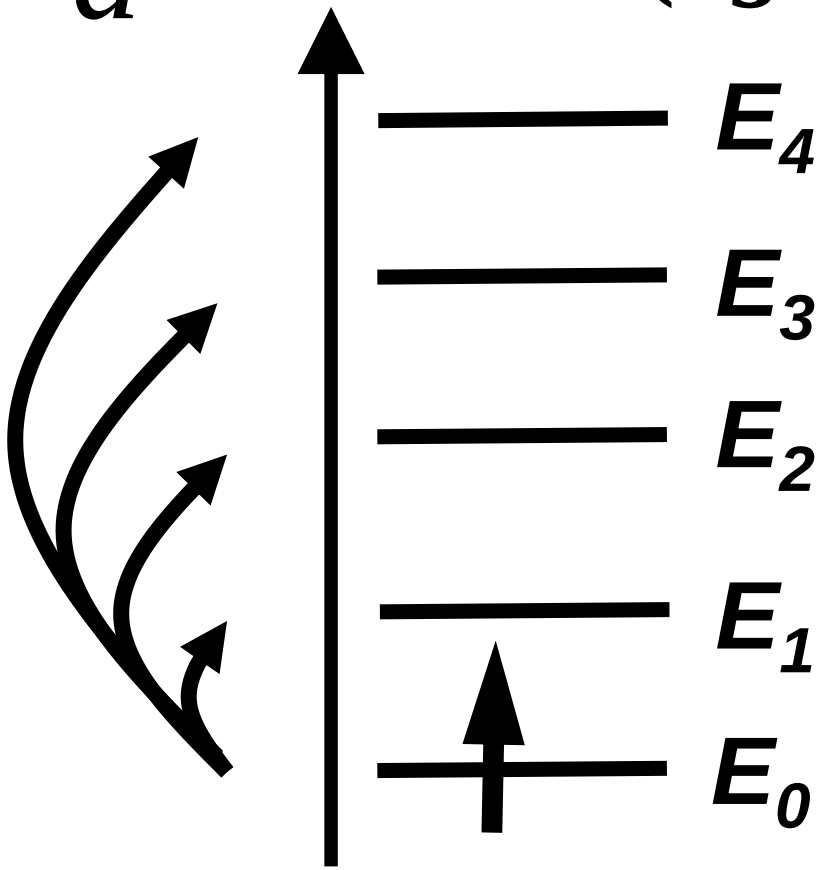
	L_x	L_y	L_z
z^2	$-i\sqrt{3}(yz)$	$i\sqrt{3}(xz)$	0
x^2-y^2	$-i(yz)$	$-i(xz)$	$+2(xy)$
xy	$+i(xz)$	$-i(yz)$	$-2(x^2-y^2)$
xz	$i(x^2-y^2)+i\sqrt{3}(z^2)$	$+i(xy)$	$-i(xz)$
yz	$-i(xy)$	$-i\sqrt{3}(z^2)+i(x^2-y^2)$	$+i(yz)$

$$g_{ij} \approx g_e\delta_{ij} - \frac{2\zeta_{3d}}{2S}\left(\sum_{\alpha} - \sum_{\beta}\right)\sum_{n}\frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n - E_0}$$

g tensor calculation
(*ligand field*)

$$\lambda = +\frac{\zeta_{3d}}{2S}$$

d^1



$$g_x \approx g_e - \frac{2\zeta_{3d}}{2S}\left(\frac{1}{E_1 - E_0}\right)$$

$$g_y \approx g_e - \frac{2\zeta_{3d}}{2S}\left(\frac{1}{E_2 - E_0}\right)$$

$$g_z \approx g_e - \frac{2\zeta_{3d}}{2S}\left(\frac{4}{E_4 - E_0}\right)$$

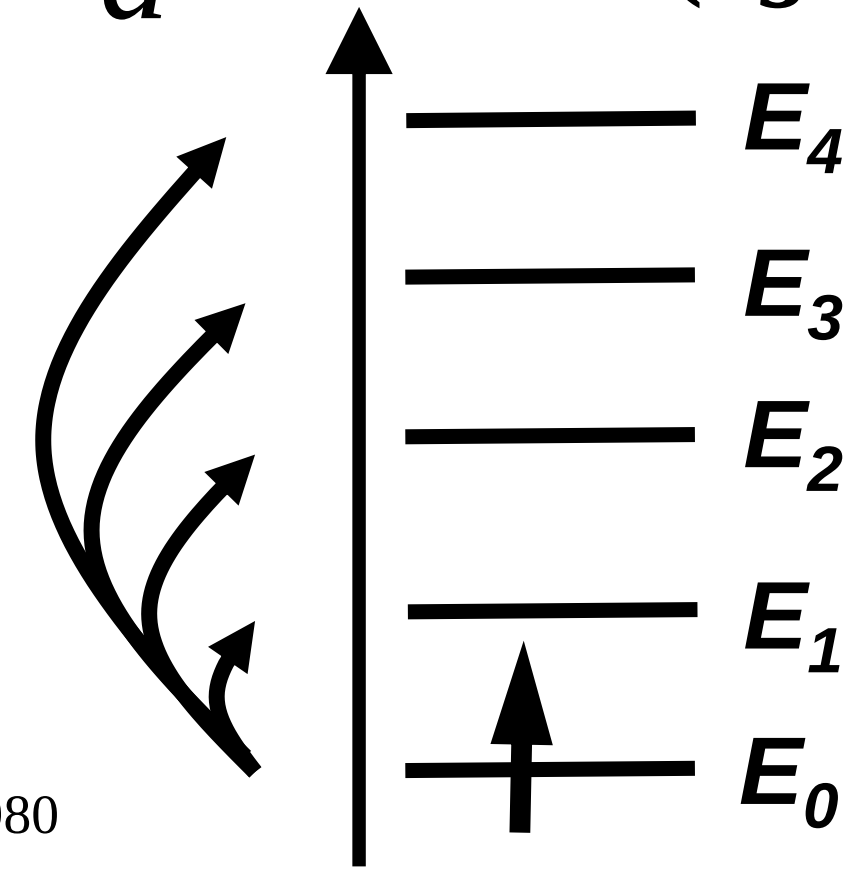
g_e~2

$$g_{ij} \approx g_e\delta_{ij} - \frac{2\zeta_{3d}}{2S}\left(\boxed{\sum_{\alpha}} - \sum_{\beta}\right)\sum_{n}\frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n - E_0}$$

g tensor calculation (*ligand field*)

$$\lambda = +\frac{\zeta_{3d}}{2S}$$

d^1



$Ti^{3+}(d^1)$	g_1	g_2	g_3
TiO_6	1.828	1.898	1.979
TiO_6	1.921	1.921	2.000
TiO_4F_2	1.932	1.932	1.968
$Ticp_2F_2$	1.979	1.988	1.998
$Ticp_2Ge_2$	1.977	1.993	2.001
$Ticp_2H_2$	1.994	1.994	1.994
$Ticp_2H_2$	1.992	1.992	1.992

$Sc^{2+}(H_2O)_6$
1.971
1.974
1.980

$Ti^{3+}(H_2O)_6$
1.953
1.966
1.970

$V^{4+}(H_2O)_6$
1.930
1.930
1.992

$V^{2+}(d^3) \sim 1.980$

DFT : $V^{2+}(H_20)_6$

1.977

1.980

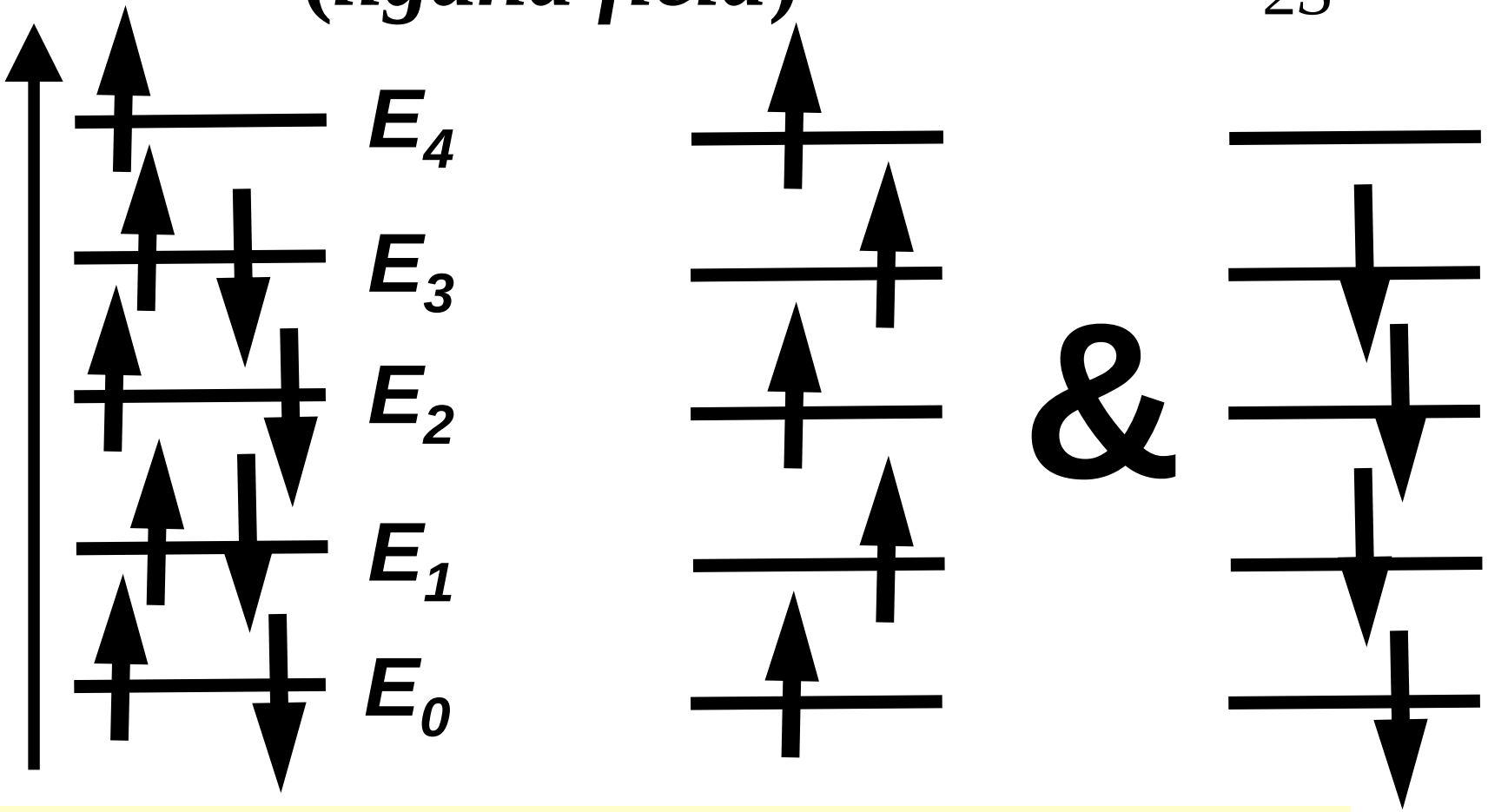
1.981

$$g_{ij} \approx g_e \delta_{ij} \boxed{-\frac{2\zeta_{3d}}{2S}} \left(\sum_{\alpha} \right) \sum_{n} \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0}$$

g tensor calculation
(*ligand field*)

d^9

$$\lambda = \pm \frac{\zeta_{3d}}{2S}$$

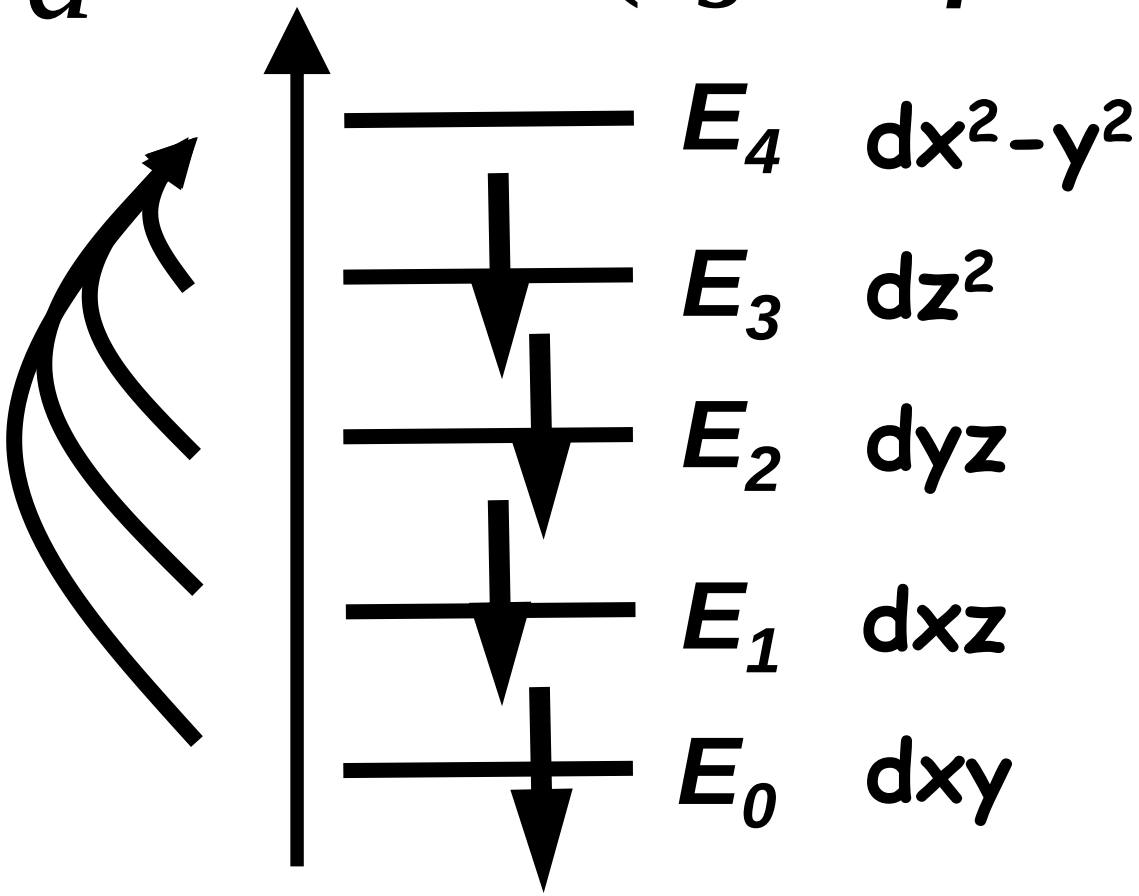


$$g_{ij} \approx g_e \delta_{ij} - \frac{2\zeta_{3d}}{2S}\left(\sum_{\alpha} \boxed{-\sum_{\beta}} \right) \sum_{n} \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0}$$

g tensor calculation (*ligand field*)

$$\lambda = -\frac{\zeta_{3d}}{2S}$$

d^9



$$g_x \approx g_e + \frac{2\zeta_{3d}}{2S}\left(\frac{1}{E_4 - E_2}\right)$$

$$g_y \approx g_e + \frac{2\zeta_{3d}}{2S}\left(\frac{1}{E_4 - E_1}\right)$$

$$g_z \approx g_e + \frac{2\zeta_{3d}}{2S}\left(\frac{4}{E_4 - E_0}\right)$$

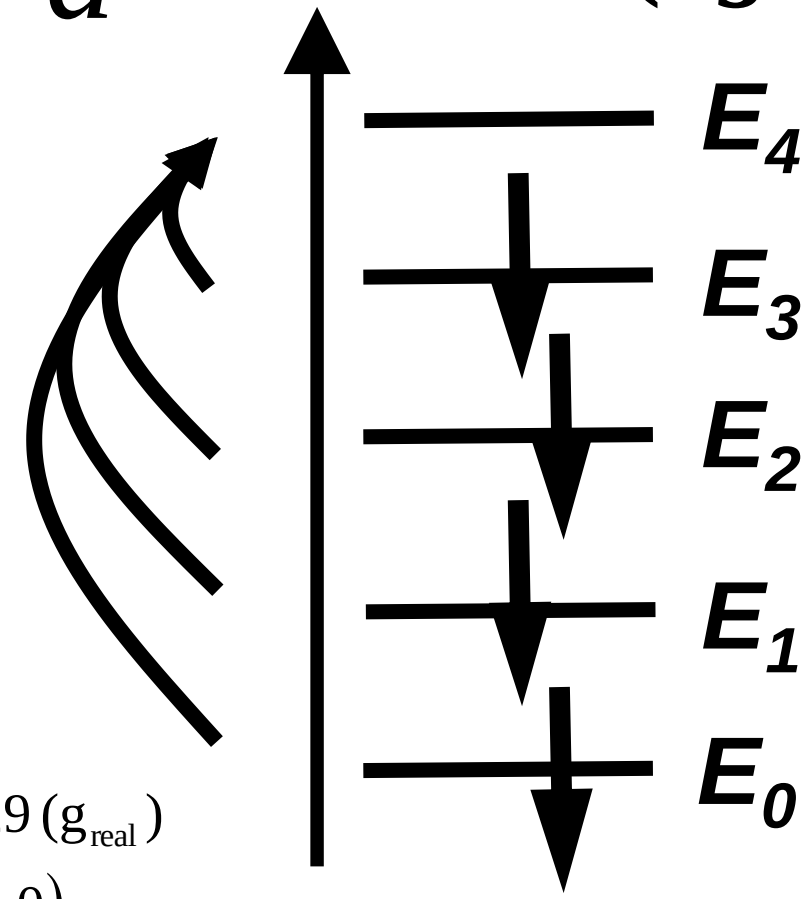
$$g_{ij} \approx g_e \delta_{ij} + \frac{2\zeta_{3d}}{2S}\left(\sum_{\beta}\right)\sum_{n}\frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n - E_0}$$

g_e~2

g tensor calculation (*ligand field*)

$$\lambda = -\frac{\zeta_{3d}}{2S}$$

d^9



$Cu^{2+}(d^9)$	g_1	g_2	g_3
CuO_6	2.465	2.465	2.099
CuN_6	2.064	2.064	2.273
CuN_6	2.082	2.082	2.248
CuN_6	2.134	2.159	2.053
CuN_6	2.06	2.12	2.52
CuN_6	2.143	2.152	2.060
CuO_6	2.22	2.23	2.08
CuO_6	2.07	2.07	2.37

$Cu^{2+}(H_2O)_6$

2.077

2.077

2.214

$Co^{2+}(d^7) \sim 2.29\ (g_{real})$

$DFT: Co^{2+}(H_2 0)_6$

2.016

2.106

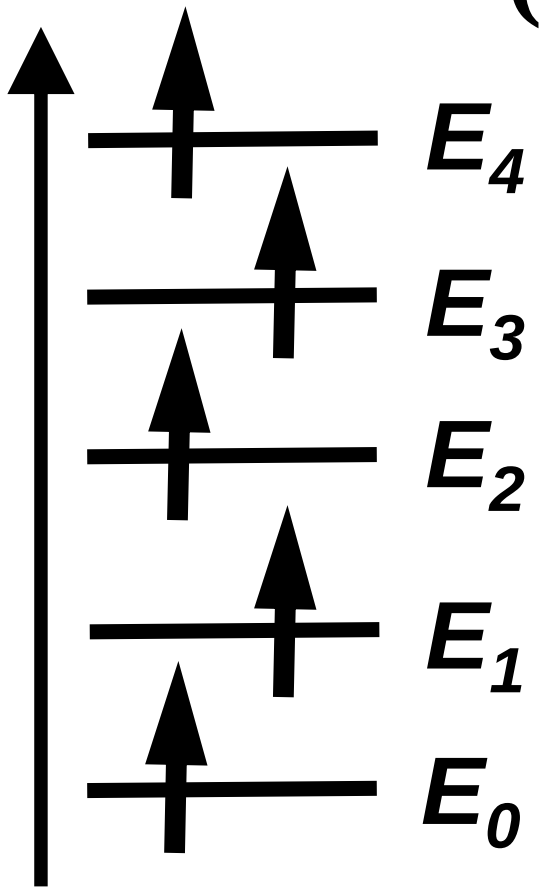
2.117

No ZFS !

$$g_{ij} \approx g_e \delta_{ij} + \frac{2\zeta_{3d}}{2S}\left(\sum_{\beta}\right)\sum_{n}\frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n - E_0}$$

g tensor calculation
(*ligand field*)

d^5



High Spin
(S=5/2)

$$g_x \approx g_e$$

$$g_y \approx g_e$$

$$g_z \approx g_e$$

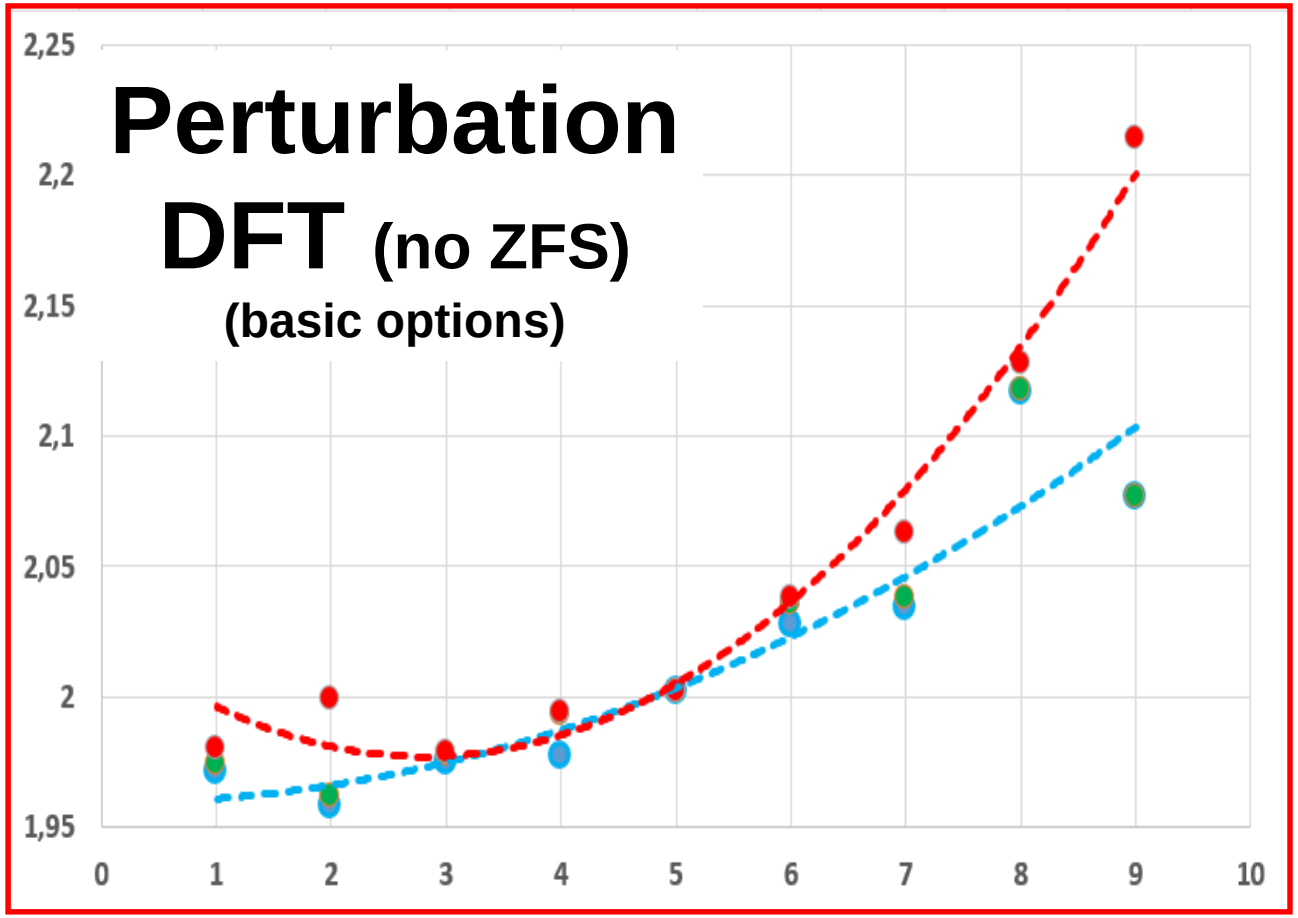
$Mn^{2+}(H_2O)_6$
2.002
2.002
2.002

$$g_{ij} \approx g_e \delta_{ij} - \frac{2\zeta_{3d}}{2S}\left(\sum_{\alpha} - \sum_{\beta} \right) \sum_{n} \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0}$$

g_e~2

Perturbative treatment of spin-orbit coupling

M_2+	d_n	g_min	g_int	g_max	g-av
Sc	1	1,971	1,974	1,98	1,975
Ti	2	1,958	1,962	1,999	1,973
V	3	1,975	1,978	1,979	1,977
Cr	4	1,977	1,993	1,994	1,988
Mn	5	2,002	2,002	2,002	2,002
Fe	6	2,028	2,036	2,038	2,034
Co	7	2,034	2,038	2,063	2,045
Ni	8	2,117	2,118	2,128	2,121
Cu	9	2,077	2,077	2,214	2,123

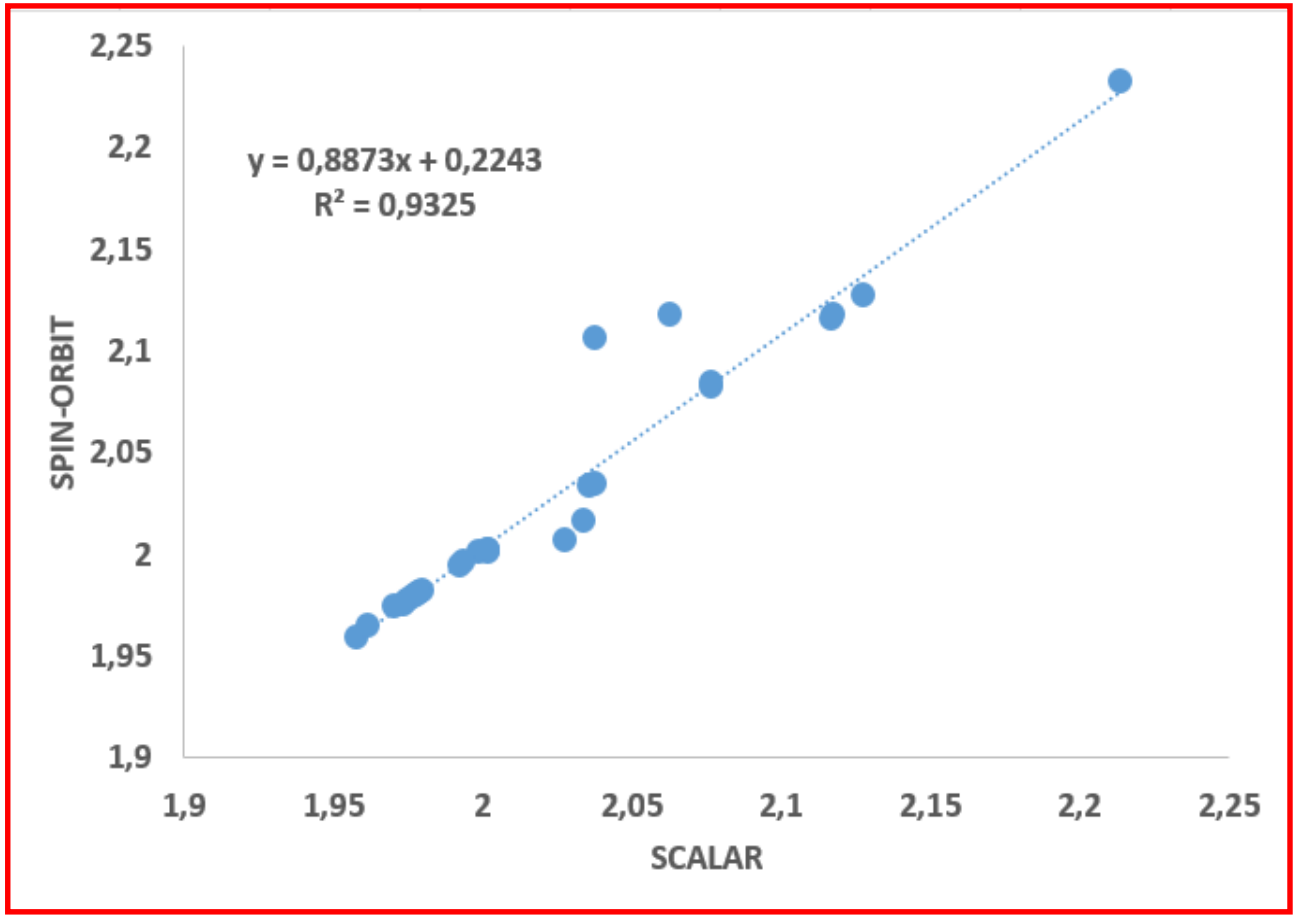


$$g_{ij} \approx g_e \delta_{ij} - \frac{2\zeta_{3d}}{2S}\left(\sum_{\alpha} - \sum_{\beta} \right) \sum_{n} \frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n - E_0}$$

High-spin $M^{2+}(H_2O)_6$

Self-consistent inclusion of spin-orbit coupling

M_2+	d_n	g_min	g_int	g_max	g-av
Sc	1	1,974	1,975	1,982	1,977
Ti	2	1,959	1,964	2,001	1,975
V	3	1,977	1,98	1,981	1,979
Cr	4	1,979	1,994	1,996	1,990
Mn	5	2,001	2,002	2,002	2,002
Fe	6	2,006	2,033	2,034	2,024
Co	7	2,016	2,106	2,117	2,080
Ni	8	2,115	2,117	2,127	2,120
Cu	9	2,082	2,084	2,232	2,133



$Co^{2+}(H_2O)_6$

$$g_{\mathrm{eff}(x)} = g_{\mathrm{real}(x)}(1 \pm \{[1 + 3(E/D)]/\sqrt{[1 + 3(E/D)^2]}\}) \quad \sim 2.2$$

$$g_{\mathrm{eff}(y)} = g_{\mathrm{real}(y)}(1 \pm \{[1 - 3(E/D)]/\sqrt{[1 + 3(E/D)^2]}\}) \quad \sim 3.9$$

$$g_{\mathrm{eff}(z)} = g_{\mathrm{real}(z)}(1 \pm \{(-2)/\sqrt{[1 + 3(E/D)^2]}\}) \quad \sim 5.2$$

$$g_{ij} \approx g_e \delta_{ij} - \frac{2\zeta_{3d}}{2S}\left(\sum_{\alpha} - \sum_{\beta}\right)\sum_{n} \frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n - E_0}$$

High-spin $M^{2+}(H_2O)_6$

J. Am. Chem. Soc. **2000,** *122,* 9206−9218

Density Functional Calculations of Electronic *g*-Tensors Using Spin−Orbit Pseudopotentials and Mean-Field All-Electron Spin−Orbit Operators

Olga L. Malkina,[†,‡] Juha Vaara,[§] Bernd Schimmelpfennig,[||] Markéta Munzarová,[⊥] Vladimir G. Malkin,[*,‡] and Martin Kaupp[*,#]

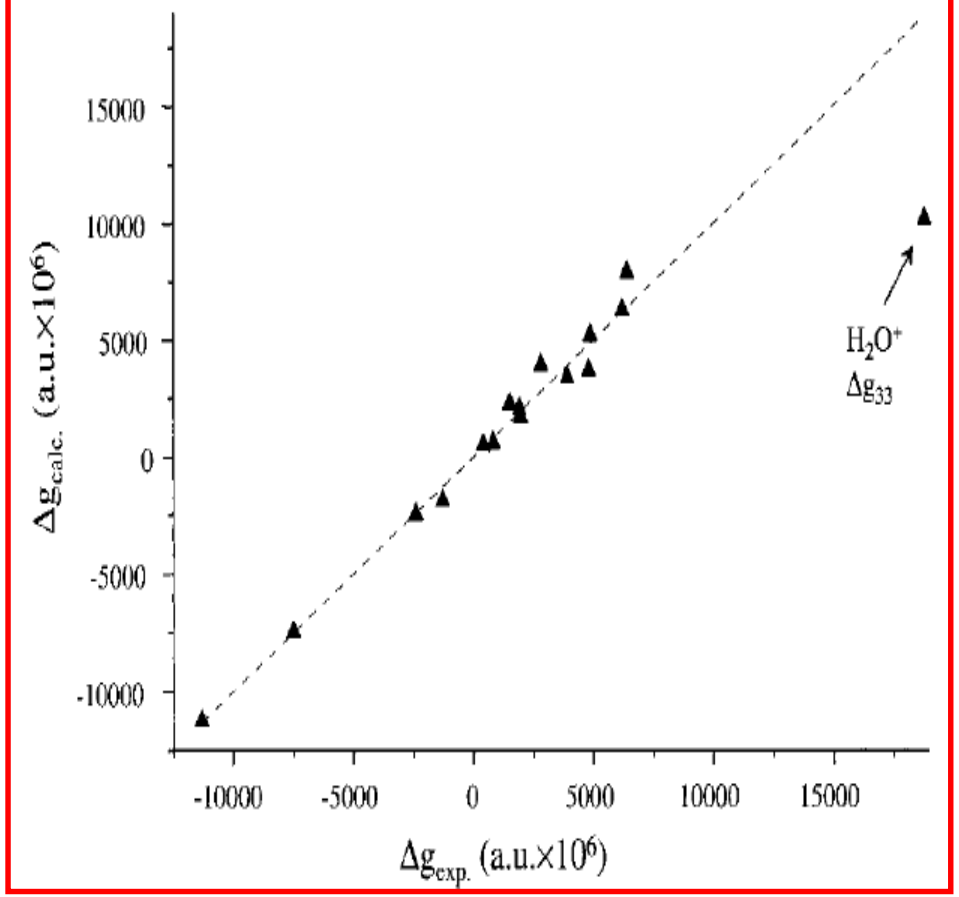


Table 3. *g*-Tensor Components (ppm) for Some Light Main Group Radicals[a]

		this work[b]	SZ[c]	Lushington (MRCI)[d]	exp.[e]	
H_2O^+	Δg_{11}	−142	103	−292	200	gas phase
	Δg_{22}	3702	5126	4217	4800	
	Δg_{33}	10205	13824	16019	18800	
CO^+	$\Delta g_{\perp}$	−2458	−3129	−2674	−2400	gas phase
	$\Delta g_{\parallel}$	−93	−138	−178	-	
HCO	Δg_{11}	−224	−270		0	matrix
	Δg_{22}	2275	2749		1500	
	Δg_{33}	−7476	−9468		−7500	
C_3H_5	Δg_{11}	−65	−115		0	matrix
	Δg_{22}	497	660		400	
	Δg_{33}	603	769		800	
NO_2	Δg_{11}	−688	−760	−235	−300	gas phase
	Δg_{22}	3400	4158	3806	3900	
	Δg_{33}	−11229	−13717	−10322	−11300	
NF_2	Δg_{11}	−617	−738		−100	matrix
	Δg_{22}	3928	4678		2800	
	Δg_{33}	6288	7619		6200	
MgF	$\Delta g_{\perp}$	−1869	−2178	−1092	−1300	matrix
	$\Delta g_{\parallel}$	14	−60	−59	−300	

[a] UDFT-BP86 results. [b] Basis BIII, UDFT-IGLO, AMFI approximation. [c] UDFT-GIAO.[12] [d] Multireference configuration interaction results.[7] [e] Experimental data as quoted in refs. 7,12.

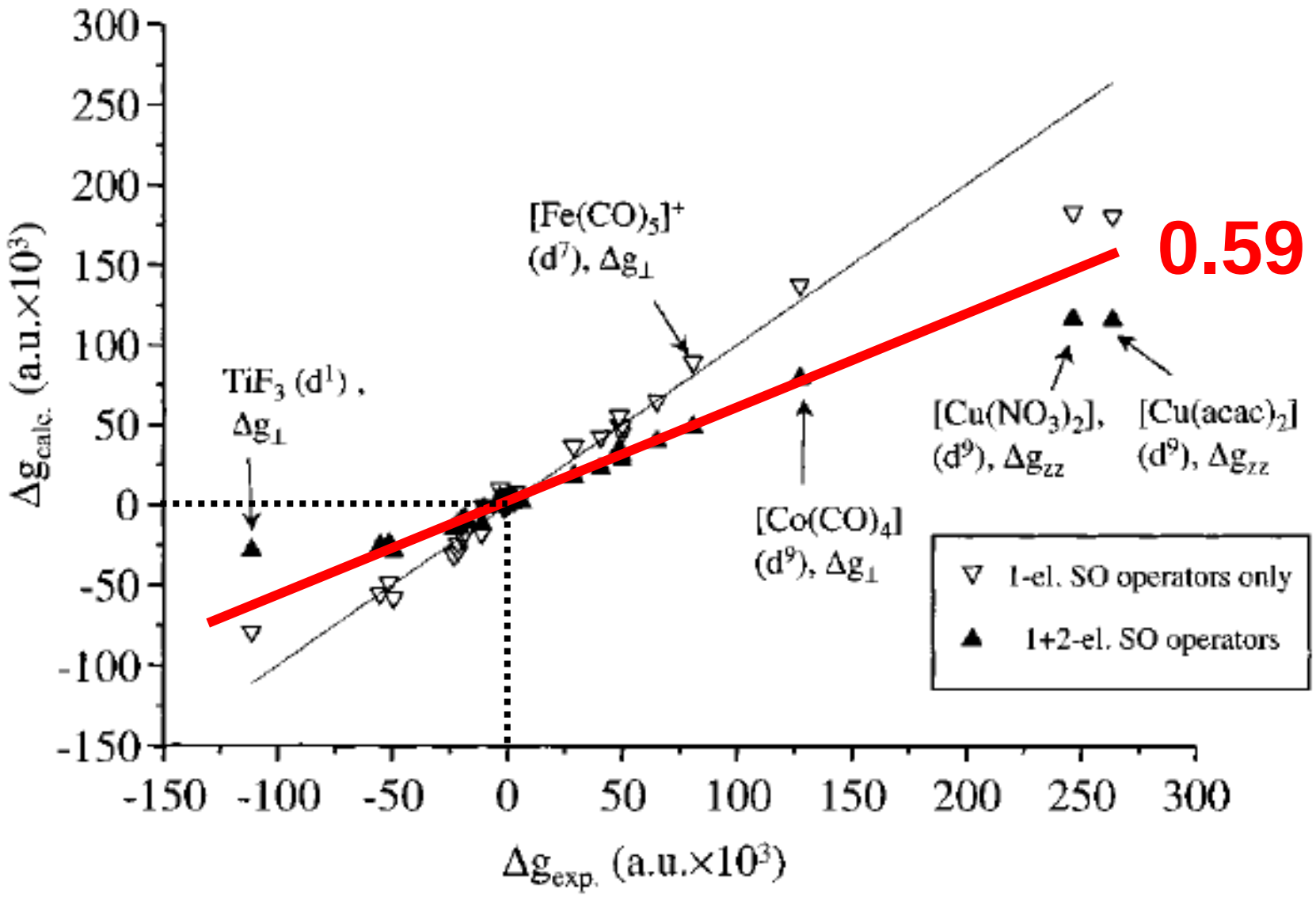
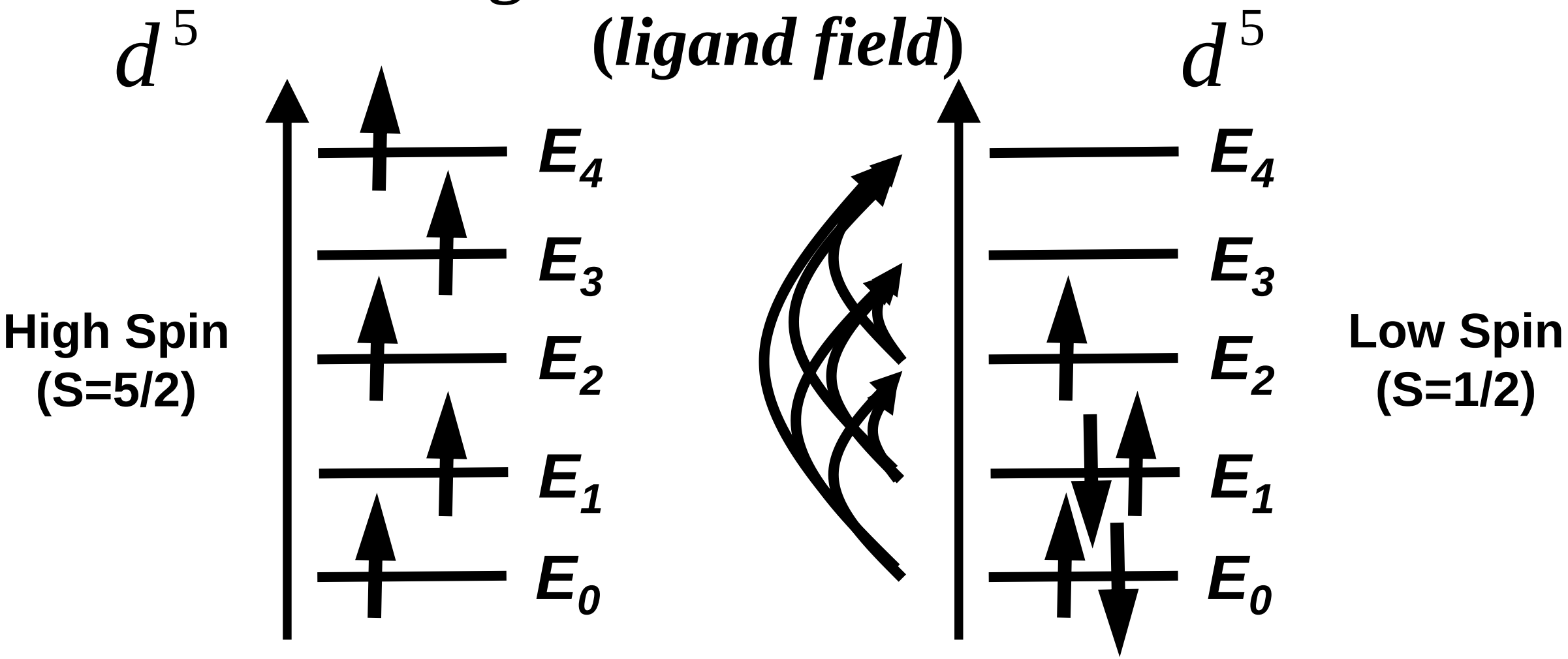


Figure 2. Comparison of calculated and experimental *g*-shift tensor components (ppt) for 3d transition metal complexes (cf. Table 10).

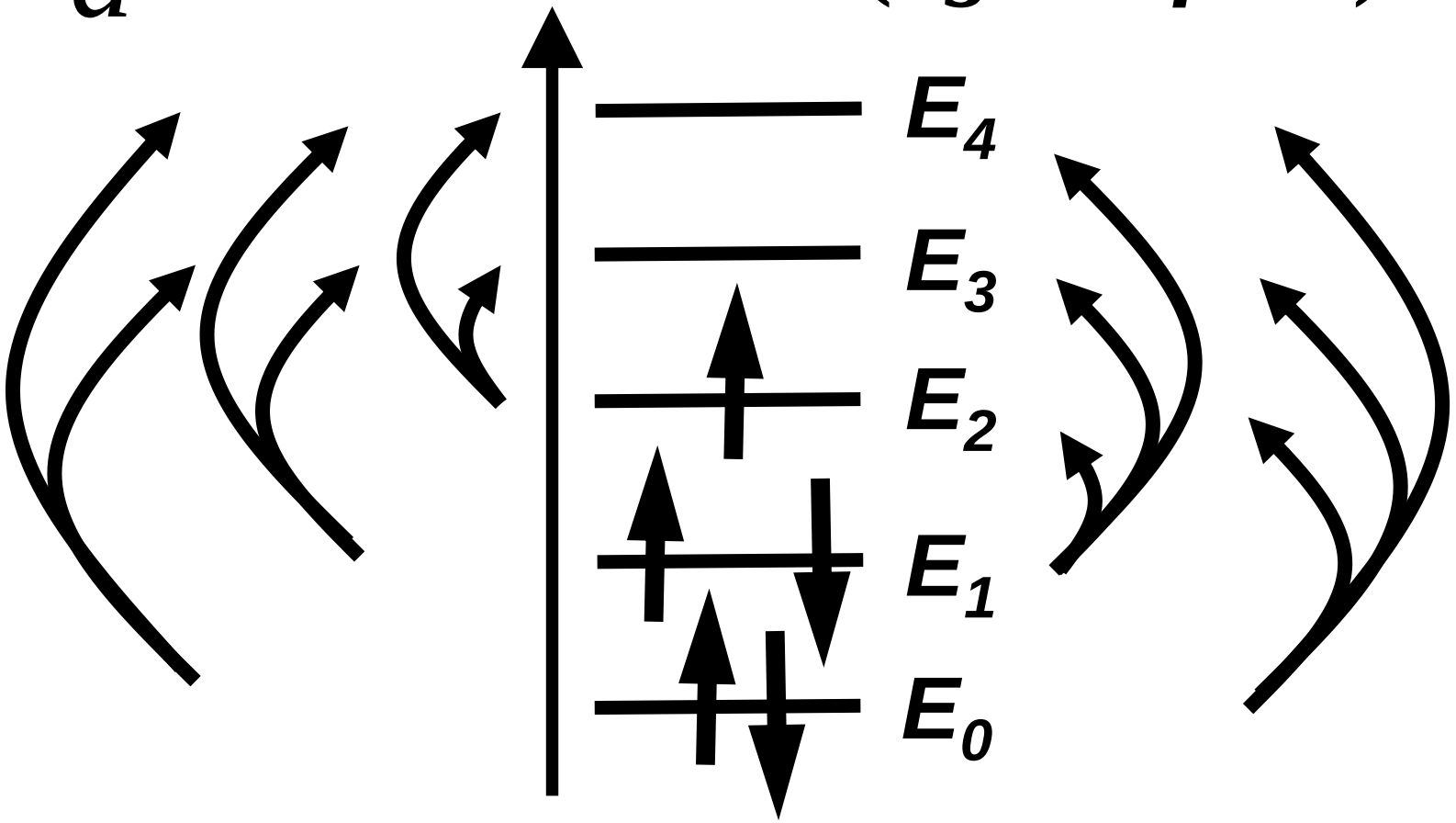
g tensor calculation
(*ligand field*)



$$g_{ij} \approx g_e \delta_{ij} - \frac{2\zeta_{3d}}{2S}\left(\sum_{\alpha} - \sum_{\beta} \right) \sum_{n} \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0}$$

g tensor calculation (*ligand field*)

d^5



Low Spin (S=1/2)

$Fe^{3+}(d^5)$	g_1	g_2	g_3
FeC_6	2.10	0.91	2.35
FeC_5N	2.177	0.845	2.995
FeC_4N_2	2.50	2.50	1.65
FeC_4N_2	2.7	2.7	1.6
FeN_6	2.615	2.727	1.459
FeN_6	2.61	2.61	1.61
FeN_6	2.64	2.64	1.38
FeN_6	2.60	2.60	1.60

$$g_{ij} \approx g_e \delta_{ij} - \frac{2\zeta_{3d}}{2S}\left(\sum_{\alpha} - \sum_{\beta}\right)\sum_{n}\frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n - E_0}$$

$Fe^{3+}(H_2O)_6$
1.935
2.072
2.110

When it does not work as simply ...

Angew. Chem. Int. Ed. **2000**, *39*

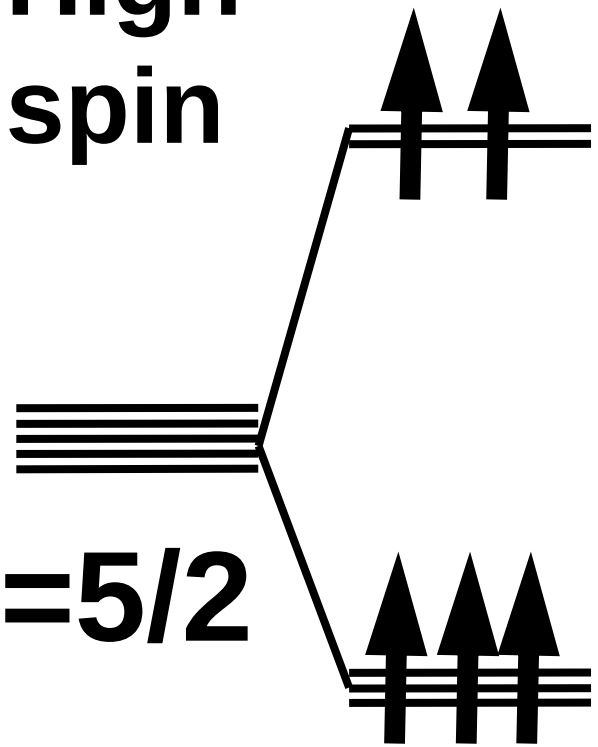
Dalton Trans., 2005, 1734–1742

Inorganica Chimica Acta 361 (2008) 4012–4016

Jean-Jacques Girerd & Marie-Laure Boillot

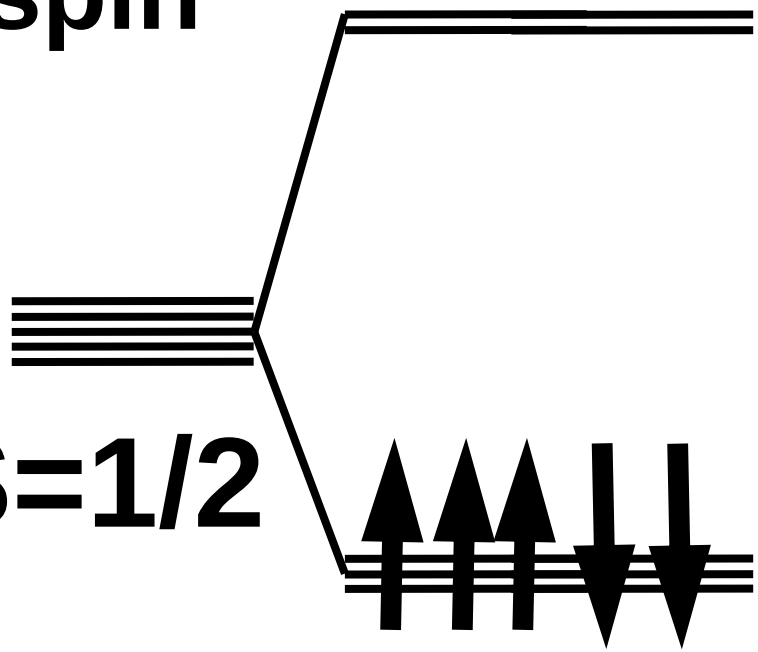
‘High spin’ versus ‘low spin’

High spin

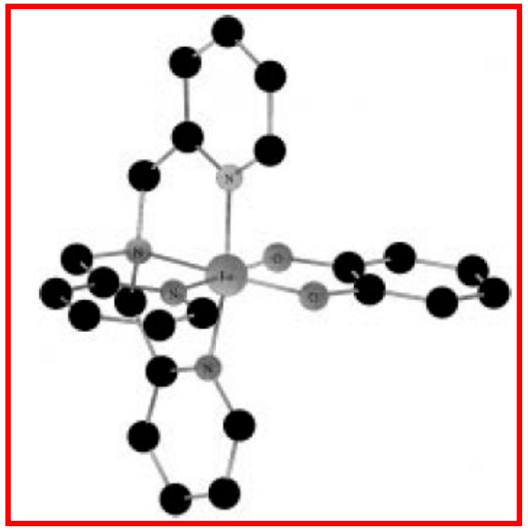


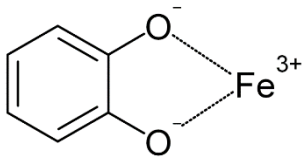
S=5/2

Low spin



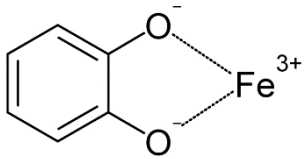
S=1/2





DBC : 2 x *ter*-Bu
CAT : 2 x H
TCC : 4 x Cl
DNC : 2 x NO_2

Experimental g tensors for a series of catecholate spin transition complexes



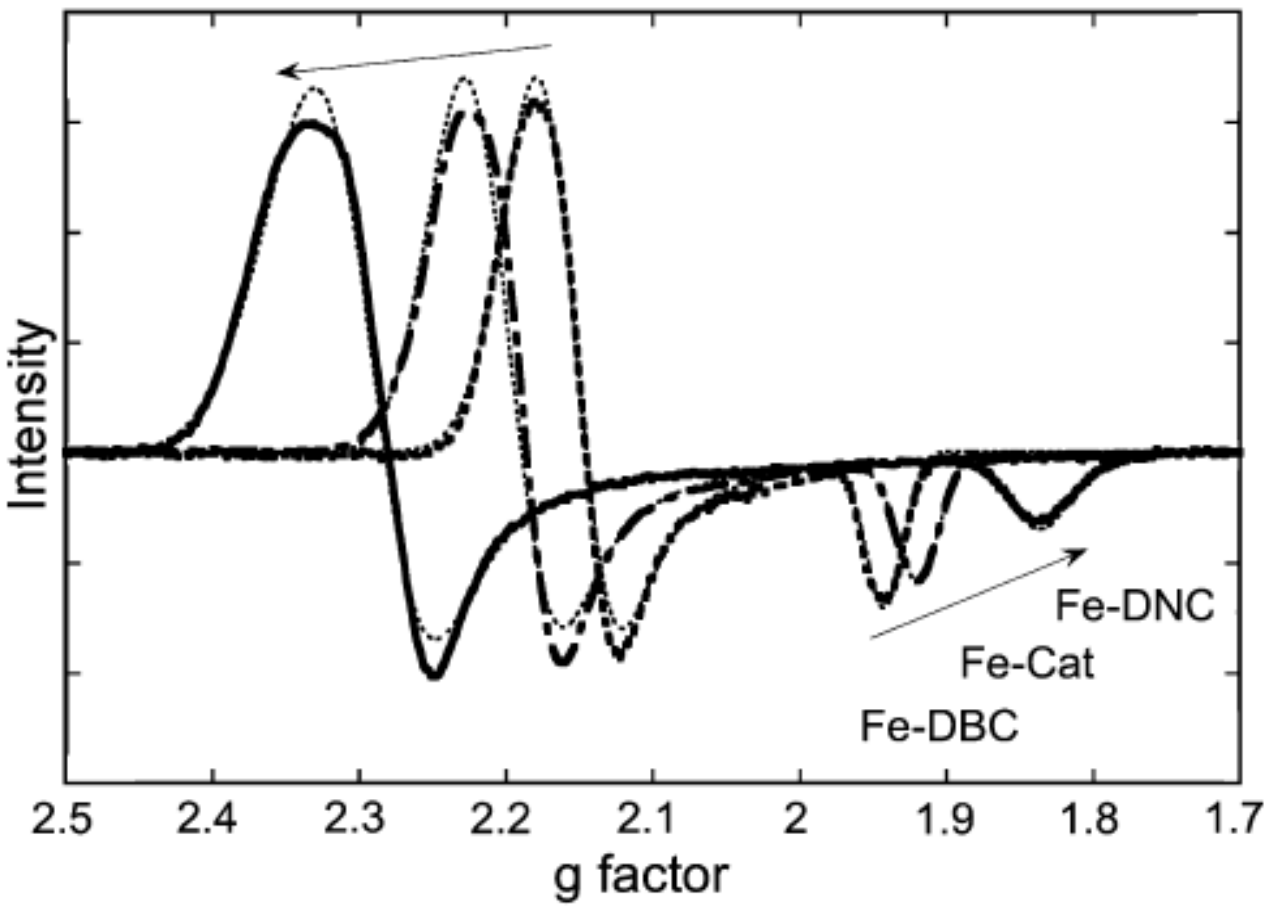
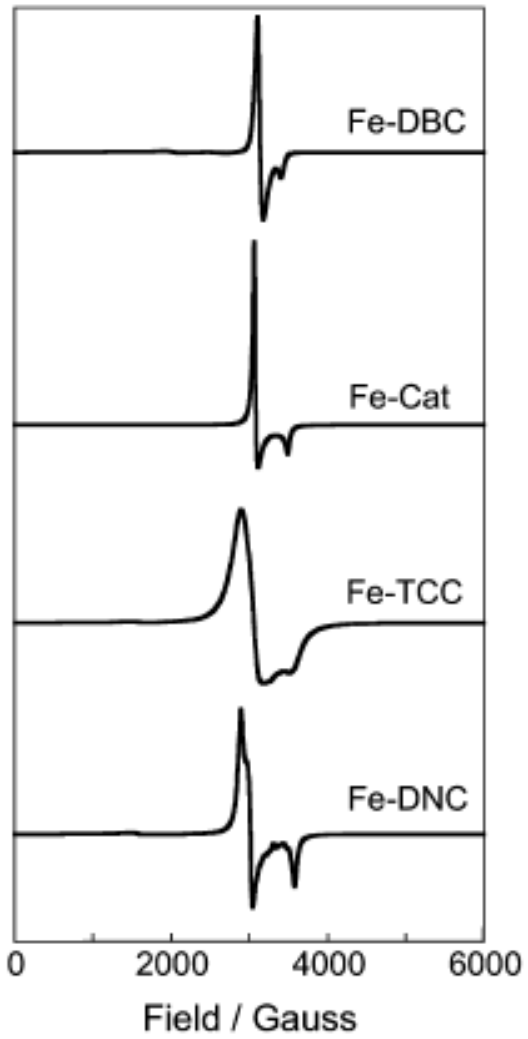


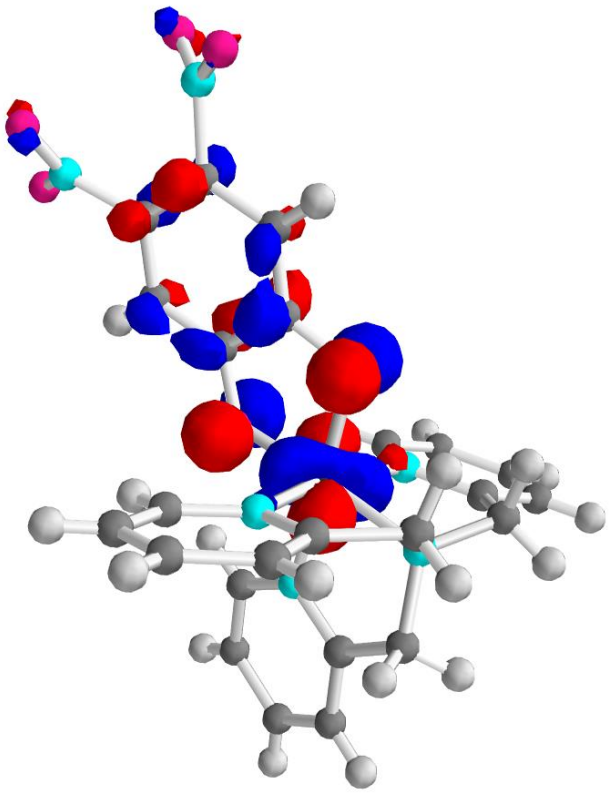
Fig. 4. Experimental LS spectra of [(TPA)Fe(R-Cat)]BPh_4 in frozen butyronitrile solutions, $T = 5$ K; the dotted lines are used for the simulated spectra.



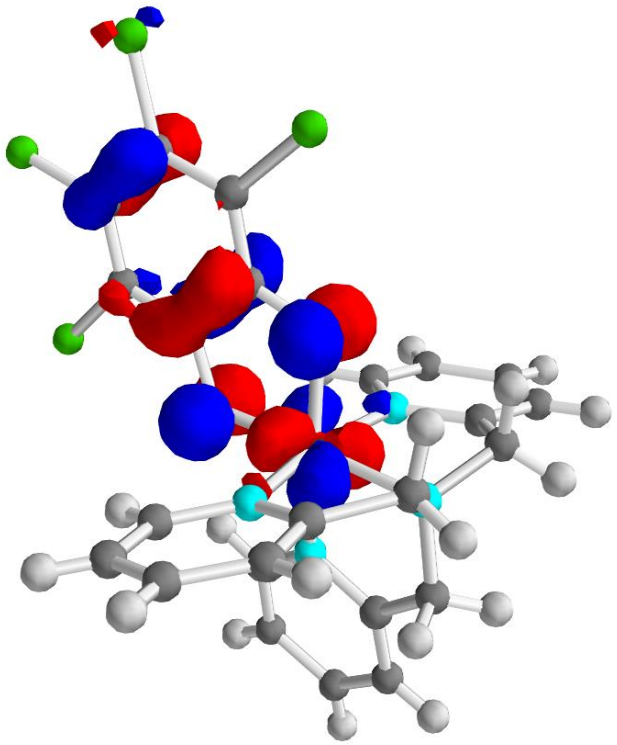
$$[g] = \lambda^2 [g_{Fe(II)SQ}] + (1 - \lambda^2)[g_{Fe(III)Cat}]$$

	PERTURB.	EXP
	1,986	1,942
DBC	2,012	2,155
	2,059	2,175
	2,002	1,918
CAT	2,018	2,190
	2,053	2,228
	2,003	1,905
TCC	2,014	2,235
	2,057	2,290
	2,002	1,826
DNC	2,033	2,278
	2,066	2,353

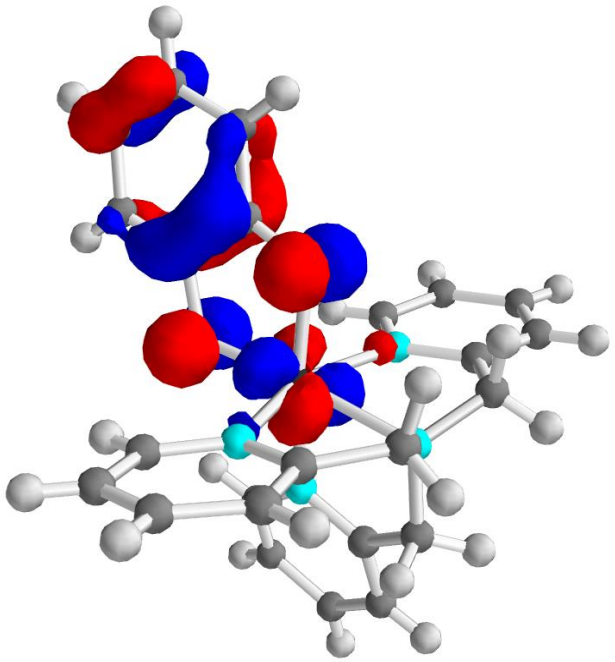
Molecular orbital delocalisation for a series of catecholate spin transition complexes



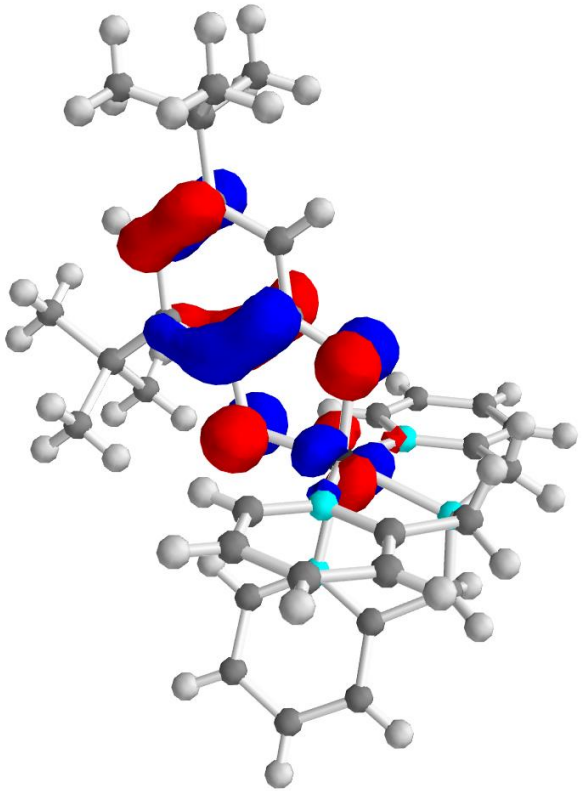
DNC



TCC



CAT



DBC

Analytical calculation of the g tensor

$$\begin{cases} \Psi_n = \alpha_n.dz^2 + \beta_n.dx^2 - y^2 + \gamma_n.dxy + \delta_n.dxz + \varepsilon_n.dyz \\ \Psi_o = \alpha_o.dz^2 + \beta_o.dx^2 - y^2 + \gamma_o.dxy + \delta_o.dxz + \varepsilon_o.dyz \end{cases}$$

$L_{Fe}.S_{Fe}$	Ψ_0^{α}	Ψ_0^{β}	Ψ_n^{α}	Ψ_n^{β}
$\Psi_0^{\alpha*}$	E_o	0	$-i.c$	$-a+i.b$
$\Psi_0^{\beta*}$	0	E_o	$a+i.b$	$i.c$
$\Psi_n^{\alpha*}$	$i.c$	$a-i.b$	E_1	0
$\Psi_n^{\beta*}$	$-a-i.b$	$-i.c$	0	E_1

$$H_{SO} = \lambda L.S = \lambda\left[L_Z S_Z + \frac{1}{2}\left(L^+S^- + L^-S^+\right)\right]$$

Analytical calculation of the g tensor

Spin-orbitals

$$
\begin{array}{c}
|\alpha\rangle \\ \\ \\ \\ \\ \\ \\ |\beta\rangle \\ \\ \\ \\ \\ \\
\end{array}
\underbrace{\begin{pmatrix}
\frac{\beta_0 - i\gamma_0}{\sqrt{2}}|2\rangle \\
\frac{i\varepsilon_0 - \delta_0}{\sqrt{2}}|1\rangle \\
\alpha_0|0\rangle \\
\frac{i\varepsilon_0 + \delta_0}{\sqrt{2}}|-1\rangle \\
\frac{\beta_0 + i\gamma_0}{\sqrt{2}}|-2\rangle \\
0 \\ 0 \\ 0 \\ 0 \\ 0
\end{pmatrix}}_{\Psi_0^{\alpha}}
\underbrace{\begin{pmatrix}
0 \\ 0 \\ 0 \\ 0 \\ 0 \\
\frac{\beta_0 - i\gamma_0}{\sqrt{2}}|2\rangle \\
\frac{i\varepsilon_0 - \delta_0}{\sqrt{2}}|1\rangle \\
\alpha_0|0\rangle \\
\frac{i\varepsilon_0 + \delta_0}{\sqrt{2}}|-1\rangle \\
\frac{\beta_0 + i\gamma_0}{\sqrt{2}}|-2\rangle
\end{pmatrix}}_{\Psi_0^{\beta}}
\underbrace{\begin{pmatrix}
\frac{\beta_n - i\gamma_n}{\sqrt{2}}|2\rangle \\
\frac{i\varepsilon_n - \delta_n}{\sqrt{2}}|1\rangle \\
\alpha_0|0\rangle \\
\frac{i\varepsilon_n + \delta_n}{\sqrt{2}}|-1\rangle \\
\frac{\beta_n + i\gamma_n}{\sqrt{2}}|-2\rangle \\
0 \\ 0 \\ 0 \\ 0 \\ 0
\end{pmatrix}}_{\Psi_n^{\alpha}}
\underbrace{\begin{pmatrix}
0 \\ 0 \\ 0 \\ 0 \\ 0 \\
\frac{\beta_n - i\gamma_n}{\sqrt{2}}|2\rangle \\
\frac{i\varepsilon_n - \delta_n}{\sqrt{2}}|1\rangle \\
\alpha_0|0\rangle \\
\frac{i\varepsilon_n + \delta_n}{\sqrt{2}}|-1\rangle \\
\frac{\beta_n + i\gamma_n}{\sqrt{2}}|-2\rangle
\end{pmatrix}}_{\Psi_n^{\beta}}
$$

Kramers doublet

$$\left\{\Psi_K, \Psi_K^*\right\}$$

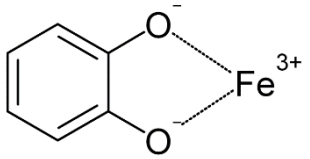
$$L_i . + g_e S_i \qquad \Psi_K \qquad \Psi_K^*$$

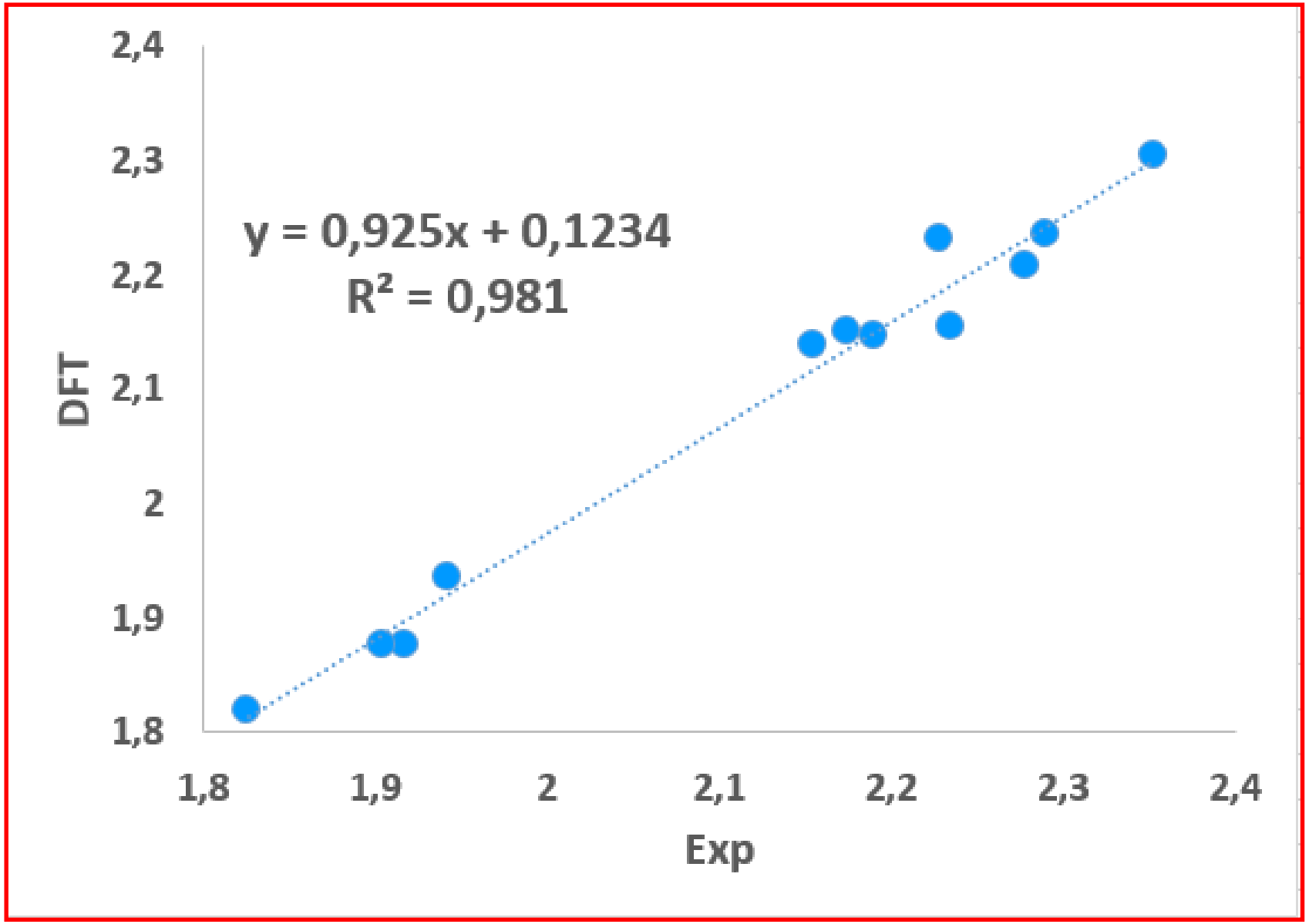
$$\Psi_K$$

$$\Psi_K^*$$

?

Analytical calculation of the g tensor



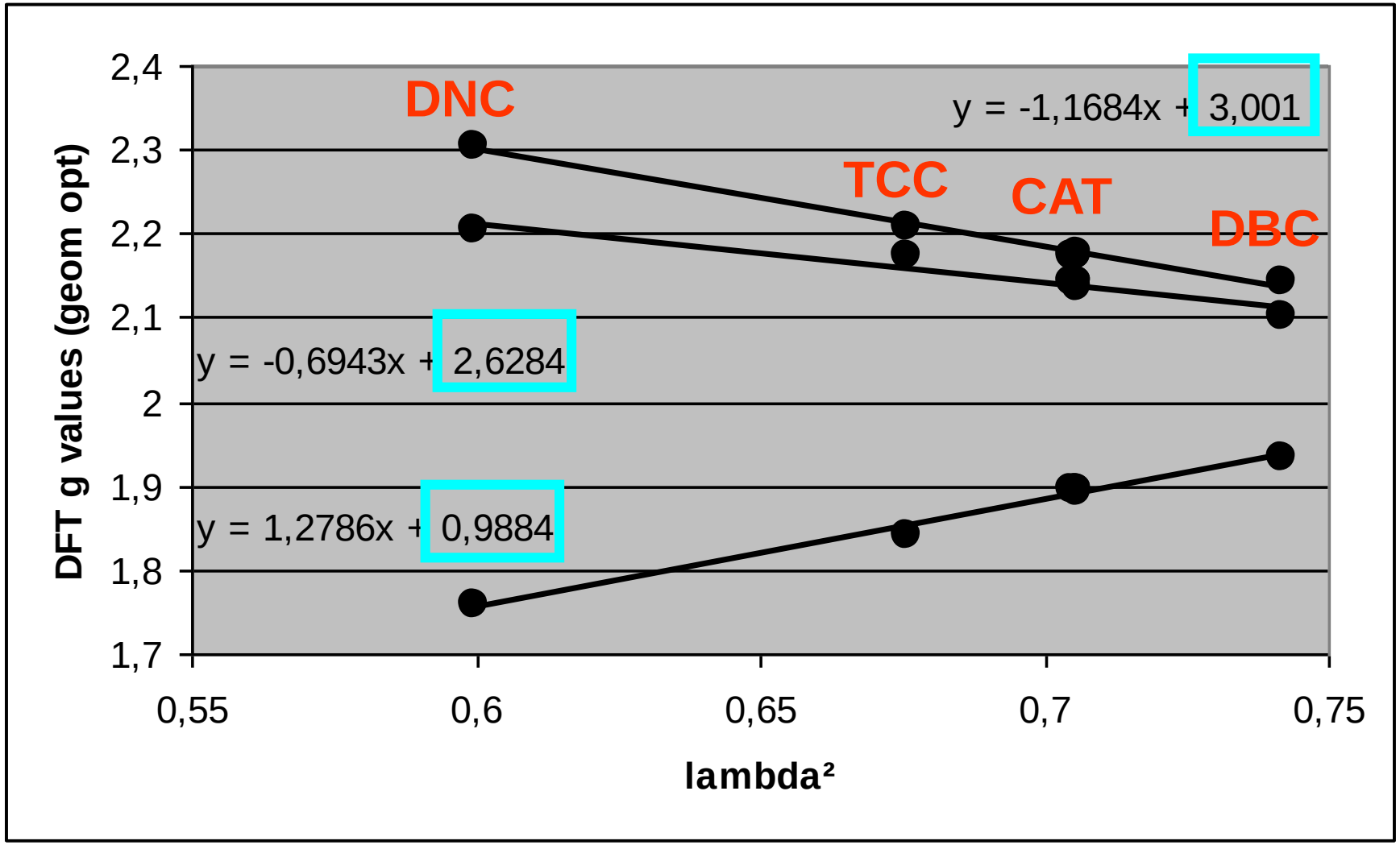


$$[g] = \lambda^2 [g_{\mathrm{Fe(II)SQ}}] + (1 - \lambda^2)[g_{\mathrm{Fe(III)Cat}}]$$

	"HYBRID"	EXP
DBC	1,934	1,942
	2,138	2,155
	2,150	2,175
CAT	1,875	1,918
	2,145	2,190
	2,230	2,228
TCC	1,875	1,905
	2,153	2,235
	2,234	2,290
DNC	1,819	1,826
	2,206	2,278
	2,304	2,353

Correlations showing non-innocence of catecholate ligands

$$\begin{cases} g_{\min}^{tot} = (1-\lambda^2) g_{\min}^{Fe}(0) + \lambda^2 \times 2.0023 \\ g_{\text{int}}^{tot} = (1-\lambda^2) g_{\text{int}}^{Fe}(0) + \lambda^2 \times 2.0023 \\ g_{\max}^{tot} = (1-\lambda^2) g_{\max}^{Fe}(0) + \lambda^2 \times 2.0023 \end{cases}$$



hemoglobins
Biophys. J., 2005, vol.89, 2628) :

$2.91 < g_{max} < 3.20$
$2.08 < g_{int} < 2.26$
$1.20 < g_{min} < 1.53$

porphyrins (Bull. Chem. Soc. Jpn, 2004, vol.77, 357) :

$2.78 < g_{max} < 3.18$
$2.29 < g_{int} < 2.31$
$1.15 < g_{min} < 1.69$

cytochroms (Phys. Chem. Chem. Phys. 2002, vol.4, p655) :

$2.93 \approx g_{max}$
$2.25 \approx g_{int}$
$1.50 \approx g_{min}$

SKIP !

G tensor calculations
- *Bilan* -

- « *ligand field* » approach
  - → not rigourous (SOC, gauge)
  - → semi-quantitative
- DFT / HF : « *sum-over-states* »
  - → gauge correction
  - → radicals *versus* metals (3d)
- Linear Response Theory

$$h\upsilon = \mu_B \vec{\mathrm{B}}.\tilde{\mathrm{g}}.\vec{\mathrm{s}}$$

$$\Delta g_{uv} = \frac{1}{\mu_{\mathrm{B}}} \frac{\partial^2 E}{\partial B_{0,u} \partial s_v}\bigg|_{\mathbf{B}=\mathbf{s}=0}$$

Directly introducing the magnetic field

SKIP !

Stone, A. J., Proc. R. Soc. A, 271, 424 (1963)

Schreckenbach & Ziegler,
J. Phys. Chem. A, 101, 3388 (1997)

→ Application to DFT, with GIAO
(Gauge-Including Atomic Orbital method)

Van Lenthe, Wormer & van der Avoird,
J. Chem. Phys., 107, 2488 (1997)

→ Application of Dirac equation (ZORA)

Neese & Solomon,
Inorg. Chem. A, 37, 6568 (1998)

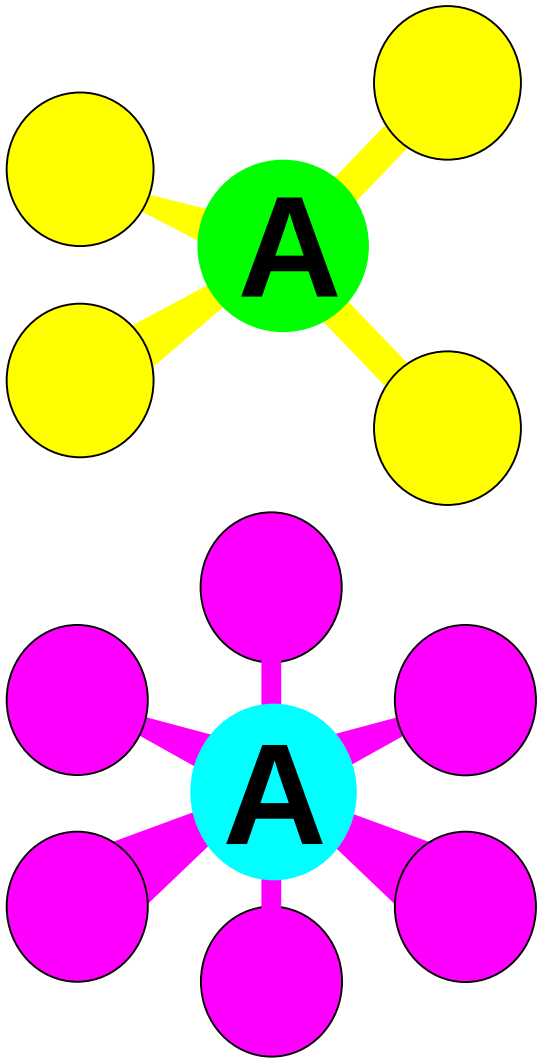
→ Formulas for g and ZFS ($S \rightarrow S \pm 1$)
implemented with INDO (semi-empirical)
(Intermediate-Neglect of Differential Orbital)

Malkina, Malkin, Kaupp *et al*,
J. Am. Chem. Soc. 122, 9206 (2000)

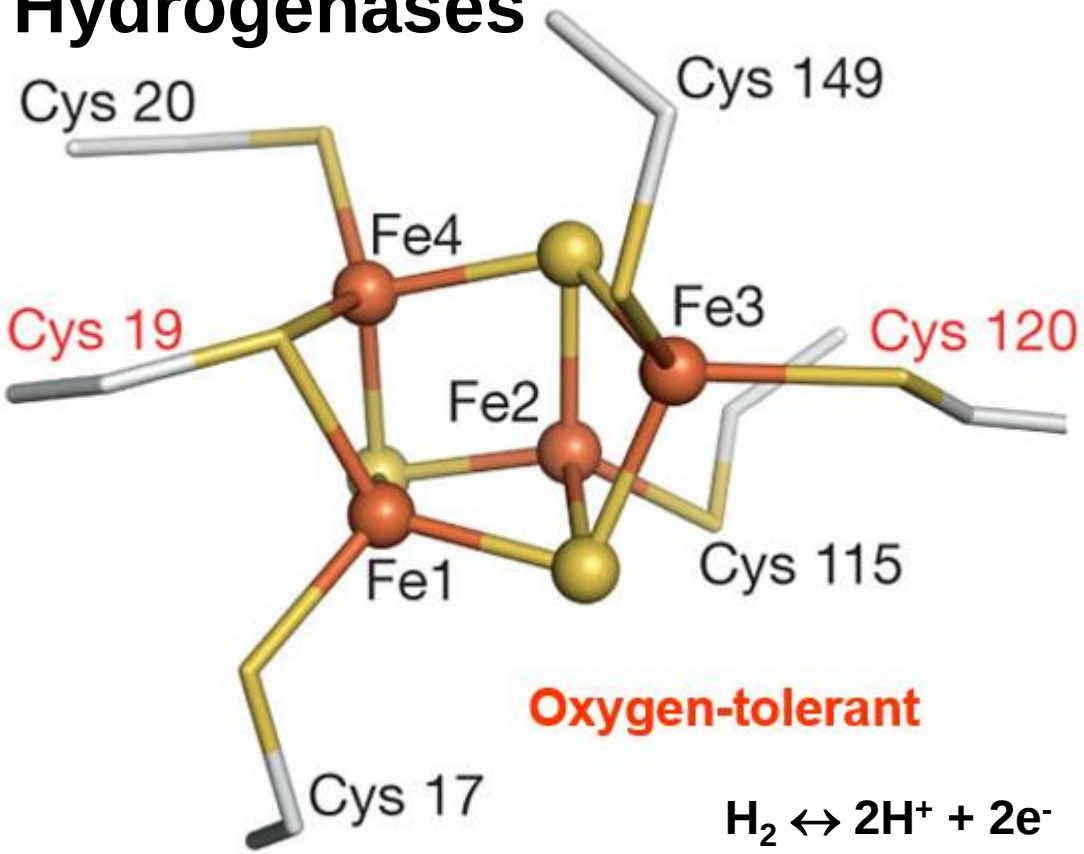
Outline of the lecture

- ***Basic introduction to DFT***
  - ***Hartree-Fock* versus *DFT***
- ***Application : (mono-metal) g-tensors***
  - ***Relativistic origin***
  - ***Perturbative & self-consisten approaches***
  - ***When it does not work ...***
- ***Polymetallic complexes***
  - ***Spin-coupling***
  - ***G-tensor (dimer)***
  - ***Hyperfine couplings (dimer)***
    - ***More complex systems : hyperfine & Mössbauer***
- ***Conclusions***

Spin coupling & spectroscopies



Hydrogenases



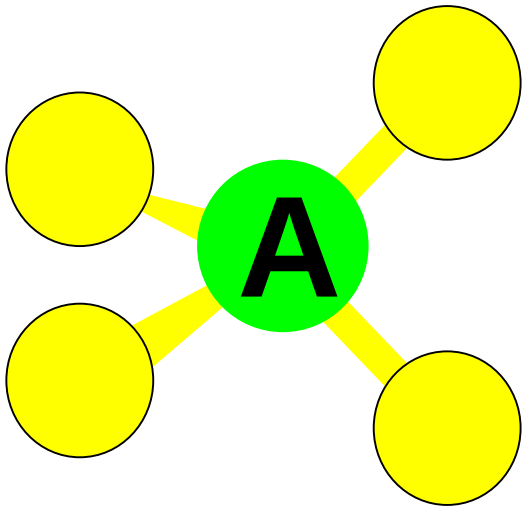
Oxygen-tolerant

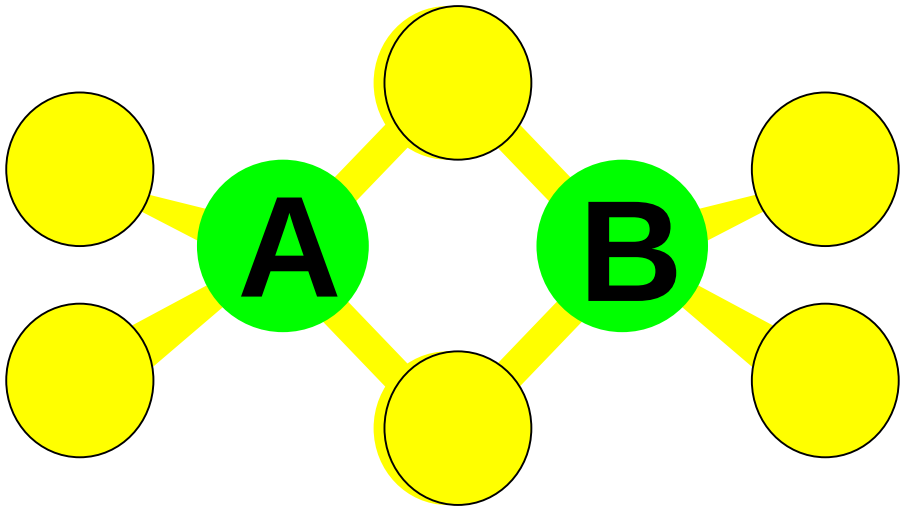
$H_2 \leftrightarrow 2H^+ + 2e^-$

charge : $\rho_e(r) = \rho_\alpha(r) + \rho_\beta(r)$

spin : $\rho_s(r) = \rho_\alpha(r) - \rho_\beta(r)$

Spin coupling & spectroscopies





Local spins

$$H_A^Z = \beta \vec{H}.\tilde{g}_A.\vec{S}_A \qquad \vec{S}_A.\tilde{A}_A.\vec{I}_A$$

$$H_B^Z = \beta \vec{H}.\tilde{g}_B.\vec{S}_B \qquad \vec{S}_B.\tilde{A}_B.\vec{I}_B$$

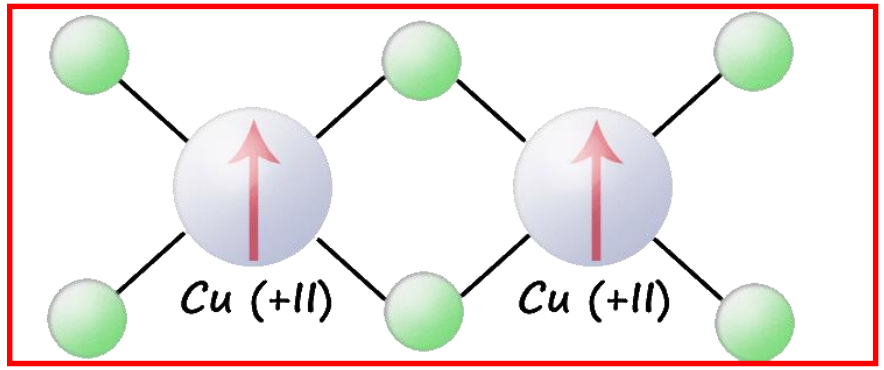
Global spin

$$H_{tot}^Z = \beta \vec{H}.\tilde{g}.\vec{S} \qquad \vec{S}.\tilde{A}_{A/S}.\vec{I}_A$$

$$H_J = J\vec{S}_A.\vec{S}_B \qquad \vec{S}.\tilde{A}_{B/S}.\vec{I}_B$$

Case of 2 Cu^{2+}(s=1/2) : triplet state (S=1)

$$\Psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(r_1)\alpha_1(s_1) & \varphi_2(r_1)\alpha_2(s_1) \\ \varphi_1(r_2)\alpha_1(s_2) & \varphi_2(r_2)\alpha_2(s_2) \end{vmatrix}$$



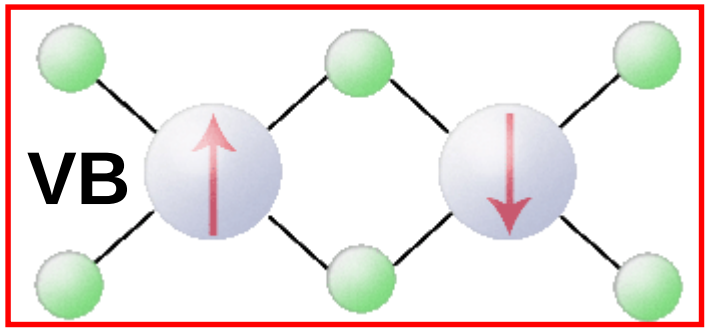
$$\left[\Phi_1(r_1)\Phi_2(r_2) - \Phi_2(r_1)\Phi_1(r_2)\right]\alpha(1)\alpha(2)$$

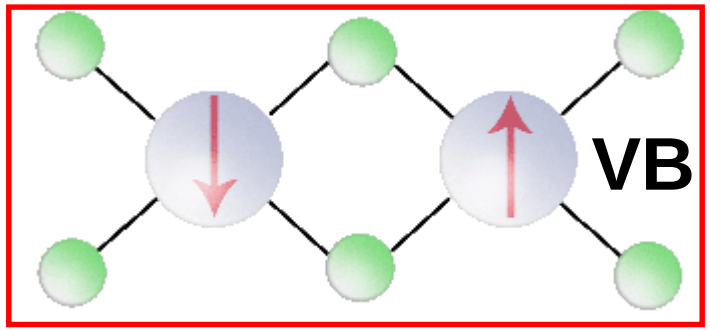
Global spin S=1

Case of 2 Cu^{2+}(s=1/2) : singlet state (S=0)

$$\Psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \Phi_1(r_1)\alpha(1) & \Phi_1(r_2)\alpha(2) \\ \Phi_2(r_1)\beta(1) & \Phi_2(r_2)\beta(2) \end{vmatrix}$$

$$\Psi_3 = \frac{1}{\sqrt{2}} \begin{vmatrix} \Phi_1(r_1)\beta(1) & \Phi_1(r_2)\beta(2) \\ \Phi_2(r_1)\alpha(1) & \Phi_2(r_2)\alpha(2) \end{vmatrix}$$





$$\left[\Phi_1(r_1)\Phi_2(r_2) + \Phi_2(r_1)\Phi_1(r_2)\right]\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

Global spin S=0

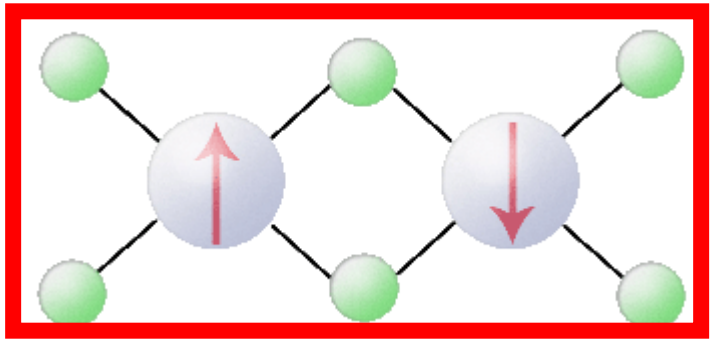
Broken symmetry state (Ms=0)

$$\Psi_S^{VB} = \frac{1}{\sqrt{2(1+S_{AB}^2)}}\left[\Phi_A^{VB}(1)\Phi_B^{VB}(2) + \Phi_B^{VB}(1)\Phi_A^{VB}(2)\right]$$

$$\Psi_T^{VB} = \frac{1}{\sqrt{2(1-S_{AB}^2)}}\left[\Phi_A^{VB}(1)\Phi_B^{VB}(2) - \Phi_B^{VB}(1)\Phi_A^{VB}(2)\right]$$

(αβ–βα) $|S,M\rangle = |0,0\rangle$

(αβ+βα) $|S,M\rangle = \begin{cases} |1,+1\rangle \\ |1,\ 0\rangle \\ |1,-1\rangle \end{cases}$

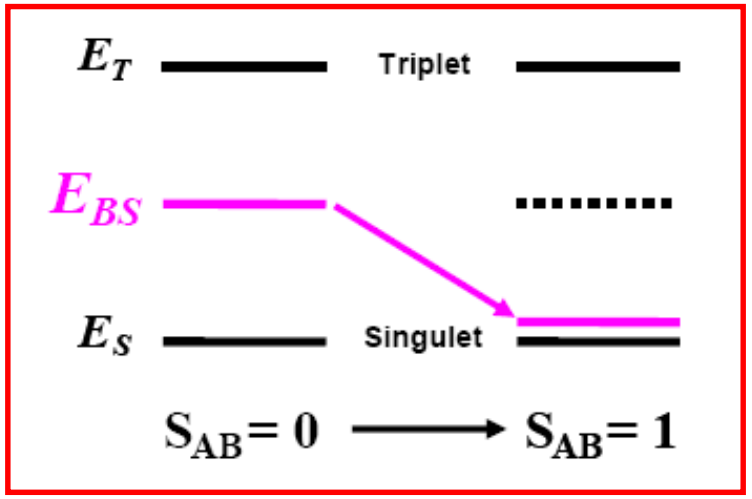


global global

local

$$\Psi_{BS}^{VB} \equiv \Phi_A^{VB}(1)\Phi_B^{VB}(2) = \sqrt{\frac{1+S_{AB}^2}{2}}\Psi_S^{VB} + \sqrt{\frac{1-S_{AB}^2}{2}}\Psi_T^{VB}$$

$$|S_A,M_A\rangle|S_B,M_B\rangle = |1/2,+1/2\rangle|1/2,-1/2\rangle$$



(3d) Transition metal dimers
Clebsch–Gordan coefficients

Global state

$$\left|S,M\right\rangle = \sum_{\{M_A,M_B\}} C^{S,S_A,S_B}_{M,M_A,M_B} \left|S_A,M_A\right\rangle \left|S_B,M_B\right\rangle$$

$$M_A + M_B = M$$

Local states

Local state

$$\left|S_A,M_A\right\rangle \left|S_B,M_B\right\rangle = \sum_{\{S\}} C^{S,S_A,S_B}_{M,M_A,M_B} \left|S,M\right\rangle$$

$$\left|S_A - S_B\right| \le S \le S_A + S_B$$

Global state

(3d) Transition metal dimers
Clebsch–Gordan coefficients

$$\left|S,M\right\rangle = \sum_{\{M_A,M_B\}} C^{S,S_A,S_B}_{M,M_A,M_B} \left|S_A,M_A\right\rangle \left|S_B,M_B\right\rangle$$

Cu^{2+}- Cu^{2+}

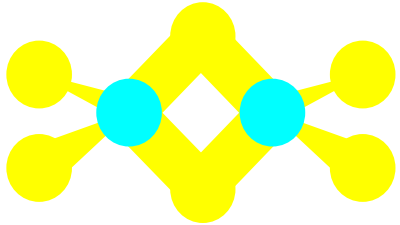
$$\begin{pmatrix} \boxed{\left|1,+1\right\rangle} \\ \left|1,\ 0\right\rangle \\ \boxed{\left|1,-1\right\rangle} \\ \left|0,\ 0\right\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{2}} & 0 \end{pmatrix} \bullet \boxed{\begin{pmatrix} \left|1/2,+1/2\right\rangle\left|1/2,+1/2\right\rangle \\ \left|1/2,+1/2\right\rangle\left|1/2,-1/2\right\rangle \\ \left|1/2,-1/2\right\rangle\left|1/2,-1/2\right\rangle \\ \left|1/2,-1/2\right\rangle\left|1/2,+1/2\right\rangle \end{pmatrix}}$$

$$triplet = \begin{cases} \left|1,+1\right\rangle \\ \left|1,\ 0\right\rangle \\ \left|1,-1\right\rangle \end{cases}$$

$$singlet = \left|0,0\right\rangle$$

$$\boxed{|5,+5\rangle} = |5/2,+5/2\rangle|5/2,+5/2\rangle$$

HS



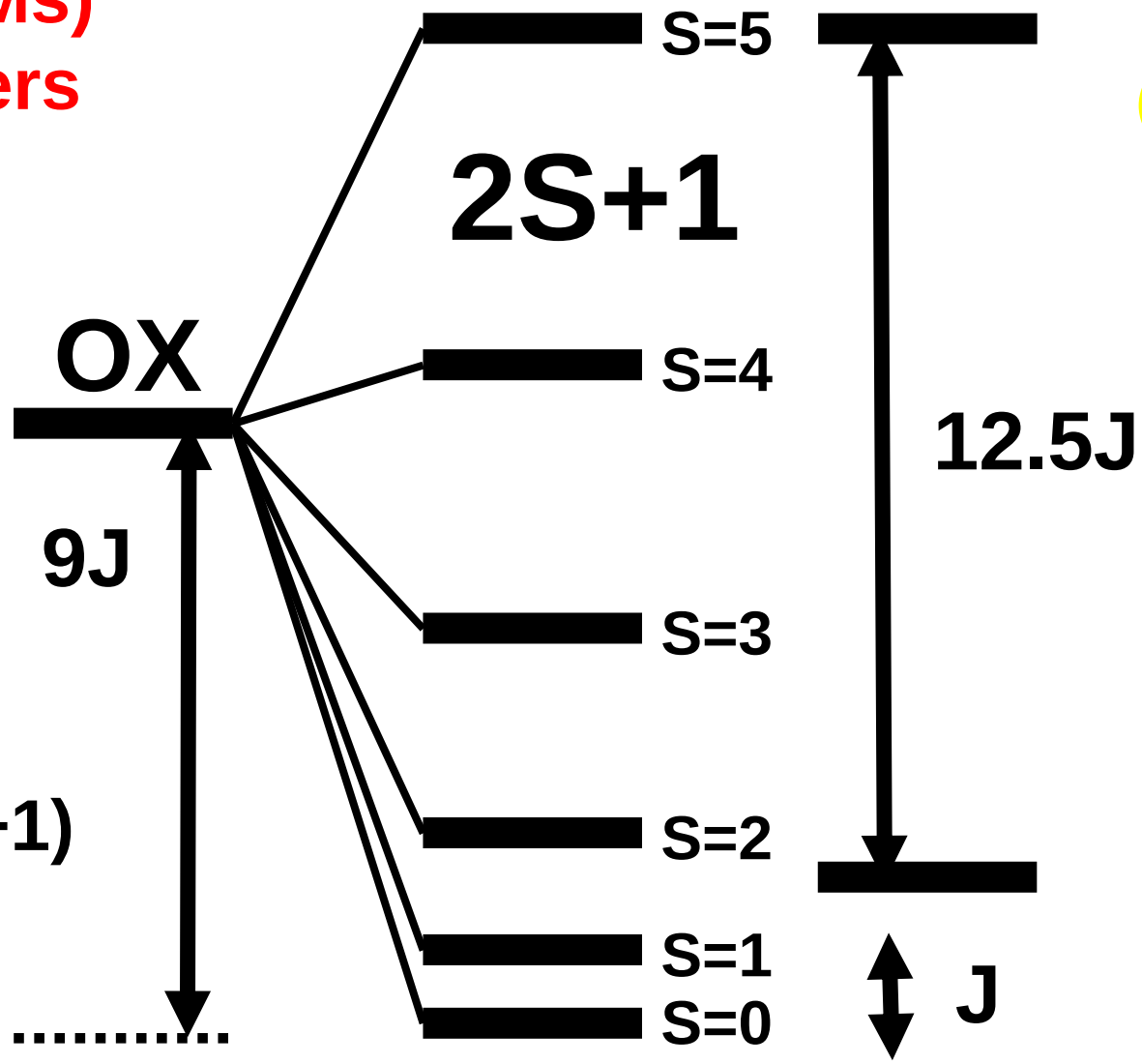
Fe^{3+}- Fe^{3+}

$$\begin{bmatrix} |5,0\rangle \\ |4,0\rangle \\ |3,0\rangle \\ |2,0\rangle \\ |1,0\rangle \\ |0,0\rangle \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{252}} & \frac{5}{\sqrt{252}} & \frac{5}{\sqrt{63}} & \frac{5}{\sqrt{63}} & \frac{5}{\sqrt{252}} & \frac{1}{\sqrt{252}} \\ \frac{1}{\sqrt{28}} & \frac{3}{\sqrt{28}} & \frac{1}{\sqrt{7}} & -\frac{1}{\sqrt{7}} & -\frac{3}{\sqrt{28}} & -\frac{1}{\sqrt{28}} \\ \sqrt{\frac{5}{36}} & \frac{7}{\sqrt{180}} & -\frac{2}{\sqrt{45}} & -\frac{2}{\sqrt{45}} & -\frac{7}{\sqrt{180}} & \sqrt{\frac{5}{36}} \\ \sqrt{\frac{25}{84}} & \sqrt{\frac{1}{84}} & -\sqrt{\frac{4}{21}} & \sqrt{\frac{4}{21}} & -\sqrt{\frac{1}{84}} & -\sqrt{\frac{25}{84}} \\ \sqrt{\frac{5}{14}} & -\sqrt{\frac{9}{70}} & \sqrt{\frac{1}{70}} & \sqrt{\frac{1}{70}} & -\sqrt{\frac{9}{70}} & \sqrt{\frac{5}{14}} \\ \frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \end{bmatrix} \bullet \begin{bmatrix} \boxed{|5/2,5/2\rangle|5/2,-5/2\rangle} \\ |5/2,3/2\rangle|5/2,-3/2\rangle \\ |5/2,1/2\rangle|5/2,-1/2\rangle \\ |5/2,-1/2\rangle|5/2,1/2\rangle \\ |5/2,-3/2\rangle|5/2,3/2\rangle \\ \boxed{|5/2,-5/2\rangle|5/2,5/2\rangle} \end{bmatrix}$$

BS

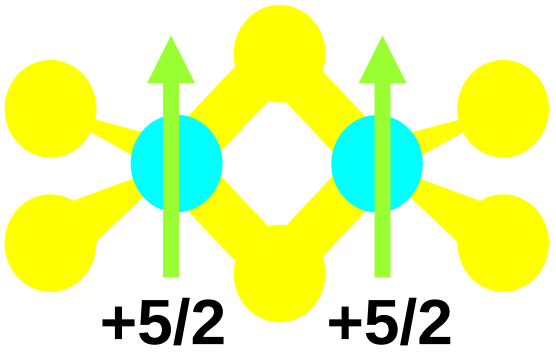
Broken symmetry state

Artificial state (Ms)
Sum of monomers



$H_{Heis.}=JS_1.S_2$

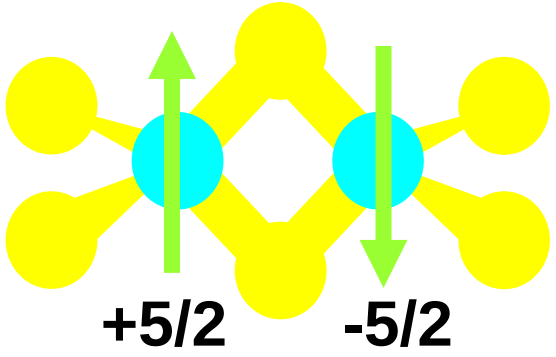
$E_{Heis.}=(J/2)S(S+1)$



HS=|+5/2,+5/2>

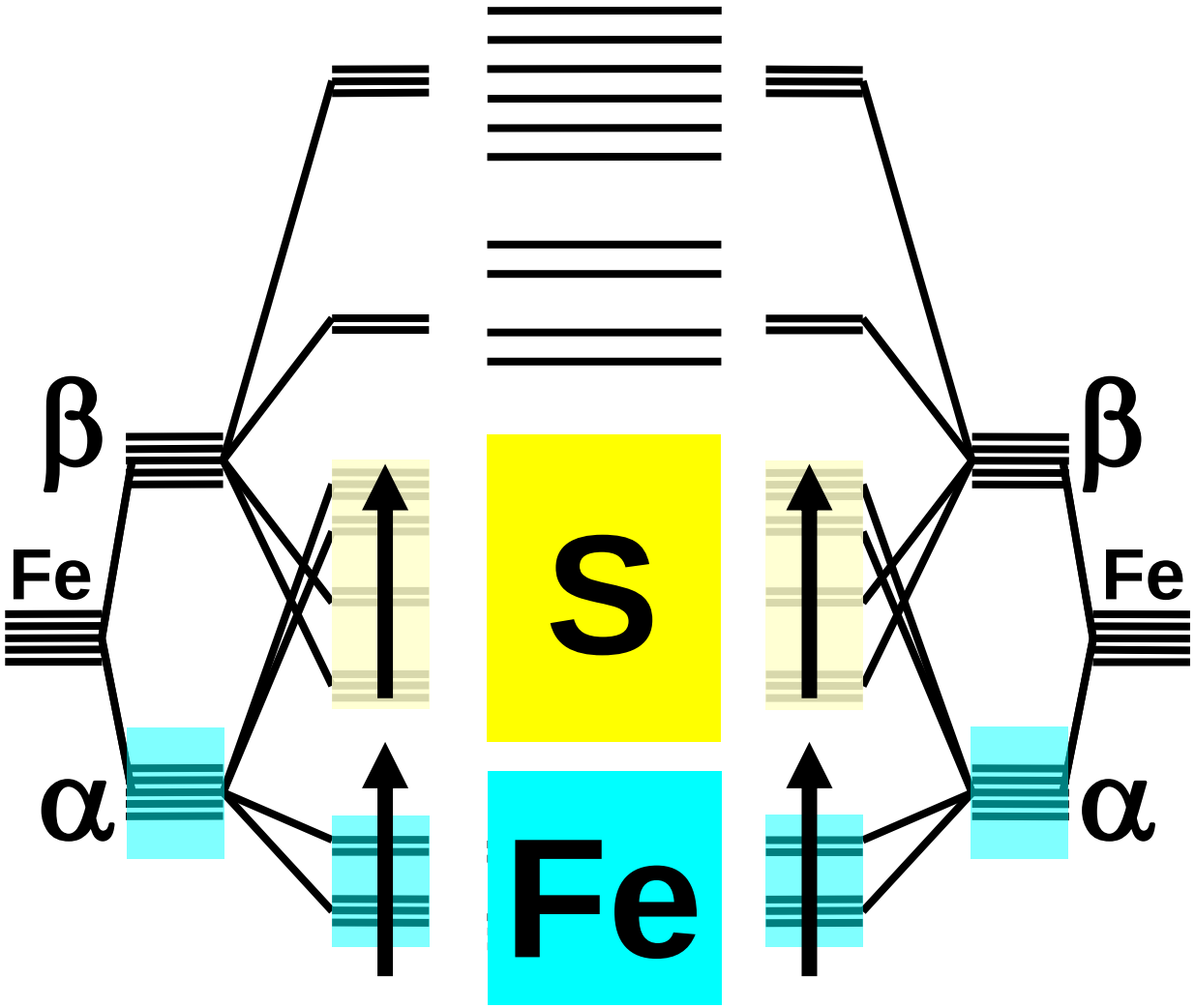
+ spin flip !

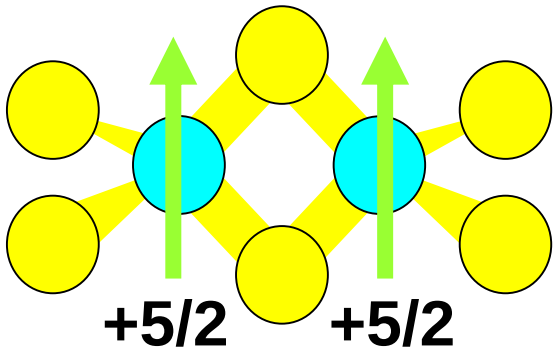
BS=|+5/2,-5/2>



High-spin states of [2Fe2S] clusters

SKIP !





HS

S=5

$$\boxed{|9/2,+9/2\rangle} = |5/2,+5/2\rangle|4/2,+4/2\rangle$$ **HS**

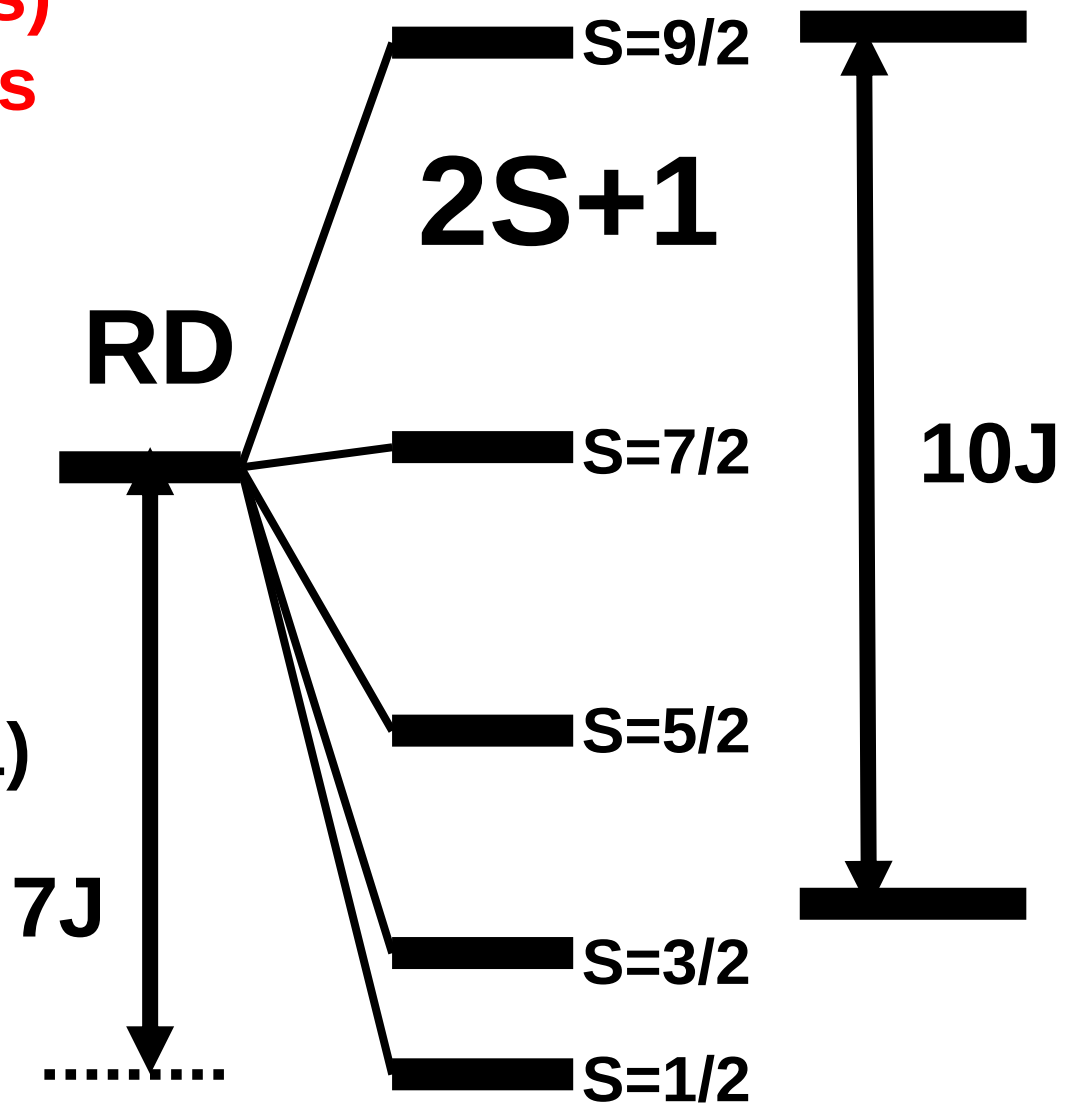
Fe^{3+}- Fe^{2+}

$$\begin{bmatrix} |9/2,1/2\rangle \\ |7/2,1/2\rangle \\ |5/2,1/2\rangle \\ |3/2,1/2\rangle \\ |1/2,1/2\rangle \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{126}} & \sqrt{\frac{10}{63}} & \sqrt{\frac{10}{21}} & \sqrt{\frac{20}{63}} & \sqrt{\frac{10}{252}} \\ \sqrt{\frac{4}{63}} & \frac{11}{\sqrt{315}} & \sqrt{\frac{4}{105}} & -\sqrt{\frac{14}{45}} & -\sqrt{\frac{64}{315}} \\ \sqrt{\frac{3}{14}} & \sqrt{\frac{6}{35}} & \sqrt{\frac{8}{35}} & 0 & \sqrt{\frac{27}{70}} \\ \sqrt{\frac{8}{21}} & -\sqrt{\frac{2}{105}} & -\sqrt{\frac{2}{35}} & \sqrt{\frac{5}{21}} & -\sqrt{\frac{32}{105}} \\ \frac{1}{\sqrt{3}} & \frac{-2}{\sqrt{15}} & \frac{1}{\sqrt{5}} & -\sqrt{\frac{2}{15}} & \sqrt{\frac{1}{15}} \end{bmatrix} \bullet \begin{bmatrix} \boxed{|5/2,5/2\rangle|2,-2\rangle} \\ |5/2,3/2\rangle|2,-1\rangle \\ |5/2,1/2\rangle|2,0\rangle \\ |5/2,-1/2\rangle|2,1\rangle \\ |5/2,-3/2\rangle|2,2\rangle \end{bmatrix}$$

BS

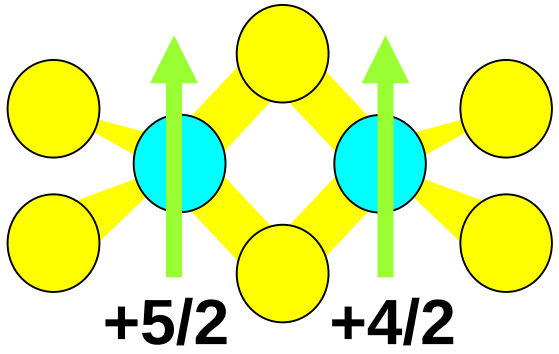
Broken symmetry state

Artificial state (Ms)
Sum of monomers



$H_{Heis.}=JS_1.S_2$

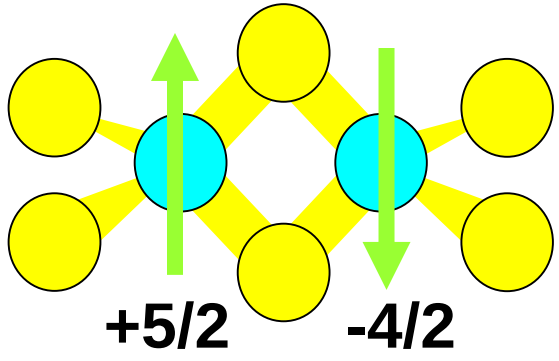
$E_{Heis.}=(J/2)S(S+1)$



HS=|+5/2,+4/2>

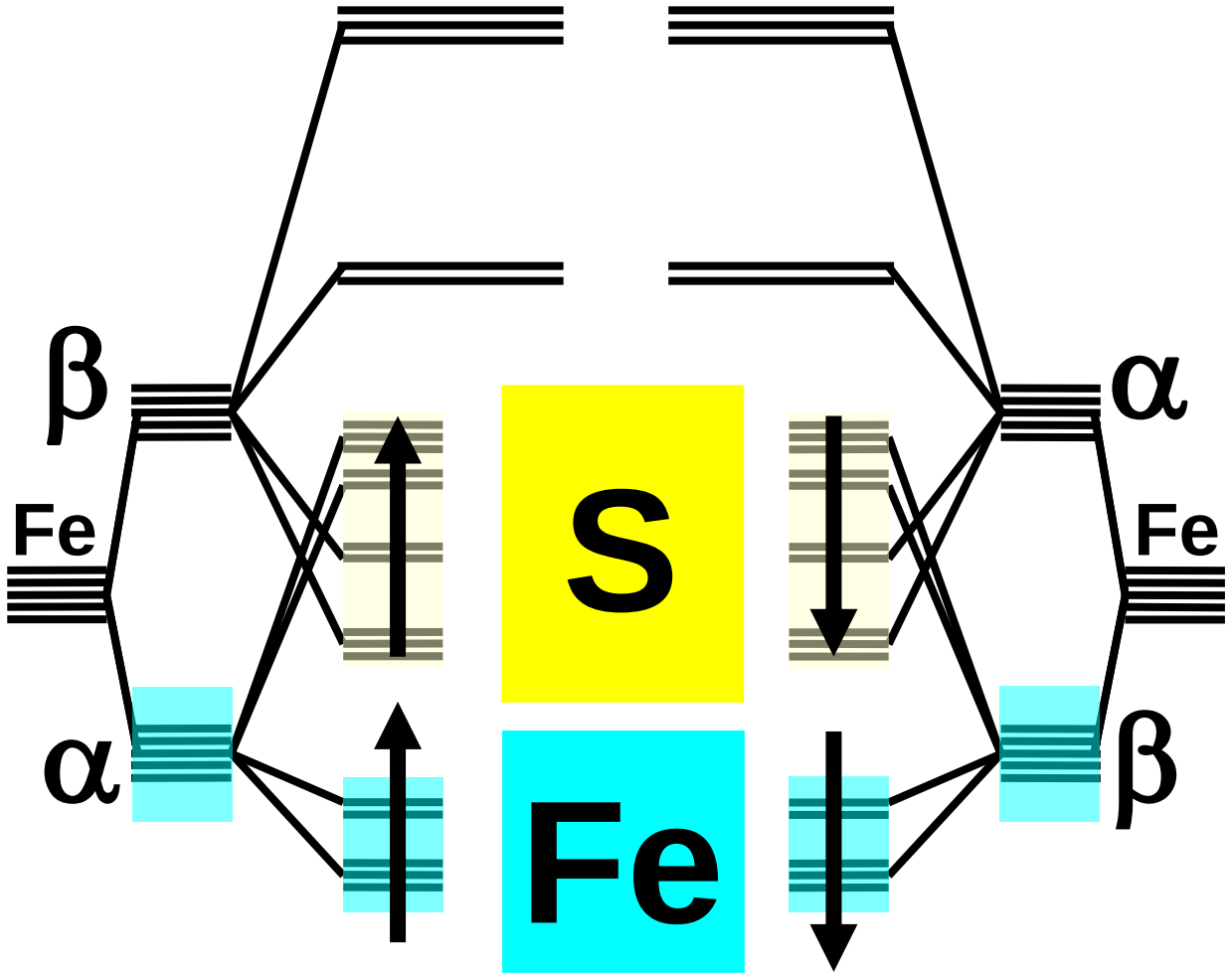
+ spin flip !

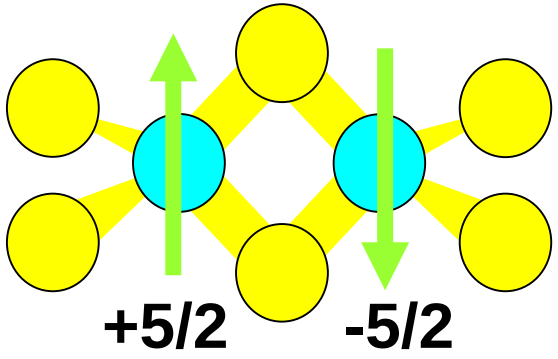
BS=|+5/2,-4/2>



SKIP !

BS states of [2Fe2S] clusters





BS

$M_{SA}=5/2$

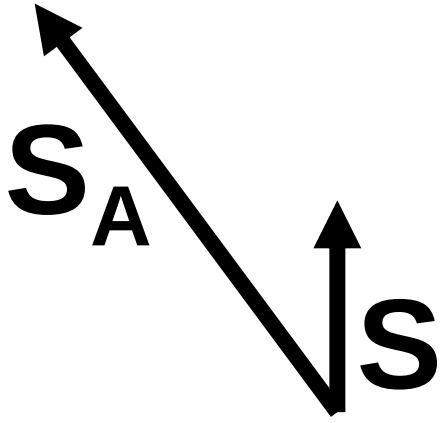
Spin coupling

$$\left|S,M\right\rangle = \sum_{\{M_A,M_B\}} C^{S,S_A,S_B}_{M,M_A,M_B} \left|S_A,M_A\right\rangle \left|S_B,M_B\right\rangle$$

Global representation ⟷ **Local representation**

$$\left\langle S,M\left|S_z\right|S,M\right\rangle = M$$

$$\left\langle S,M\left|S_{Az}\right|S,M\right\rangle = \sum_{\{M_A,M_B\}} M_A \left(C^{S,S_A,S_B}_{M,M_A,M_B}\right)^2$$



$$\tilde{A}_{global} \equiv \underbrace{\frac{\left\langle S,M\left|S_{Az}\right|S,M\right\rangle}{\left\langle S,M\left|S_z\right|S,M\right\rangle}}_{K_A} \tilde{A}_{local}$$

$$\vec{S}_A.\tilde{A}_{local}.\vec{I}_A$$

$$\Downarrow$$

$$\vec{S}.\tilde{A}_{global}.\vec{I}_A$$

Spin coupling

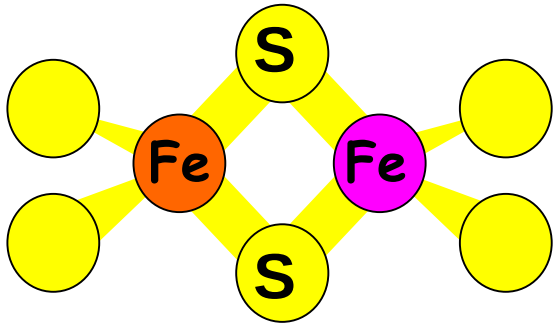
$$S_A + S_B = S$$

$$K_A + K_B = 1$$

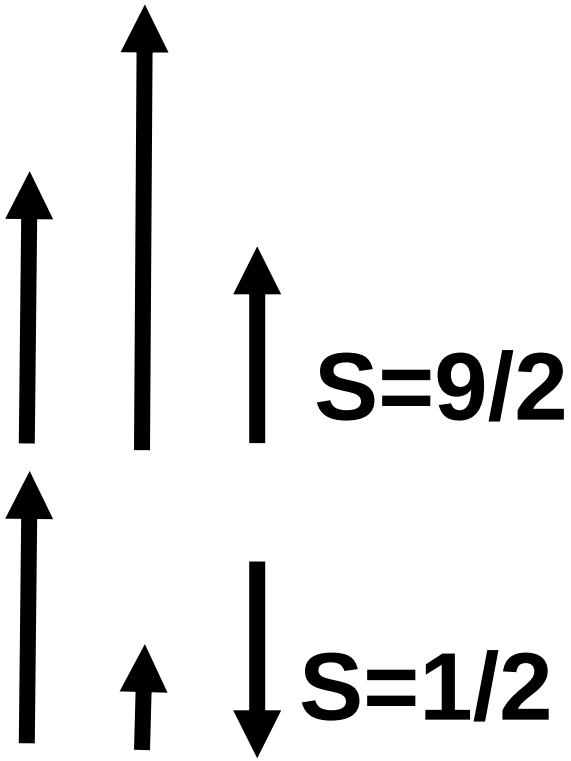
$$K_A \equiv \frac{S(S+1) + S_A(S_A+1) - S_B(S_B+1)}{2S(S+1)}$$

$$K_B \equiv \frac{S(S+1) + S_B(S_B+1) - S_A(S_A+1)}{2S(S+1)}$$

$S_A = 5/2$
$S_B = 2$



S	K_A	K_B
$9/2$	$+5/9$	$+4/9$
$7/2$	$+37/63$	$+26/63$
$5/2$	$+23/35$	$+12/35$
$3/2$	$+13/15$	$+2/15$
$1/2$	$+7/3$	$-4/3$



SKIP !

Spin coupling and EPR/ENDOR spectroscopies

$$\left|S,M\right\rangle = \sum_{\{M_A,M_B\}} C^{S,S_A,S_B}_{M,M_A,M_B} \left|S_A,M_A\right\rangle \left|S_B,M_B\right\rangle$$

Global representation ⟷ **Local representation**

$$H^Z_A = \beta \vec{H}.\tilde{g}_A.\vec{S}_A \qquad \vec{S}_A.\tilde{A}_A.\vec{I}_A$$

$$H^Z_B = \beta \vec{H}.\tilde{g}_B.\vec{S}_B \qquad \vec{S}_B.\tilde{A}_B.\vec{I}_B$$

⟷

$$H^Z_{tot} = \beta \vec{H}.\tilde{g}.\vec{S} \qquad \vec{S}.\tilde{A}_{A/S}.\vec{I}_A$$

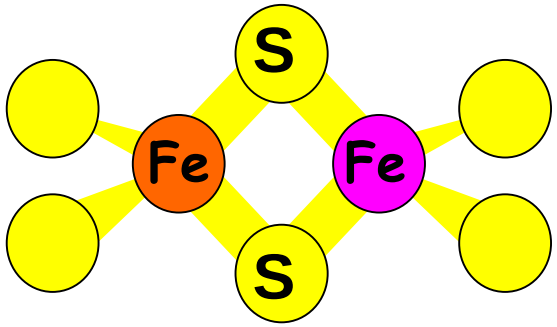
$$H_J = J\vec{S}_A.\vec{S}_B \qquad \vec{S}.\tilde{A}_{B/S}.\vec{I}_B$$

Spin coupling and EPR/ENDOR spectroscopies

$S_A + S_B = S$

$$\tilde{g} = K_A \tilde{g}_A + K_B \tilde{g}_B$$

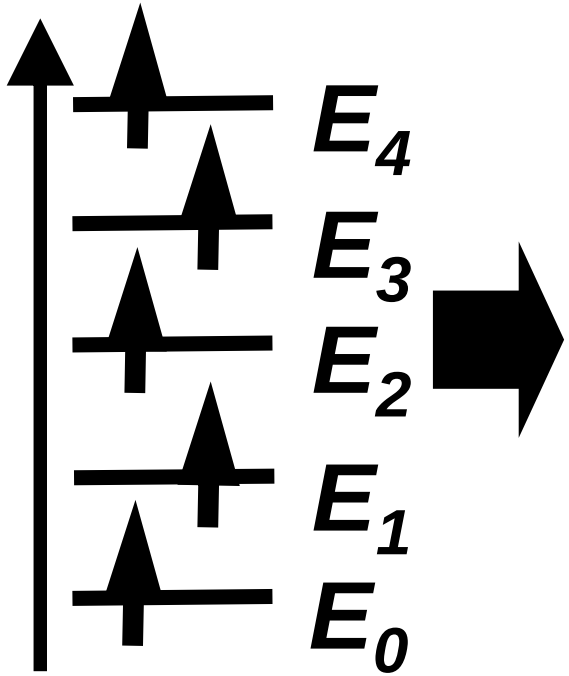
$S_A = 5/2$
$S_B = 2$



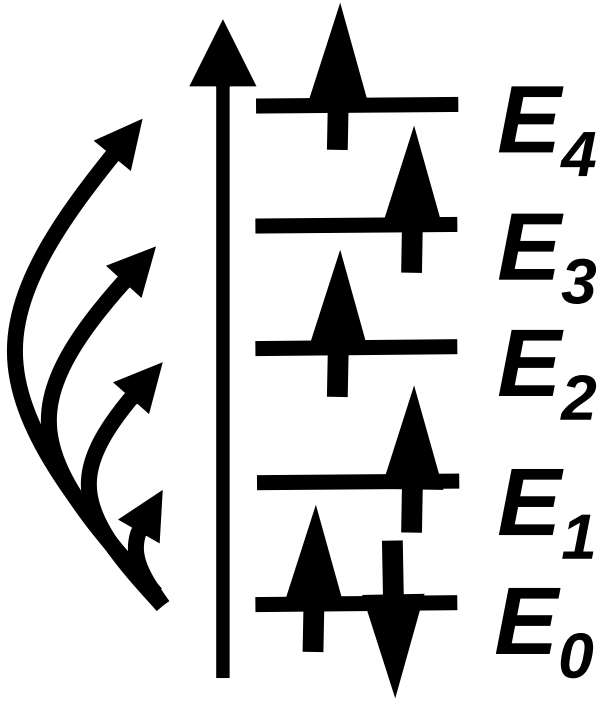
S	K_A	K_B
$9/2$	$+5/9$	$+4/9$
$7/2$	$+37/63$	$+26/63$
$5/2$	$+23/35$	$+12/35$
$3/2$	$+13/15$	$+2/15$
$1/2$	$+7/3$	$-4/3$

Spin coupling and EPR/ENDOR spectroscopies

$$\tilde{g} = (7/3)\tilde{g}_A - (4/3)\tilde{g}_B$$

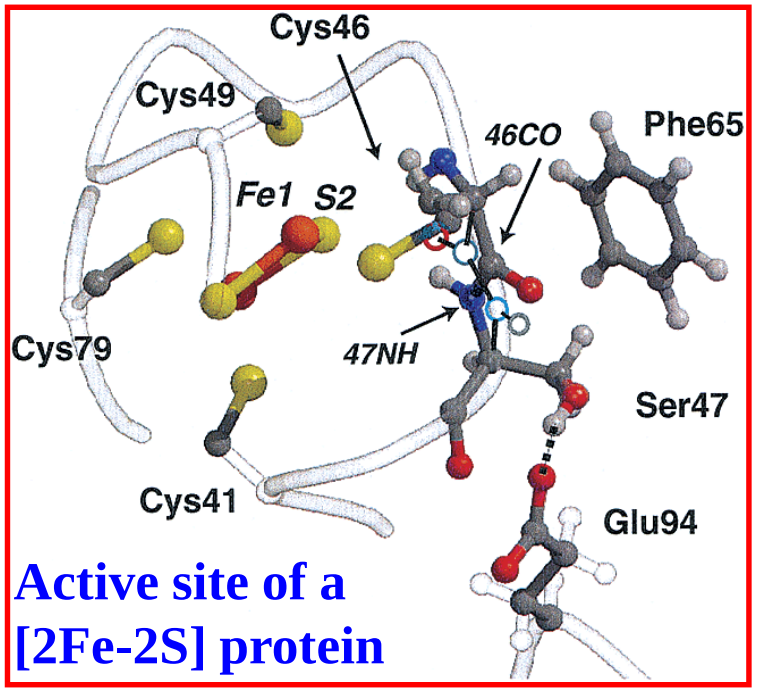


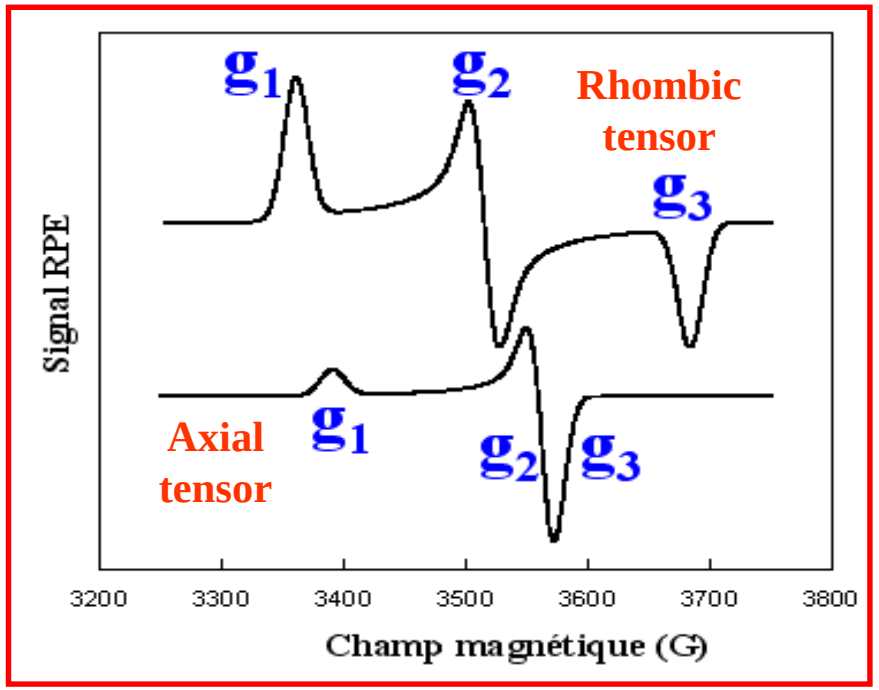
$$g_x \approx g_e$$
$$g_y \approx g_e$$
$$g_z \approx g_e$$

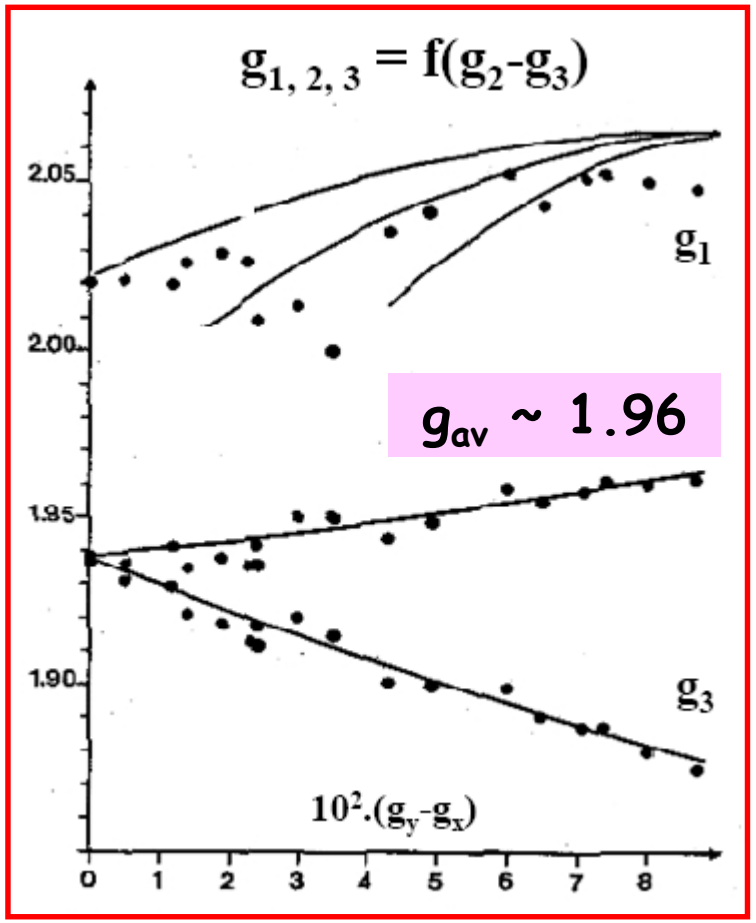


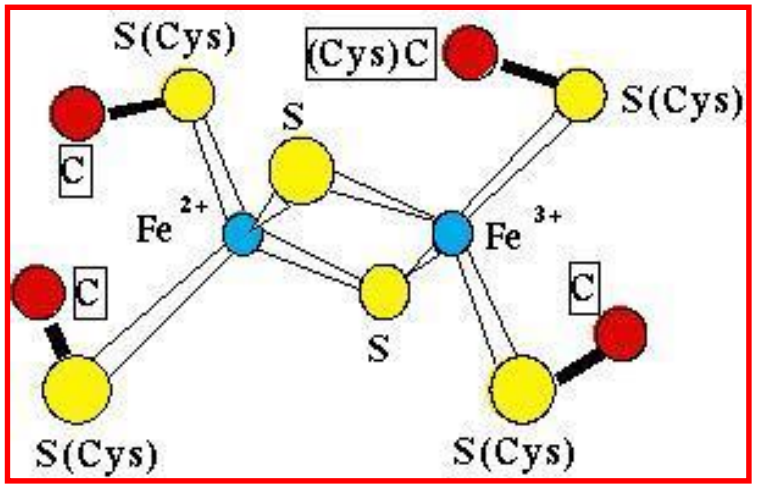
$$g_x \approx g_e + \frac{2\zeta_{3d}}{2S}\left(\frac{1}{E_1 - E_0}\right)$$
$$g_y \approx g_e + \frac{2\zeta_{3d}}{2S}\left(\frac{1}{E_2 - E_0}\right)$$
$$g_z \approx g_e + \frac{2\zeta_{3d}}{2S}\left(\frac{1}{E_4 - E_0}\right)$$

Example of magneto-structural correlation









Correlation between the Magnetic g Tensors and the Local Cysteine Geometries for a Series of Reduced [2Fe–2S*] Protein Clusters. A Quantum Chemical Density Functional Theory and Structural Analysis

Serge Gambarelli* and Jean-Marie Mouesca*

Inorg. Chem. **2004**, *43*, 1441–1451

Variation of Average *g* Values and Effective Exchange Coupling Constants among [2Fe–2S] Clusters: A Density Functional Theory Study of the Impact of Localization (Trapping Forces) versus Delocalization (Double-Exchange) as Competing Factors

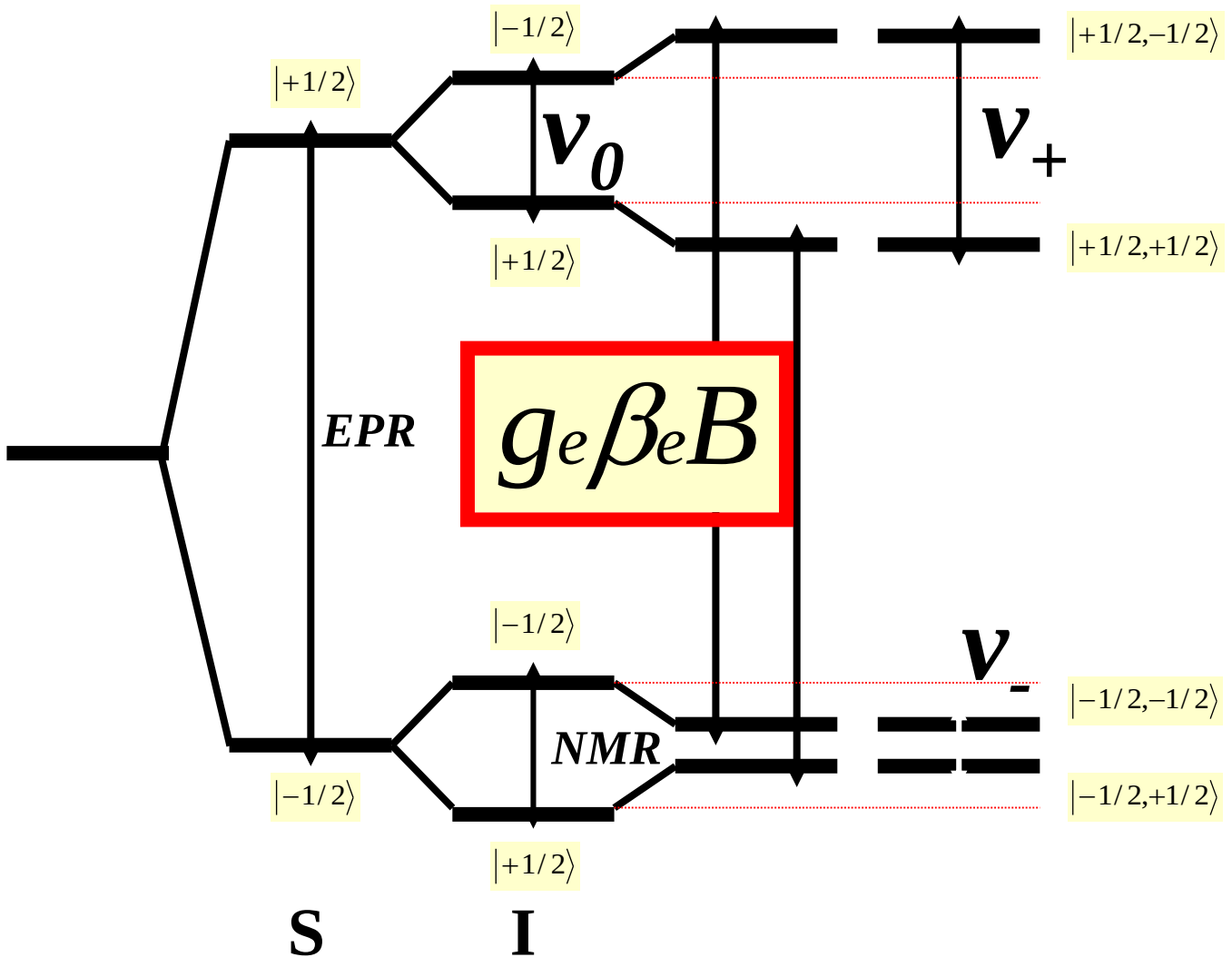
Maylis Orio and Jean-Marie Mouesca*

Inorg. Chem. **2008**, *47*, 5394–5416

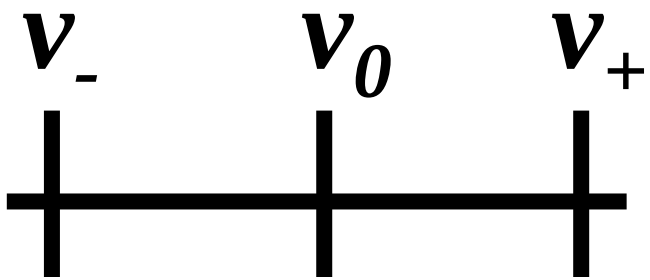
P.Bertrand and J.-P.Gayda, *Biochim.Biophys.Acta* 579, p.107 (1979)

SKIP !

Zeeman interactions + hyperfine couplings



$$A\vec{S}.\vec{I}$$



$$\nu_+ = \nu_0 + A/2$$

$$\nu_- = \nu_0 - A/2$$

SKIP !

Hyperfine tensor

Isotropic ***Anisotropic***

Contact ***Orbital*** ***Dipolar***

$$A_{cont}\vec{S}.\vec{I}$$

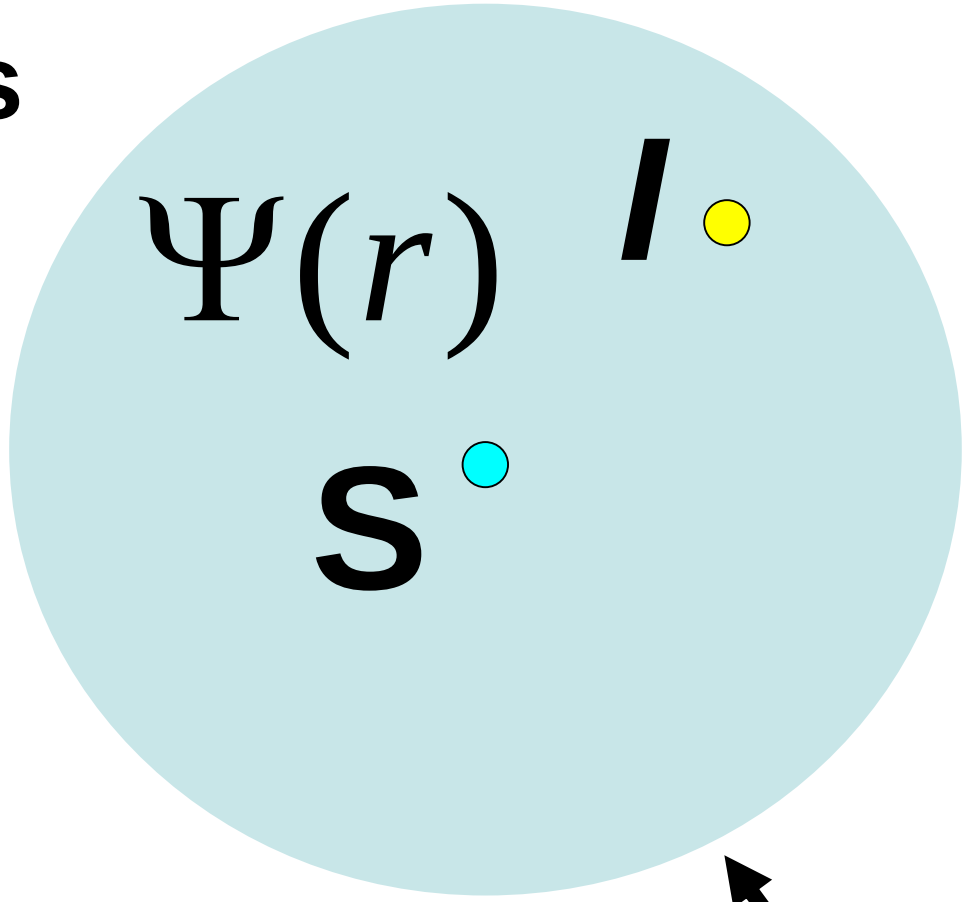
$$\vec{S}.\tilde{A}_{orb}.\vec{I}$$

$$\vec{S}.\tilde{A}_{dip}.\vec{I}$$

SKIP !

Hyperfine couplings

$$\vec{S}.\tilde{A}_I.\vec{I}$$



Fermi contact

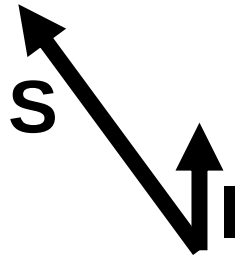
$$A_{cont}\vec{S}.\vec{I}$$

$$A_{cont} = \frac{1}{2S}\frac{8\pi}{3} g_e \beta_e g_I \beta_I \Psi^2(r_I)$$

$$\vec{S}.\tilde{A}_{orb}.\vec{I}$$

$$\tilde{A}_{orb} = \vec{S}.\left[\frac{1}{g_e}\left(\tilde{g} - g_e \tilde{I} d\right)\tilde{A}(dip)\right].\vec{I}$$

Pseudo-contact



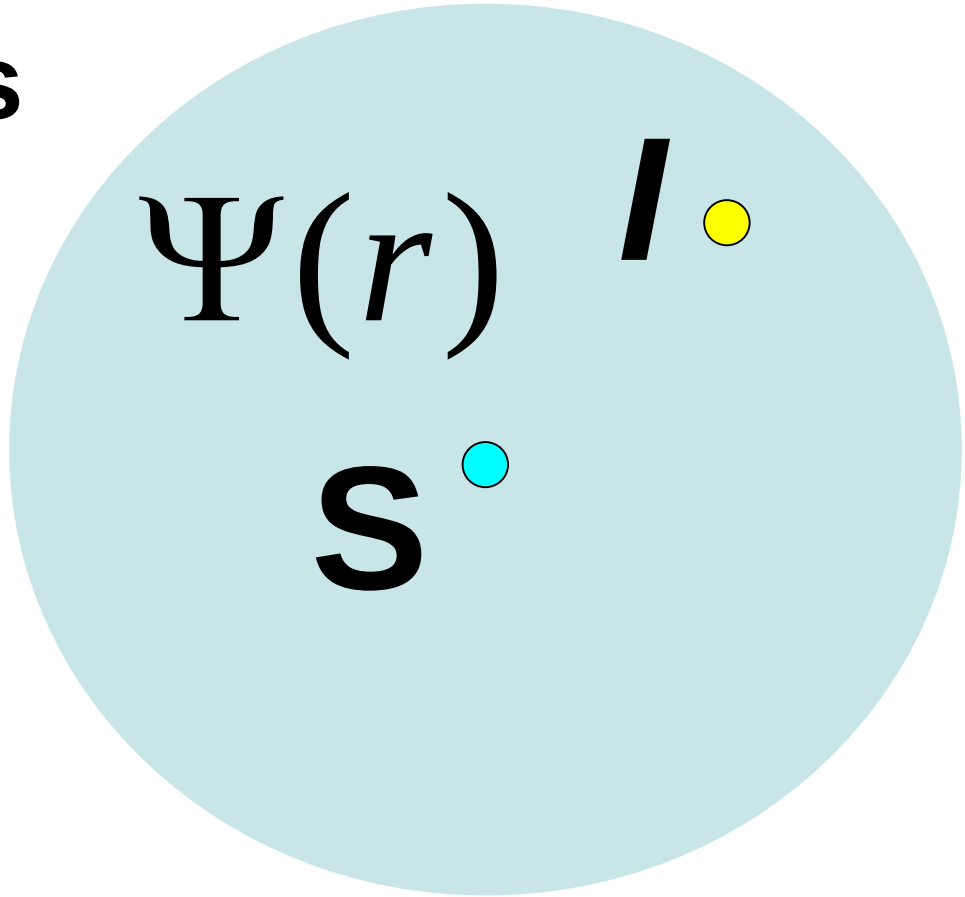
$$\vec{S}.\tilde{A}_{dip}.\vec{I}$$

$$\tilde{A}_{dip} = \frac{g_e \beta_e g_I \beta_I}{2S} \iiint_r \frac{1}{r^5}\left[-\vec{S}.\vec{I} r^2 + 3(\vec{S}.\vec{r})(\vec{I}.\vec{r})\right]\Psi^2(r)dr$$

SKIP !

Hyperfine couplings

$$\vec{S}.\tilde{A}_I.\vec{I}$$



$$A_{cont}\vec{S}.\vec{I}$$

$$A_{cont} = \frac{1}{2S}\frac{8\pi}{3} g_e \beta_e g_I \beta_I \left(\Psi_\alpha^2(r_I) - \Psi_\beta^2(r_I)\right)$$

$$\left(\frac{\mu_0}{4\pi}\right) g_e \beta_e g_I \beta_I /(hr^3)$$

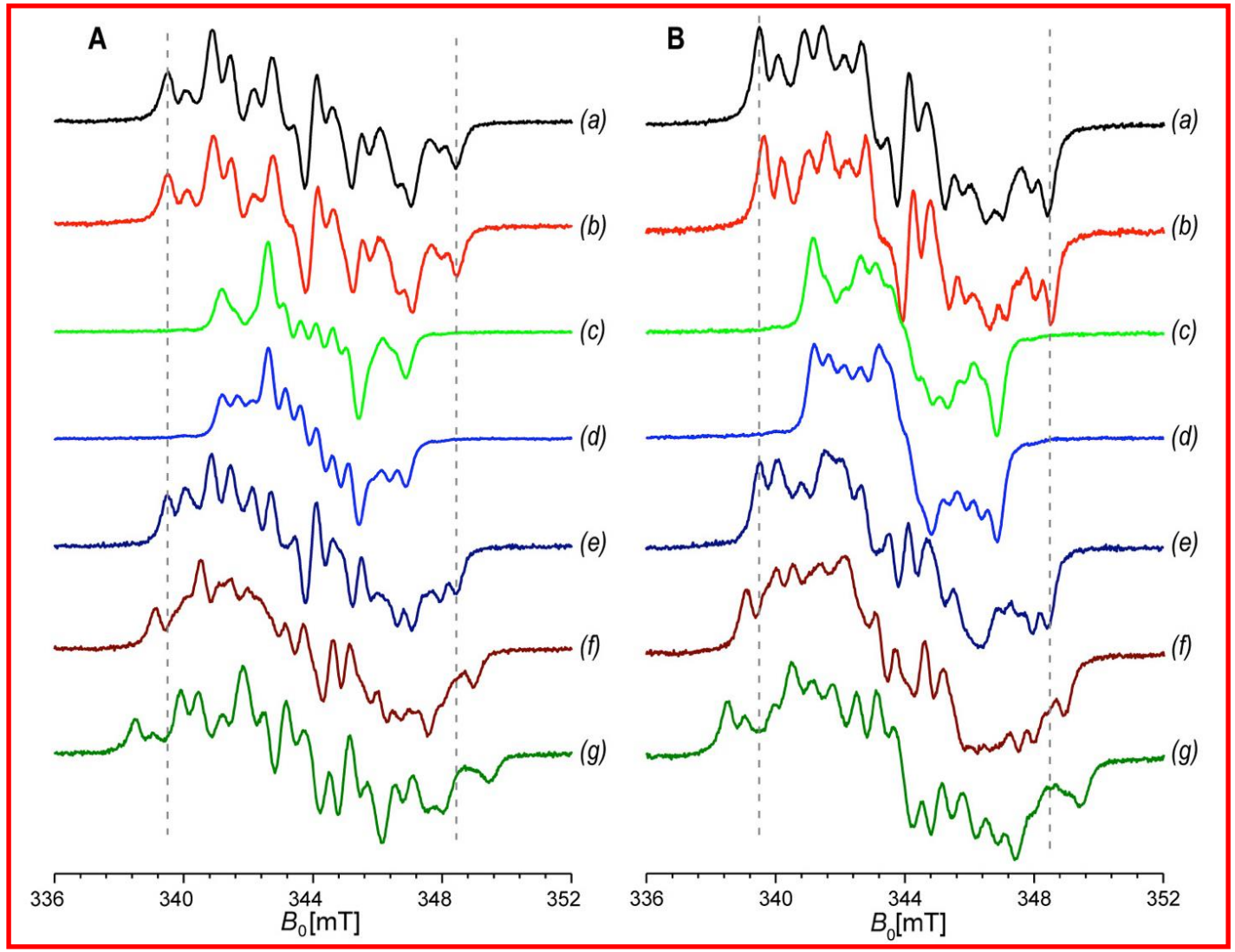
In MHz:

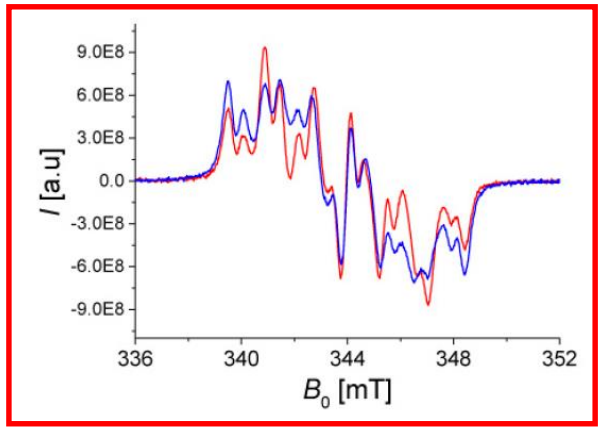
Proton (^1H)	79.1
Carbone (^{13}C)	19.9
Nitrogen (^{14}N)	5.7
Fer (^{57}Fe)	2.55

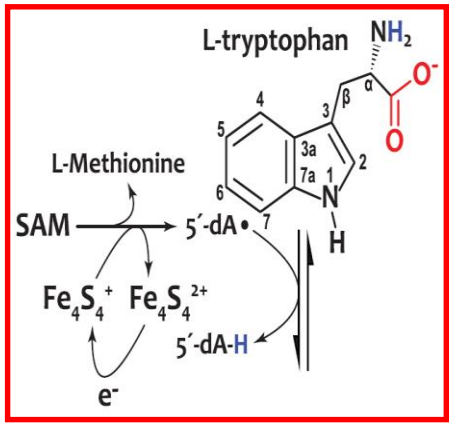
$$^1\mathrm{H}(1\mathrm{s}:100\%)$$

$$\rightarrow 1420\ \mathrm{MHz}$$

SKIP ! Organic radicals *versus* Metallic complexes







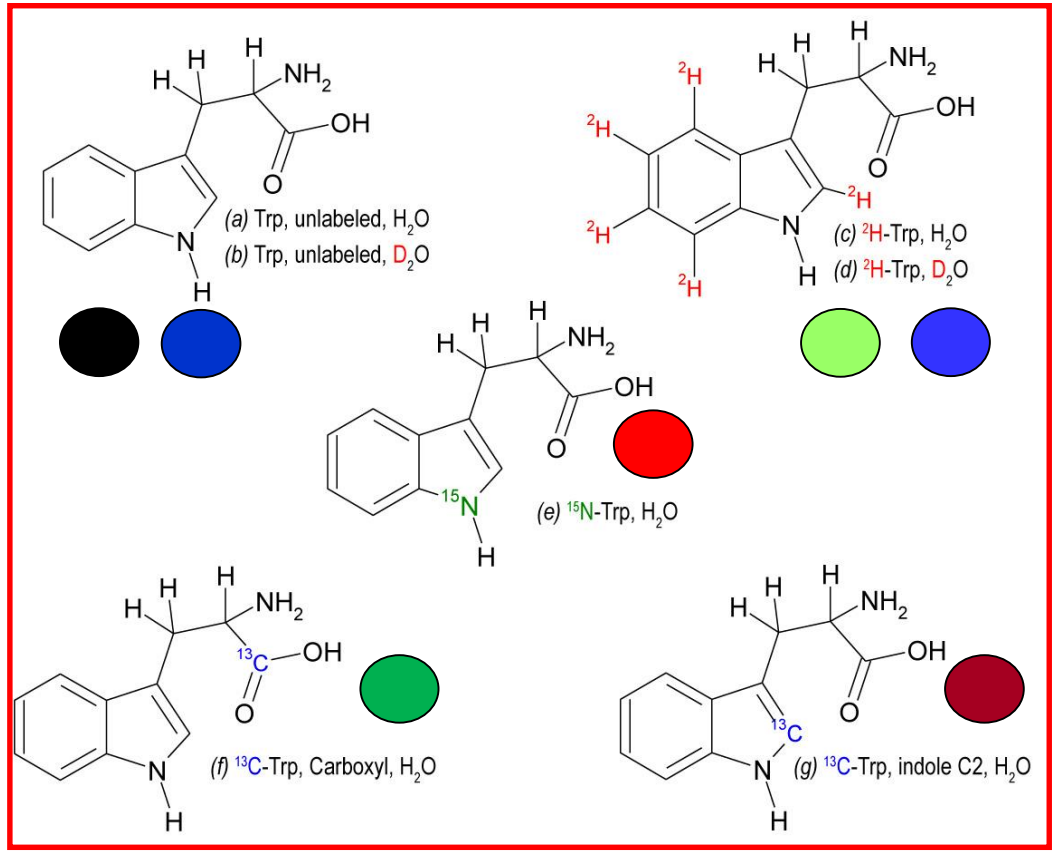
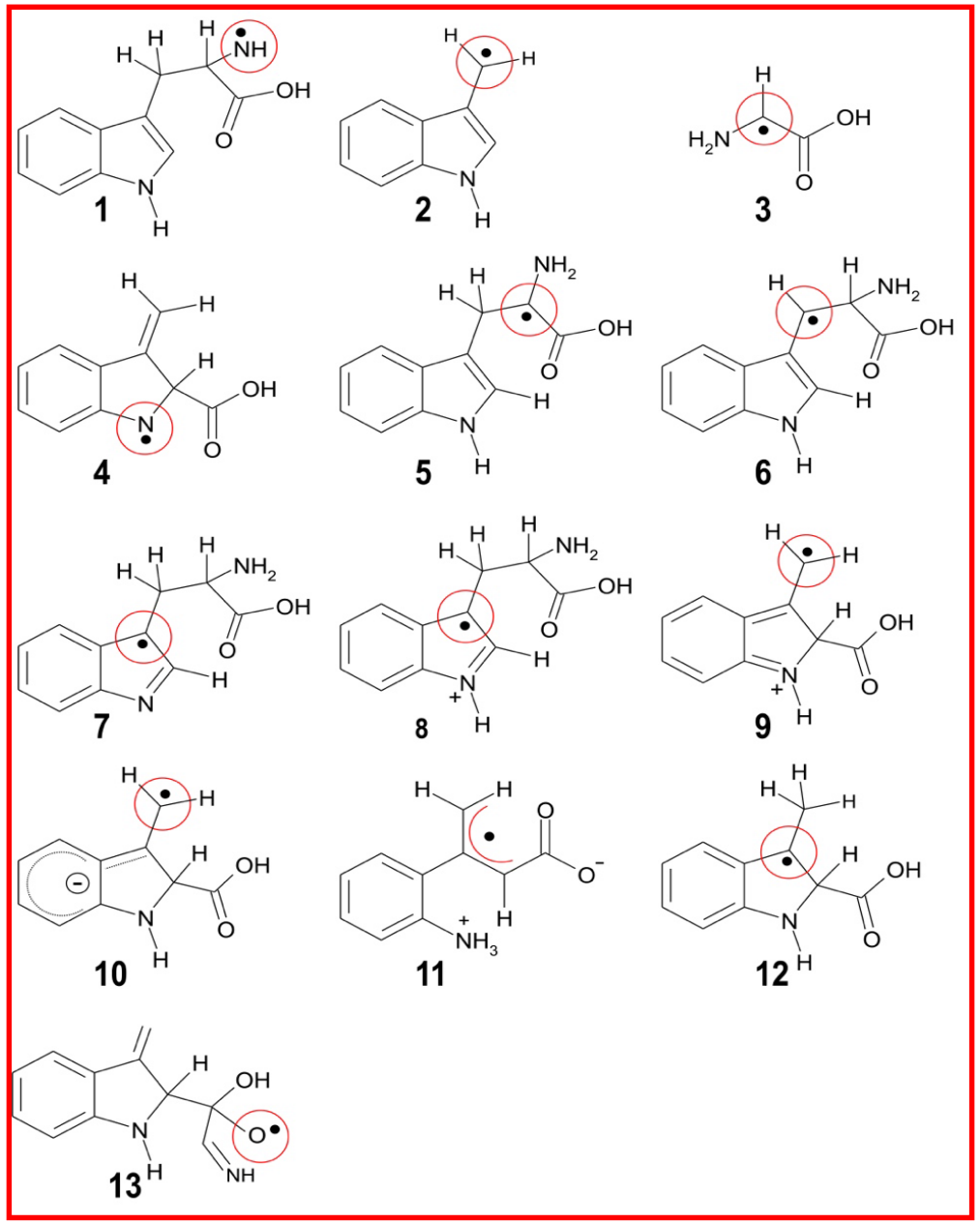
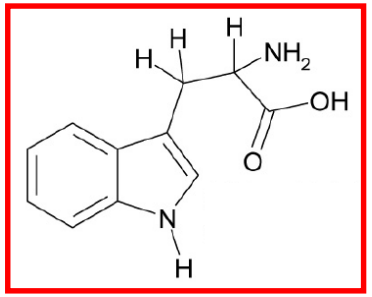


Figure S6. Raw spectra (*X*-band, 9.65 GHz) for unlabeled L-tryptophan (Trp) in H_2O (*a*, *black*), ^{15}N-Trp (*b*, *red*), ^{2}H-Trp in H_2O (*c*, *light green*), ^{2}H-Trp in D_2O (*d*, *blue*), unlabeled Trp in D_2O (*e*, *navy*), ^{13}C-Trp (*f*, indole, *brown*), ^{13}C-Trp (*g*, COOH, *dark green*); quenching time of the reaction: 45 s. (**A**) temperature 80 K, (**B**) temperature 60 K.

SKIP !

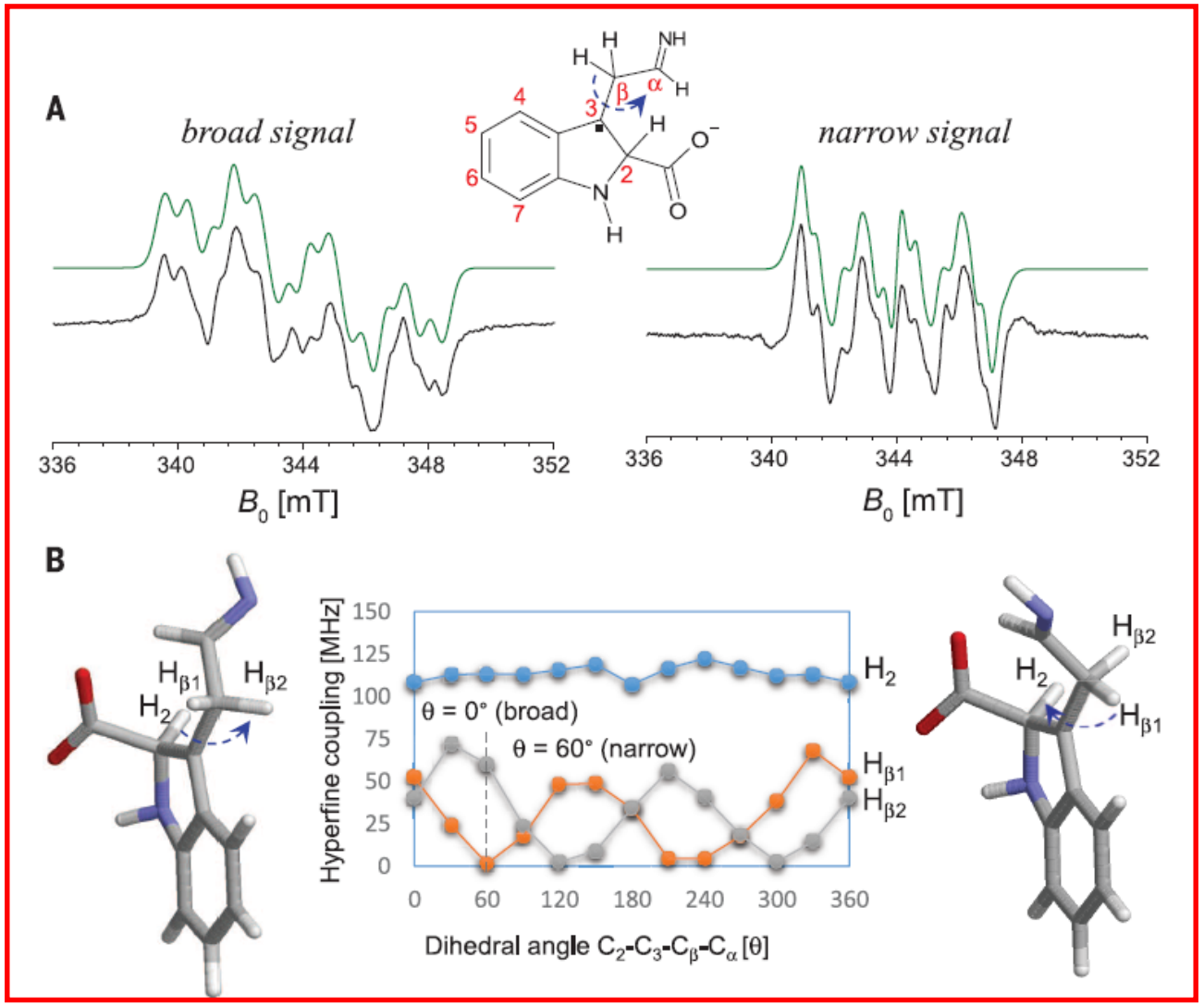




Fine-tuning of a radical-based reaction by radical *S*-adenosyl-L-methionine tryptophan lyase

Science 2016, vol.351, p.1320

Giuseppe Sicoli,[1,2] Jean-Marie Mouesca,[1,2] Laura Zeppieri,[3] Patricia Amara,[3] Lydie Martin,[3] Anne–Laure Barra,[4] Juan C. Fontecilla-Camps,[3] Serge Gambarelli,[1,2*] Yvain Nicolet[3*]



Organic radicals *versus* Metallic complexes

3s

2s

1s

Ions	1s	2s	3s	total
Fe^{2+}	+0.07	+2.37	-1.44	≡ 1.00
Fe^{3+}	+0.09	+2.83	-1.91	≡ 1.00

Watson & Freeman (1961)

$$FC = A_{cont}$$

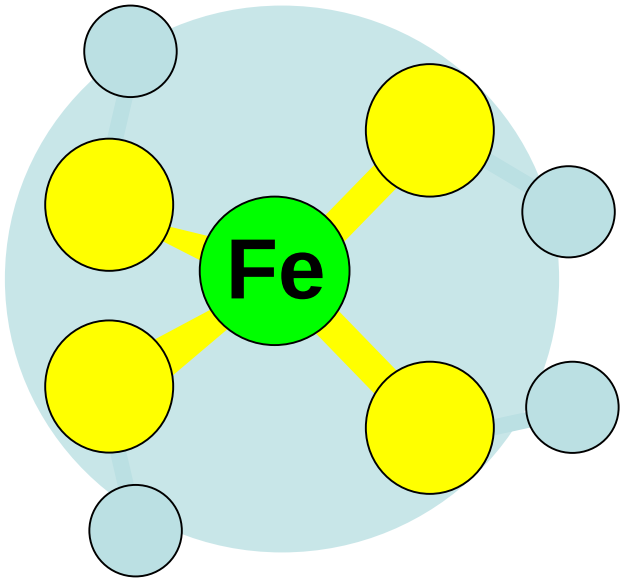
$$PC = A_{orb}$$

The Mössbauer Parameters of the Proximal Cluster of Membrane-Bound Hydrogenase Revisited: A Density Functional Theory Study

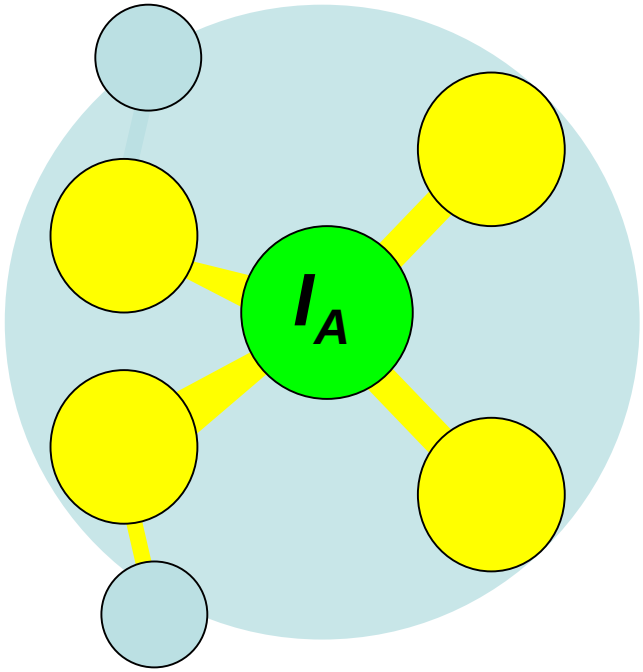
Shadan Ghassemi Tabrizi,[†] Vladimir Pelmenschikov,[†] Louis Noodleman,[‡] and Martin Kaupp*[,†]

J. Chem. Theory Comput. 2016, 12, 174–187

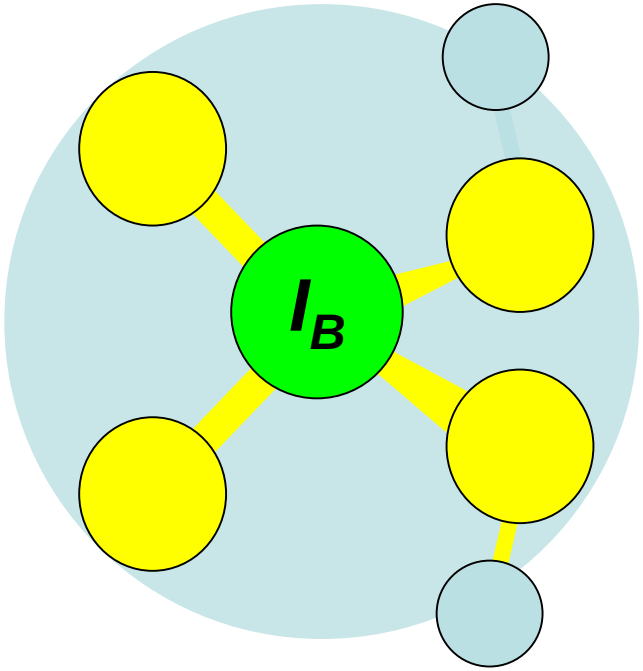
	FC	PC	FC+PC	FC^{scal}	PC^{scal}	FC^{scal} $+PC^{scal}$	A_{iso}^{exp}
Fe^{II}PorOAc	-18.5	+1.3	-16.8	-35.9	+4.7	-31.2	-21.8
Fe^{II}SR3	-14.7	+2.3	-12.4	-28.5	+8.3	-20.2	-14.9
Fe^{III}Az	-15.8	+4.6	-11.1	-30.7	+16.6	-14.0	-13.47
Fe^{III}OEPPy	-16.6	+6.2	-10.4	-32.2	+22.4	-9.8	-6.8
Fe^{III}MAC	-3.2	+1.0	-2.1	-6.2	+3.6	-2.6	-15.4
Fe^{III}PorOAc	-16.6	+0.1	-16.4	-32.2	+0.4	-31.8	-27.5
Fe^{III}PorO2	-13.3	+0.7	-12.6	-25.8	+2.5	-23.3	-32.1
Fe^{IV}PorO	-9.6	-0.7	-10.4	-18.6	-2.5	-21.2	-25.2
Fe^{IV}MAC	-8.2	+0.3	-7.9	-15.9	+1.1	-14.8	-20
Rd_{red} Fe^{2+}	-13.49	+1.37	-12.12	-26.2	+4.9	-21.2	-23.4
Rd_{ox} Fe^{3+}	-12.19	+0.61	-11.58	-23.6	+2.2	-21.4	-22.5



Spin coupling



Fe^{3+}



Fe^{2+}

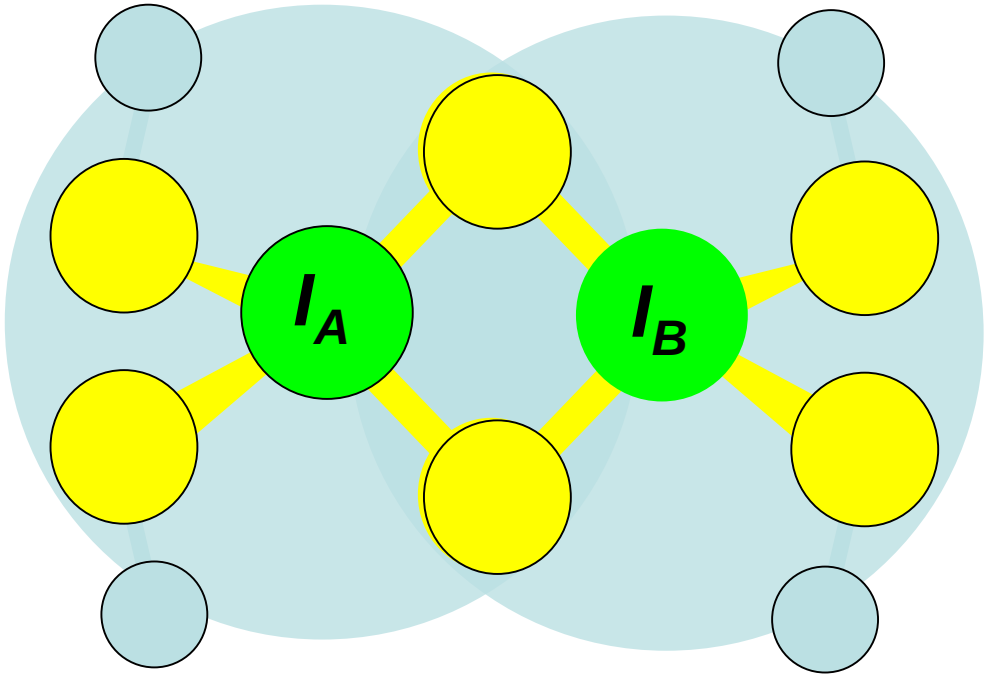
$$\vec{S}_A.(\tilde{A}_{cont}(loc)_{AA}).\vec{I}_A$$

$$\vec{S}_B.(\tilde{A}_{cont}(loc)_{BB}).\vec{I}_B$$

$$\tilde{A}_{cont}(loc)_{AA} \approx -22\,MHz$$

$$\tilde{A}_{cont}(loc)_{BB} \approx -23\,MHz$$

Spin coupling



^{57}Fe

$$K_A = +7/3$$

$$K_B = -4/3$$

$$K_A \tilde{A}_{cont}(loc)_{AA} = -51\,MHz$$

$$K_B \tilde{A}_{cont}(loc)_{BB} = +27\,MHz$$

S=1/2

Spin coupling effect on hyperfine couplings

Exp.	14.6	[-3.2, -0.5, 3.6]	[11.4, 14.1, 18.2]
	13.0	[-1.5, -1.5, 3.0]	[11.5, 11.5, 16.0]

$$\vec{S}_A.(\tilde{A}_{cont}(loc)_{AA}).\vec{I}_A$$

$$\tilde{A}_{cont}(loc)_{BS12} \sim 36\ MHz$$

$$\tilde{A}_{cont}(loc)_{BS13} \sim 37\ MHz$$

$$\tilde{A}_{cont}(loc)_{BS14} \sim -5\ MHz$$

BS State	Model	A_{iso}^{UBS}	T^{UBS}	$A^{UBS} = A_{iso}^{UBS} + T^{UBS}$
BS12	S-OX_P^{5+}	38.0	[-8.0, -1.6, 9.5]	[30.0, 36.4, 47.5]
	S-OX_D^{5+}	34.4	[-10.4, 3.1, 7.3]	[24.0, 37.5, 41.7]
	S-$OX_{D\text{-}H}^{5+}$	35.8	[-9.8, 0.8, 9.0]	[26.1, 36.6, 44.8]
BS13	S-OX_P^{5+}	41.2	[-8.7, -1.8, 10.5]	[32.5, 39.5, 51.7]
	S-OX_D^{5+}	35.2	[-10.8, 3.1, 7.8]	[24.3, 38.2, 43.0]
	S-$OX_{D\text{-}H}^{5+}$	37.1	[-10.4, 1.1, 9.3]	[26.8, 38.2, 46.4]
BS34	S-OX_P^{5+}	9.5	[-4.5, 0.2, 4.3]	[5.0, 9.7, 13.7]
	S-OX_D^{5+}	-2.5	[-7.0, 2.0, 5.0]	[-9.4, -0.5, 2.5]
	S-$OX_{D\text{-}H}^{5+}$	-5.3	[-6.1, 2.0, 4.1]	[-11.4, -3.3, -1.3]

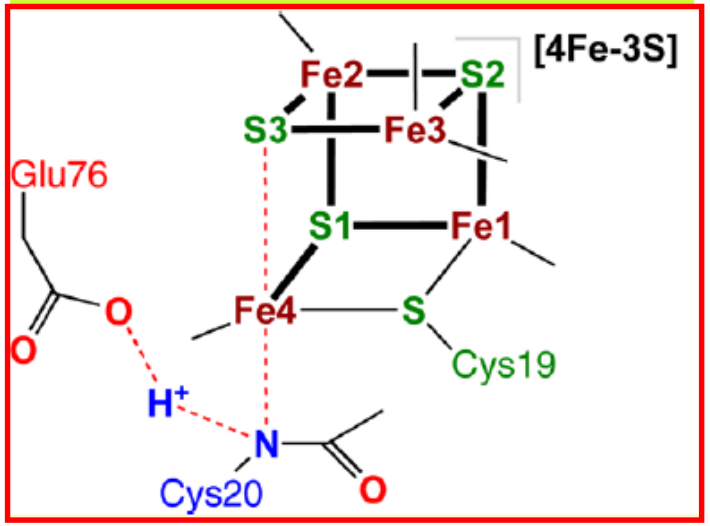


Table S9. 'Raw' Unrestricted Broken-Symmetry (UBS) DFT Hyperfine Parameters (MHz) of the Fe4-bound Cys20 Amide Nitrogen Atom N20 in Different Structural Arrangements of the Superoxidized Proximal Cluster Computed using PBE and B3LYP Functionals for the Broken-Symmetry States BS12, BS13, and BS34[a]

Spin coupling effect on hyperfine couplings

Redox-Dependent Structural Transformations of the [4Fe-3S] Proximal Cluster in O_2-Tolerant Membrane-Bound [NiFe]-Hydrogenase: A DFT Study

Vladimir Pelmenschikov and Martin Kaupp,
J. Am. Chem. Soc. 2013, 135, 11809−11823

$$K_{ij}\tilde{A}_{cont}(loc)_{BSij}$$

$$K_{BS12} = 0.47$$
$$K_{BS13} = 0.47$$
$$K_{BS34} = 0.33$$

Signal/DFT Model	BS State	A_{iso}	T	$A = A_{iso} + T$
N_{C20} (ENDOR)[19]	–	14.6	[-3.2, -0.5, 3.6]	[11.4, 14.1, 18.2]
N1 (HYSCORE)[20]	–	13.0	[-1.5, -1.5, 3.0]	[11.5, 11.5, 16.0]
$S\text{-}OX_{D\text{-}H}^{5+}$ (B3LYP)	BS12	16.8	[-4.6, 0.4, 4.2]	[12.3, 17.2, 21.1]
	BS13	17.5	[-4.9, 0.5, 4.4]	[12.6, 18.0, 21.8]
	BS34	-1.8	[-2.0, 0.7, 1.4]	[-3.8, -1.1, -0.4]

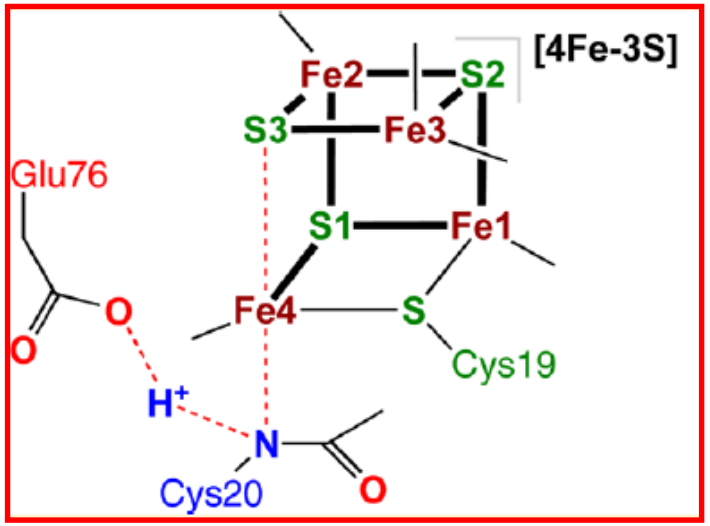


Table S10. Spin-Projected ^{14}N Hyperfine Parameters (MHz) of the Fe4-bound Cys20 Amide Nitrogen Atom N20 in Different Structural Arrangements of the Superoxidized Proximal Cluster Computed using B3LYP Functional for the Broken-Symmetry States BS12, BS13, and BS34, Compared to ENDOR and HYSCORE Data[a]

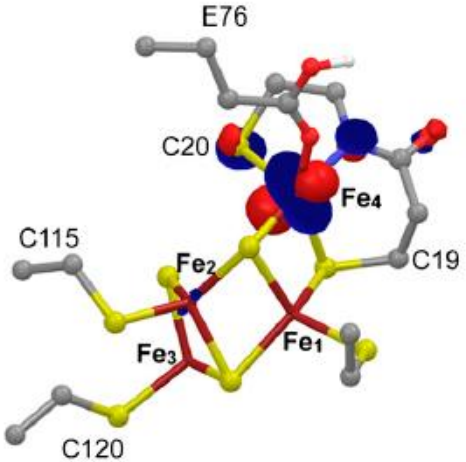
Spin coupling effect on charges (Mössbauer)

X-ray crystallographic and computational studies of the O_2-tolerant [NiFe]-hydrogenase 1 from *Escherichia coli*

PNAS 2012, vol. 109, p.5305–5310

Anne Volbeda[a,1], Patricia Amara[a,1], Claudine Darnault[a], Jean-Marie Mouesca[b], Alison Parkin[c], Maxie M. Roessler[c,d], Fraser A. Armstrong[c,d], and Juan C. Fontecilla-Camps[a,2]

Exp	2.41	0.60	0.60	1.23



BS13	-4/2	+5/2	-5/2	+5/2
BS24	+5/2	-5/2	+5/2	-4/2
BS34	+5/2	+5/2	-5/2	-4/2
BS23	+5/2	-4/2	-5/2	+5/2
BS12	-4/2	-5/2	+5/2	+5/2
BS14	-5/2	+5/2	+5/2	-4/2

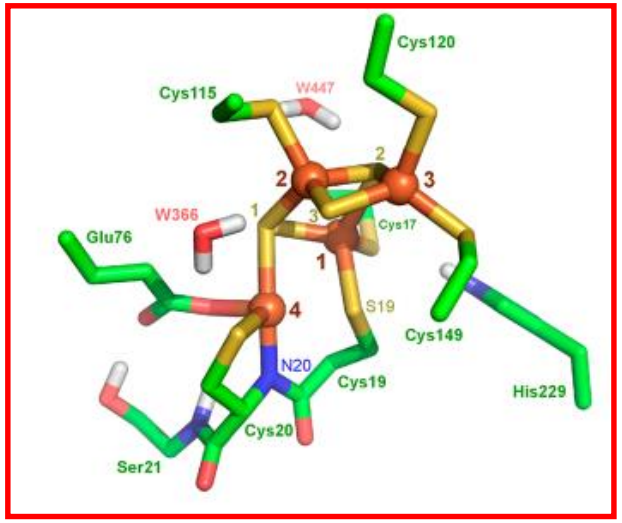
Electronic State	Relative energies (kJ/mol)	ΔE_Q Fe_1 (η)	ΔE_Q Fe_2 (η)	ΔE_Q Fe_3 (η)	ΔE_Q Fe_4 (η)
BS13	8.1	2.36 (0.21)	0.31 (0.44)	-0.31 (0.29)	0.96 (0.60)
BS24	**0.0**	2.14 (0.21)	0.27 (0.45)	-0.35 (0.24)	2.09 (0.77)
BS34	9.9	1.65 (0.93)	0.49 (0.52)	-0.20 (0.46)	2.12 (0.51)
BS23	58.7	0.56 (0.62)	1.11 (0.68)	0.72 (0.40)	1.35 (0.40)
BS12	1.4	1.54 (0.97)	0.44 (0.33)	-0.24 (0.22)	0.80 (0.83)
BS14	60.4	1.23 (0.70)	0.37 (0.97)	-0.45 (0.37)	1.55 (0.28)

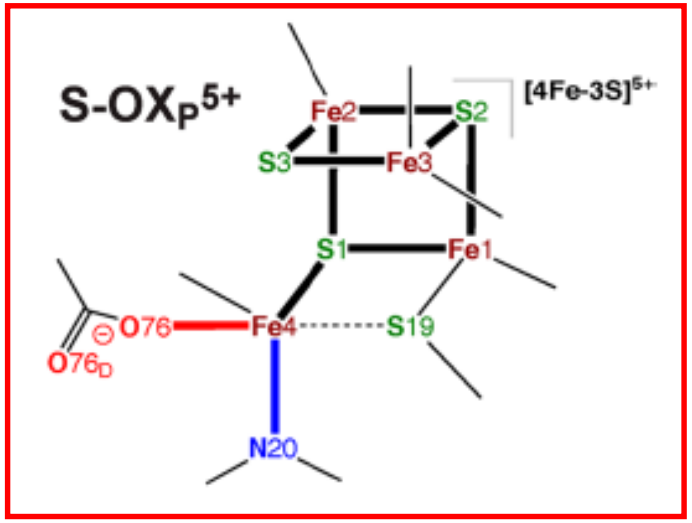
Spin coupling effect (Mössbauer & hyperfine)

The Mössbauer Parameters of the Proximal Cluster of Membrane-Bound Hydrogenase Revisited: A Density Functional Theory Study

Shadan Ghassemi Tabrizi,[†] Vladimir Pelmenschikov,[†] Louis Noodleman,[‡] and Martin Kaupp*[,†]

J. Chem. Theory Comput. 2016, 12, 174−187





	site	A_{iso} [a]	A_{iso} [b]	T_{xx} [c]	T_{yy}	T_{zz}
BS13 S-OX_p^{5+}						
	N_{C20}	+16.0	–	−3.5	+0.1	+3.5
^{14}N exp.	N_{C20}^{ENDOR}	+14.6		−3.2	−0.5	+3.6
	$N_{C20}^{HYSCORE}$	+13.0		−1.5	−1.5	+3.0

Table 3. Computed Mössbauer Parameters for the S-OX_p^{5+} Model at PBE/B3LYP Levels in Different BS States As Compared to Experimental Data[a]

S-OX_p^{5+} PBE/B3LYP Mössbauer parameters					
state	site	ΔE_Q (mms^{-1})	δ (mms^{-1})	η	A_{iso}
S-OX exp.[20]	S	(+)2.45	0.46	0.5	+25.7
		(+)0.70	0.39	1.0	−47.9
		(+)0.60	0.28	0.3	+33.4
		(−)1.00	0.40	0.7	−33.6
BS12	$Fe1^{2+}$	+1.67/+2.51	0.48/0.50	0.93/0.70	+
	$Fe2^{3+}$	−0.55/−0.66	0.37/0.35	0.71/0.86	+
	$Fe3^{3+}$	−0.41/+0.47	0.32/0.29	0.89/0.95	–
	$Fe4^{3+}$	−1.63/−1.66	0.58/0.47	0.39/0.20	–
BS13	$Fe1^{2+}$	+2.51/+3.42	0.48/0.55	0.21/0.35	+
	$Fe2^{3+}$	+0.54/+0.53	0.32/0.30	0.42/0.57	–
	$Fe3^{3+}$	+0.66/+0.78	0.36/0.33	0.87/0.66	+
	$Fe4^{3+}$	−1.34/−1.26	0.59/0.50	0.85/0.85	–
BS34	$Fe1^{2+}$	+1.82/+2.70	0.50/0.51	0.69/0.50	–
	$Fe2^{3+}$	−0.54/−0.64	0.41/0.40	0.16/0.64	–
	$Fe3^{3+}$	+0.37/+0.46	0.33/0.31	0.78/0.68	+
	$Fe4^{3+}$	+2.51/+2.89	0.53/0.51	0.25/0.19	+

DFT codes are very useful ...
But they are not black boxes !

- Some cases are « easily » treated :
  - Most organic molecules
  - Most (metallic) monomeric complexes
    - g-tensors, hyperfine couplings ... but also ZFS
    - « most » → possible degenerescence problems
- Polymetallic complexes :
  - Beware of spin coupling !
  - Computation of Broken Symmetry states
- Almost each problem is unique
  - Know your system before DFT calculations

Original papers

- *Inhomogeneous Electron Gas*, P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- *Self Consistent Equations Including Exchange and Correlation Effects*, W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

Review Articles

- *Nobel Lecture: Electronic structure of matter–wave functions and density functionals*, W. Kohn, Rev. Mod. Phys. **71**, 1253 (1998).
- *The density functional formalism, its applications and prospects*, R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

Books

- *Density-Functional Theory of Atoms and Molecules*, R.G Parr and W. Yang, Oxford University Press, New York (1989).
- *A Chemist's Guide to Density Functional Theory*, W. Koch and M.C. Holthausen, WILEY-VCH (2001).

REPORT

THEORETICAL CHEMISTRY

ORIGINAL ARTICLE Medvedev, M. G. *et al.* Density functional theory is straying from the path toward the exact functional. *Science* **355**, 49–52 (2017)

Density functional theory is straying from the path toward the exact functional

Michael G. Medvedev,[1,2,3]*† Ivan S. Bushmarinov,[1]*† Jianwei Sun,[4]‡ John P. Perdew,[4,5]† Konstantin A. Lyssenko[1]†

The theorems at the core of density functional theory (DFT) state that the energy of a many-electron system in its ground state is fully defined by its electron density distribution. This connection is made via the exact functional for the energy, which minimizes at the exact density. For years, DFT development focused on energies, implicitly assuming that functionals producing better energies become better approximations of the exact functional. We examined the other side of the coin: the energy-minimizing electron densities for atomic species, as produced by 128 historical and modern DFT functionals. We found that these densities became closer to the exact ones, reflecting theoretical advances, until the early 2000s, when this trend was reversed by unconstrained functionals sacrificing physical rigor for the flexibility of empirical fitting.

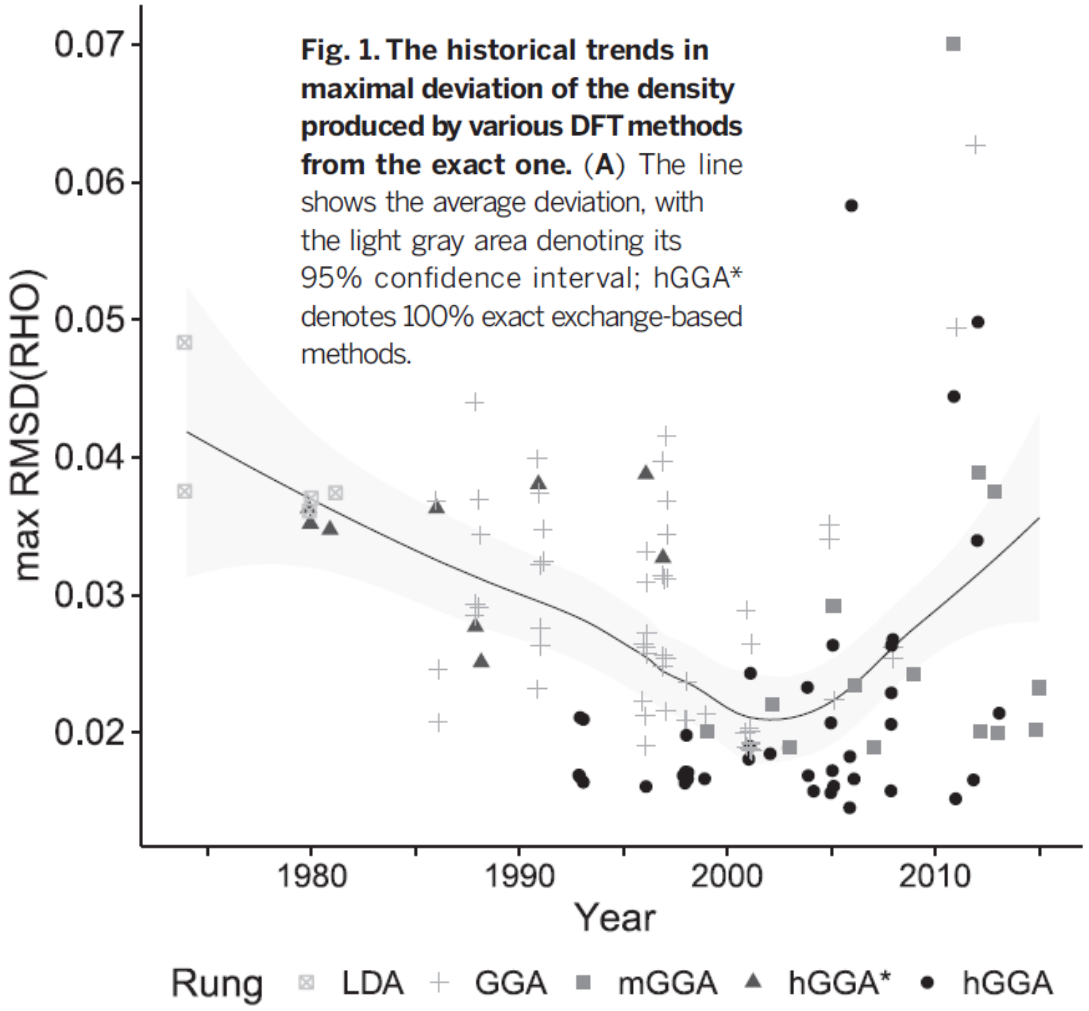


Fig. 1. The historical trends in maximal deviation of the density produced by various DFT methods from the exact one. (**A**) The line shows the average deviation, with the light gray area denoting its 95% confidence interval; hGGA* denotes 100% exact exchange-based methods.

QUANTUM CHEMISTRY

Gabriella Graziano

DFT's midlife crisis

Nature Reviews Chemistry

Published online 1 Feb 2017

doi:10.1038/s41570-017-0019

Review

Prediction of molecular properties and molecular spectroscopy with density functional theory: From fundamental theory to exchange-coupling

Frank Neese

Lehrstuhl für Theoretische Chemie, Universität Bonn, Institut für Physikalische und Theoretische Chemie, Wegelerstrasse 12, D-53115 Bonn, Germany

Coordination Chemistry Reviews 253 (2009) 526–563

Coordination Chemistry Reviews
Volume 253, Issues 5–6, Pages 523-826 (March 2009)
Theory and Computing in Contemporary Coordination Chemistry
Edited by A. Ghosh

REVIEW ARTICLE www.rsc.org/pccp | Physical Chemistry Chemical Physics

Density functional theory for transition metals and transition metal chemistry

Christopher J. Cramer* and Donald G. Truhlar*

Phys. Chem. Chem. Phys., 2009, **11**, 10757–10816

Chem. Rev. **2004**, *104*, 419–458

Electronic Structures of Metal Sites in Proteins and Models: Contributions to Function in Blue Copper Proteins

Edward I. Solomon,*,† Robert K. Szilagyi,† Serena DeBeer George,‡ and Lipika Basumallick†

CHEMICAL REVIEWS

Chem. Rev. 2012, 112, 289–320
dx.doi.org/10.1021/cr200107z

Challenges for Density Functional Theory

Aron J. Cohen,* Paula Mori-Sánchez,* and Weitao Yang*

June 1998

Density functional theory of one-dimensional two-particle systems

H. L. Neal

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Applications of density functional theory to iron-containing molecules of bioinorganic interest

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Review

Challenging Density Functional Theory Calculations with Hemes and Porphyrins

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