Origin and Interpretation of Spin Hamiltonian Parameters

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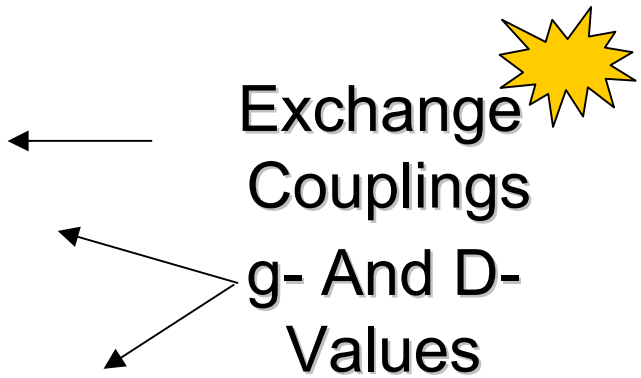
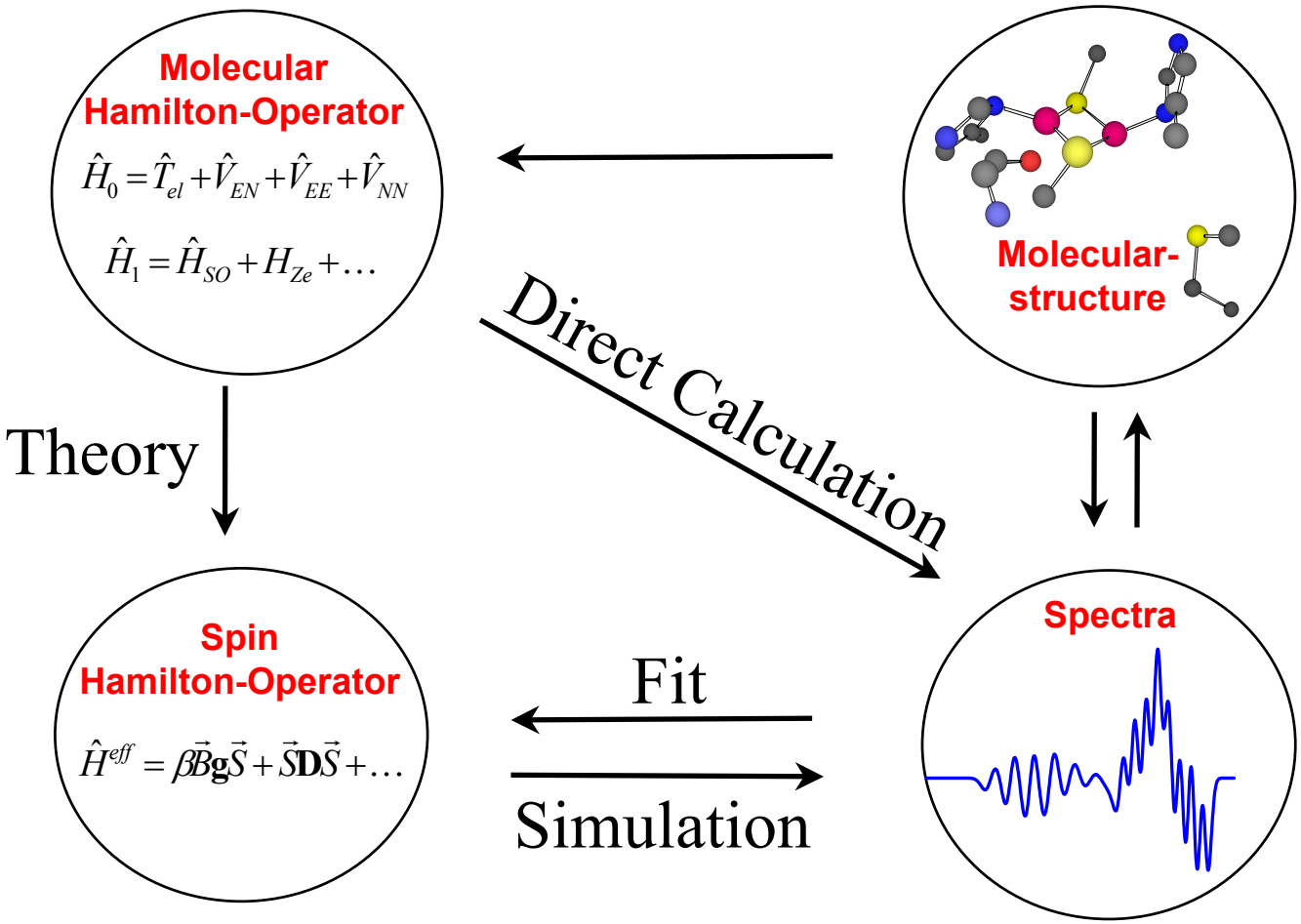
Outline

1. **Introduction**
2. **Molecular Electronic Structure**
   a) Construction of Many Electron States
   b) The Non-Relativistic Hamiltonian
   c) Relativistic Quantum Theory
3. **Ligand Field Theory as a Simple Model**
   a) One Electron in a Ligand Field
   b) Many Electrons in a Ligand Field
   c) Tanabe Sugano Diagrams and Optical Spectra
4. **Perturbation Theory of Spin-Hamiltonian Parameters**
   a) Partitioning Theory and Effective Hamiltonians
   b) g-Tensor
   c) D-Tensor
5. **Spin-Hamiltonian Parameters in d^N Configurations**

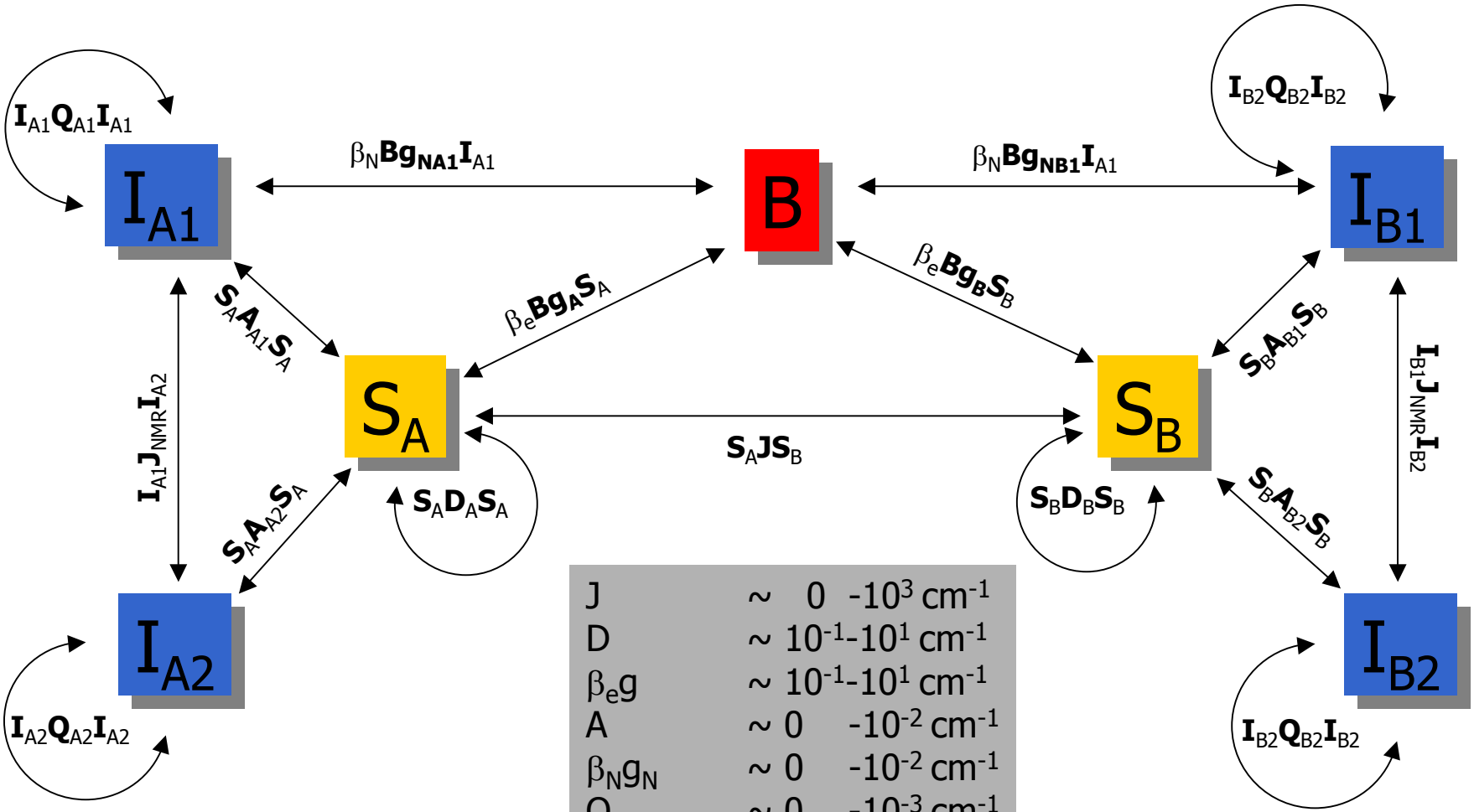


Why a Spin-Hamiltonian ?



Reviews: (1) FN (**2003**) *Curr. Op. Chem. Biol.*, 7, 125
(2) FN; Solomon, E.I. in: Miller, JS, Drillon, M. (Eds) *Magnetism Vol. IV*, Wiley-VCH, **2003**, pp 345-466

Terms in the Spin Hamiltonian



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}

One Electron Systems

Properties of Electrons:

- Mass : m_e
- Electric Charge : $-e_0$
- Spin : s=1/2 („up“=m_s=1/2 or „down“=m_s=-1/2)
- Magnetic Dipole Moment : $|\mu|=s(s+1)g_e\beta$ ~ 1.5 β (g_e=2.002319...)

Schrödinger‘s Nonrelativistic Equation for a Single Electron:

$$\hat{H}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

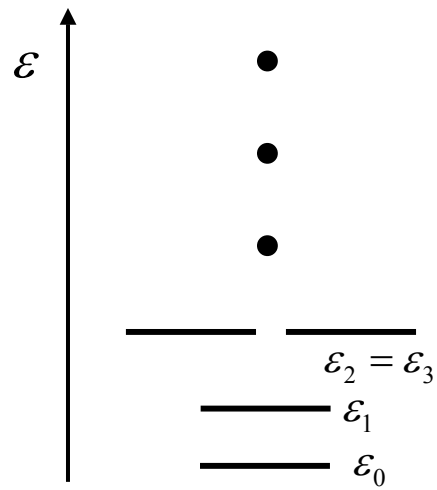
$\hat{H}$: „Hamiltonian“. Includes all Energy Terms and Interactions (H=T+V)

$\psi_i(\mathbf{r})$: An „Orbital“ (=Square Integrable One-Electron Wavefunction)

$|\psi_i(\mathbf{r})|^2$ = Probability per Unit Volume of Finding the Electron at **r**

$\int |\psi_i(\mathbf{r})|^2 d\mathbf{r} = 1$ ~ „We are Sure it‘s Somewhere“

ε_i :„Orbital Energy“. Energy of the Electron in Orbital ψ_i



Nonrelativistic Many Electron Systems

In many Electron Systems Orbitals are – Strictly Speaking – no Longer Well Defined or Necessary to Describe the Physics!

What Matters is the Many Electron Wavefunction $\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, ..., \mathbf{r}_N\sigma_N)$

Born-Interpretation: $\Psi^*(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, ..., \mathbf{r}_N\sigma_N)\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, ..., \mathbf{r}_N\sigma_N)$

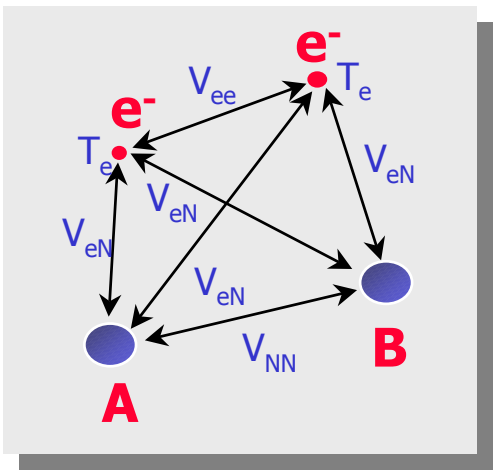
Conditional Probability for Finding Electron 1 at $\mathbf{r}_1$ with Spin σ_1, Electron 2 at $\mathbf{r}_2$ with Spin σ_2, ...

Pauli-Principle: $\Psi(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_i\sigma_i, ..., \mathbf{r}_j\sigma_j, ..., \mathbf{r}_N\sigma_N) = -\Psi(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_j\sigma_j, ..., \mathbf{r}_i\sigma_i, ..., \mathbf{r}_N\sigma_N)$

Antisymmetry with Respect to Particle Interchanges (Electrons are Fermions)

Born-Oppenheimer Hamiltonian:

$$\hat{H}_{BO} = \hat{T}_e + \hat{V}_{EN} + \hat{V}_{EE} + \hat{V}_{NN} + \cancel{\hat{T}_N}$$



Contains only the Electronic Kinetic Energy plus the Dominant Electrostatic Interactions => Looks Easy!

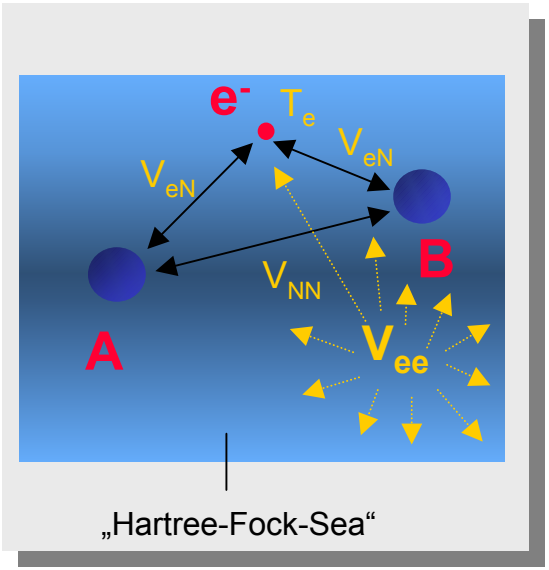
However, the BO Schrödinger Equation:

$$\hat{H}_{BO}\Psi_I(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_N\sigma_N | \mathbf{R}_1, ..., \mathbf{R}_M) = E_I\Psi_I(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_N\sigma_N | \mathbf{R}_1, ..., \mathbf{R}_M)$$

Is **Frightening** - Unsolvable Equation!

Nonrelativistic Many Electron Systems (ctd.)

Since the BO Problem Cannot be Solved Eactly (Except for the Simplest Systems) a Reasonable Approximation is the **Hartree-Fock Meanfield Theory**



Hartree-Fock Wavefunction:

$$\Psi(\mathbf{x}_1 \ldots \mathbf{x}_N) = \frac{1}{\sqrt{N!}} |\psi_1 \ldots \psi_N|$$

Slater Determinant

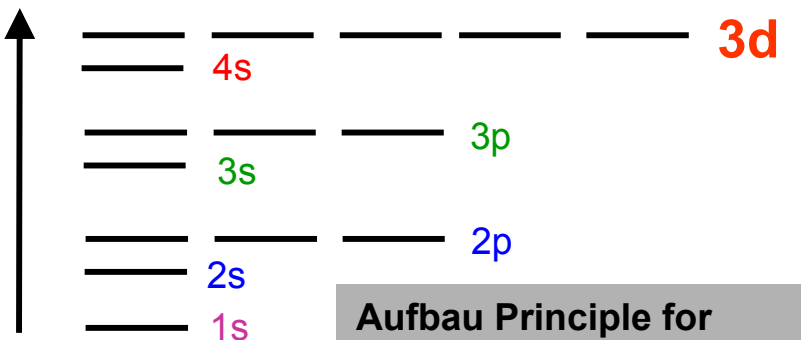
Hartree-Fock Energy:

$$E_{HF} = T_e + E_{eN} + \underbrace{J_{ee} + X_{ee}}_{E_{ee}} + E_{NN}$$

LCAO-Approximation

$$\psi_i = \sum_j c_{ji} \varphi_j(\vec{r})$$

- **Successful Approximation** (>99% of the Exact NR Energy)
- **Errors** Still Large (>100 kcal/mol)
- Need to Describe **Correlated Electron Movement**: **Post-HF**
- Nice: **Reintroduces Orbitals!**

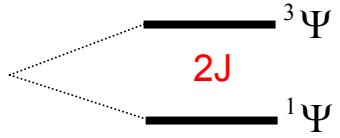


Aufbau Principle for Atoms and Molecules!

Exchange Couplings

„Exchange Coupling“

$\hat{H} = -2J\hat{S}_A\hat{S}_B$

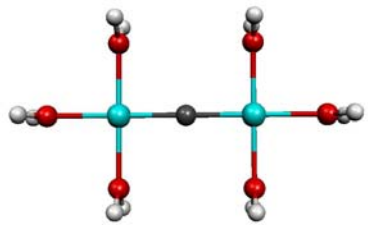


From the Talk of Dr. Glaser Recall:

1. The „Exchange Hamiltonian“ Does NOT Follow from Magnetic Interactions (There is No Such Thing as an „Exchange Interaction“ in Nature)
2. The Born-Oppenheimer Hamiltonian Is Enough to Describe the Splitting of States of the Same Configuration but Different Multiplicity
3. The Splitting is Related to the Electron-Electron Interaction and the Antisymmetry of the N-Particle Wavefunction
4. The Simplest (Anderson) Model Leads to Two Contributions:
   a) The „**Direct Exchange**“ : $K = \langle a(1)b(2)|r_{12}^{-1}|a(1)b(2)\rangle$ (Ferromagnetic)
   b) The „**Kinetic Exchange**“ : $-\beta^2/U \approx -|\langle a|f|b\rangle|^2/(E(ionic)-E(neutral))$
   $\langle a|f|b\rangle \approx\propto S$ (Antiferromagnetic)

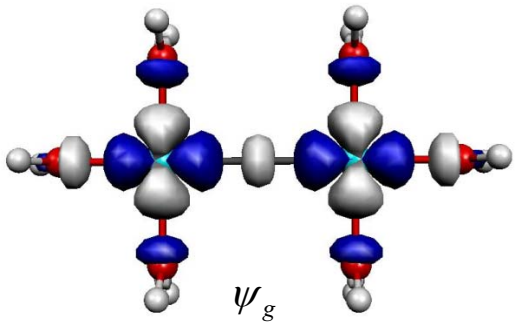
We can Talk and Argue this Way, but How do We Calculate it ?

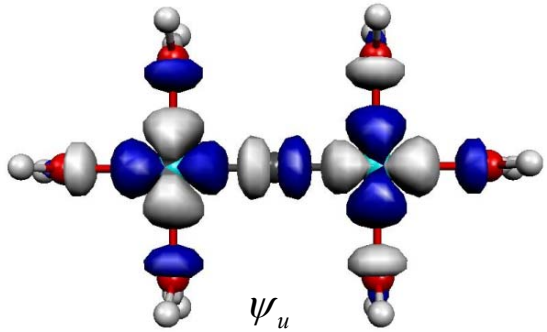
A Model Calculation: $[Cu_2(\mu\text{-}F)(H_2O)_6]^{3+}$

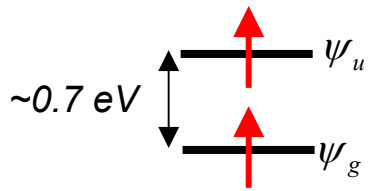


A Model Calculation: $[Cu_2(\mu\text{-}F)(H_2O)_6]^{3+}$

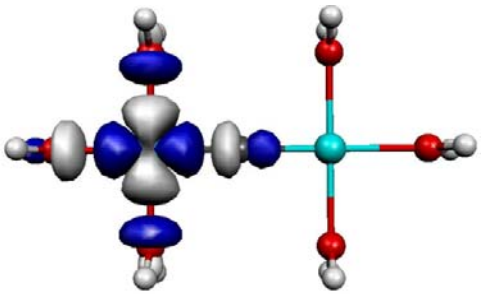
The Hartree-Fock SOMOs of the Triplet State („Active“ Orbitals)



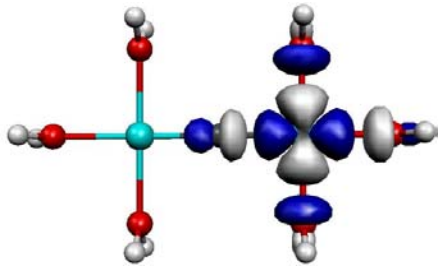




The Pseudo-Localized „Magnetic Orbitals“



$a = 2^{-1/2}(\psi_g + \psi_u)$



$b = 2^{-1/2}(\psi_g - \psi_u)$

Notes:

- ‚a‘ and ‚b‘ have Tails on the Bridge (and on the Other Side)
- ‚a‘ and ‚b‘ are Orthogonal and Normalized
- ‚a‘ and ‚b‘ do **not** Have a Definite Energy
- THE Orbitals of a Compound are not Well Defined! (ROHF, MC-SCF, DFT, Singlet or Triplet Optimized, ...)

Values of Model Parameters:

$$\hat{H} = -2J\hat{S}_A\hat{S}_B$$

„Direct“ (Potential) Exchange Term: $\left\langle a(1)b(2)\left|r_{12}^{-1}\right|a(1)b(2)\right\rangle = 17\ cm^{-1}$

Exactly Calculated „Kinetic“ Exchange Term: $-2\beta^2/U = -57\ cm^{-1}$

$$J = -40\ cm^{-1}$$

Is that Accurate? Look at the Singlet Wavefunction:

$$\left|{}^1\Psi_0\right\rangle = 99.94\%\left|neutral\right\rangle + 0.06\%\left|ionic\right\rangle$$

BUT:

- The Ionic Parts are too High in Energy and Mix too Little with the Neutral Configuration (Electronic Relaxation)
- What About Charge Transfer States?

➢ Need a More Rigorous Electronic Structure Method:

a) Difference Dedicated CI (DDCI): Malrieu, Caballol *et al.*
b) CASPT2: Roos, Pierloot
c) MC-CEPA: Staemmler

Recommended Literature:
Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, *116*, 2728
Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys* **2002**, *116*, 3985
Fink, K.; Fink, R.; Staemmler, V. *Inorg. Chem.* **1994**, *33*, 6219
Ceulemans, A.; et al., L. *Chem. Rev.* **2000**, *100*, 787

Refined *Ab Initio* Calculation

Include Relaxation and LMCT/MLCT States via the Difference Dedicated CI Procedure:

(~10^5 Configurations)

$$\left\langle a(1)b(2)\left|r_{12}^{-1}\right|a(1)b(2)\right\rangle = +17\ cm^{-1}$$
$$-2\beta^2/U = -57\ cm^{-1}$$
$$all\ others = -166\ cm^{-1}$$
$$J = -206\,cm^{-1}$$

Look at the Singlet Wavefunction

$$\left|{}^1\Psi_0\right\rangle = 92.3\%\left|neutral\right\rangle + 3.3\%\left|ionic\right\rangle + 4.4\%\left|LMCT\right\rangle$$

Reduced Increased! NEW+IMPORTANT

The Anderson Model is Not Really Realistic and Should not Be Taken Literally Even Though its CI Ideas are Reasonable.

- Relaxation of Ionic Configurations are Important („Dressing“ by Dynamic Correlation: (DDCI, CASPT2,MC-CEPA,...)
- LMCT States are Important

Treatment of LMCT States in Model Calculations: **VBCI Model**: Tuczek, F.; Solomon, E. I. *Coord. Chem. Rev.* **2001**, *219*, 1075

Exchange Coupling by DFT

The Dominant part of the Triplet Wavefunction is:

$$\left|{}^3 neutral\right\rangle = \left|core\, a_\alpha b_\alpha\right|$$

The Dominant part of the Singlet Wavefunction is:

$$\left|{}^1 neutral\right\rangle = \frac{1}{\sqrt{2}}\left[\left|core\, a_\alpha b_\beta\right| - \left|core\, a_\beta b_\alpha\right|\right]$$

This is a Wavefunction that Can NOT be Represented by a Single Slater Determinant!

- BIG Problem – DFT Can Only Do Single Determinants (Triplet: Fine,Singlet: ☹)

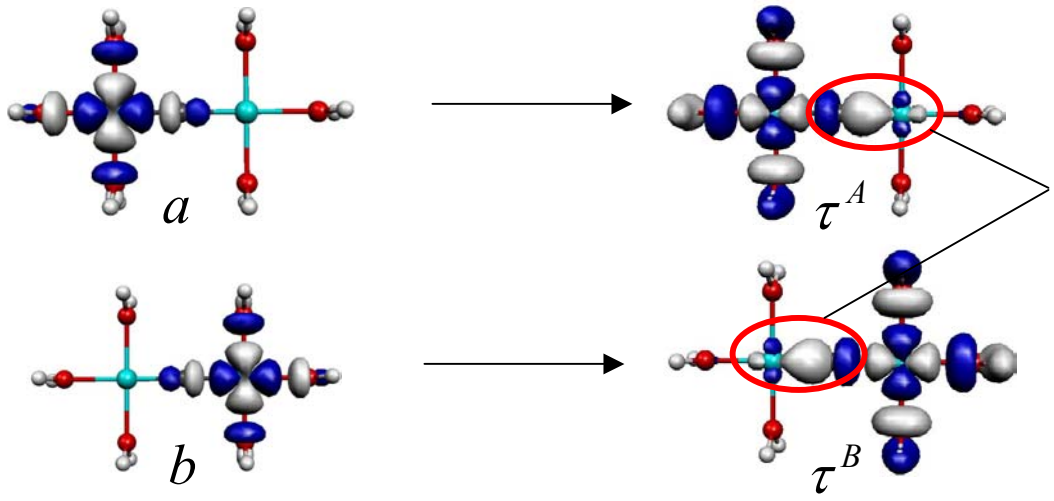
Noodleman (*J. Chem. Phys.*, (1981), 74, 5737)

- Use Only Either $\left|core\, a_\alpha b_\beta\right|$ or $\left|core\, a_\beta b_\alpha\right|$ as Starting Point BUT Reoptimize Orbitals $\left|core\, a_\alpha b_\beta\right| \xrightarrow{Minimize\ \ Energy\ !!!} \left|core\ \tau_\alpha^A \tau_\beta^B\right| \equiv \left|BS\right\rangle$
- NOTE: $\tau_\alpha^A, \tau_\beta^B$ Are No Longer Orthogonal in Their Space Parts
- ASSUME: $\left|BS\right\rangle$ ~ 50% Singlet, 50% Triplet $\boxed{J = -\frac{E_{HS} - E_{BS}}{(S_A + S_B)^2}}$

Better: $J = -\frac{E_{HS} - E_{BS}}{\left\langle S^2\right\rangle_{HS} - \left\langle S^2\right\rangle_{BS}}$ (Yamaguchi)

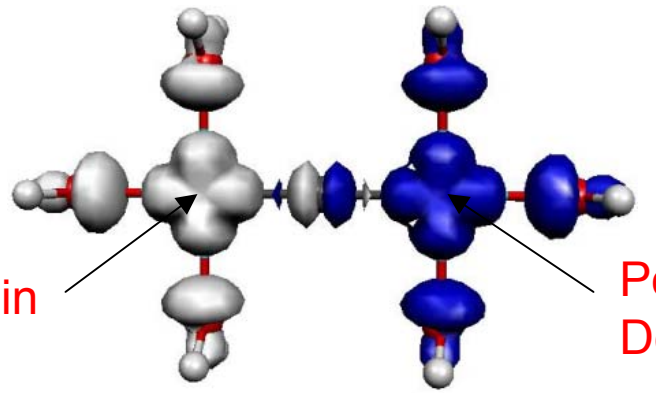
The Broken Symmetry Wavefunction

Relaxation of Orbitals ‚a' and ‚b':



Energy Gain Through Partial Delocalization Gives Nonorthogonality of Space Parts (S~0.16 here)

Terrible Mistake:



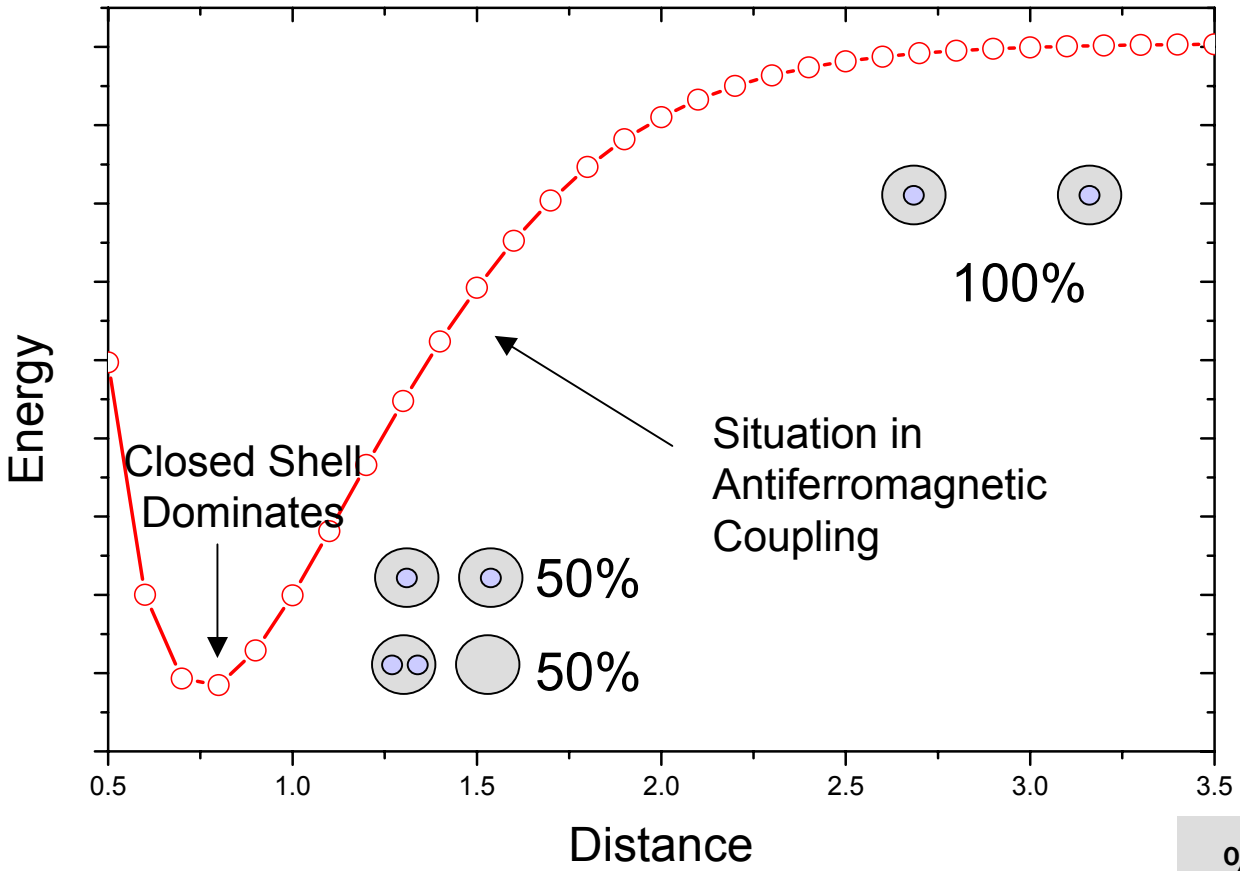
Negative Spin Density

Positive Spin Density

In the Real World Everywhere Zero for A Singlet State!!!

My View:
FN (**2003**) *J. Phys. Chem. Solids*, 65, 781

Interpretation of the BS Wavefunction



Diradical Index:

200 x Percentage Neutral Character on Top of the Closed Shell Wavefunction (=50%)

BS-DFT

$$\%d=100x(1+|S|)x(1-|S|)$$

Ab Initio CI

$$\%d=200x(c_0^2c_d^2/(c_0^2+c_d^2))^{1/2}$$

My View:
FN (**2003**) *J. Phys. Chem. Solids*, 65, 781

Corresponding Orbitals

How to Calculate the Overlap of the Relaxed Magnetic Orbitals ? (Problem: How to Find and Define them in the Many MOs composing the BS Determinant)

My Suggestion: Use the Corresponding Orbitals

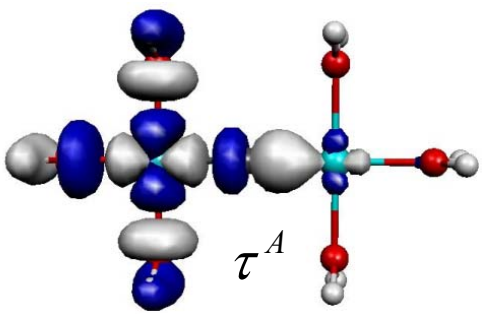
$$\psi_i^\alpha \rightarrow \sum_j U_{ji}^\alpha \psi_i^\alpha$$
$$\psi_i^\beta \rightarrow \sum_j U_{ji}^\beta \psi_i^\beta$$

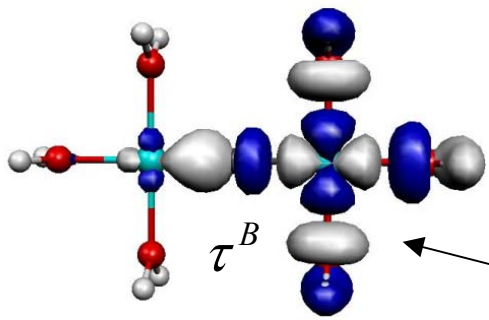
such that $\left\langle \psi_i^\alpha \middle| \psi_j^\beta \right\rangle \neq 0$ For at most 1 *j*

$$\left\langle S^2 \right\rangle_{BS} = \left(\frac{N^\alpha - N^\beta}{2} \right) \left(\frac{N^\alpha - N^\beta}{2} + 1 \right) + N^\beta - \sum_i n_i^\alpha n_i^\beta \left| S_{ii}^{\alpha\beta} \right|^2$$

Overlap

120:	1.00000
121:	1.00000
122:	0.99999
123:	0.99999
...	
146:	0.99475
147:	0.99267
148:	**0.16195...**



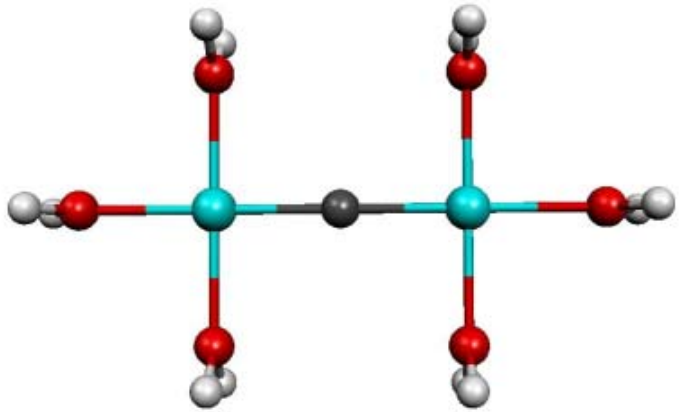


‚Magnetic Pair'

NOTE : Larger Overlap → Stronger AF Coupling
BUT : Overlap is Result of Variational Calculation NOT of Intuition

Ghosh et al. (**2003**) *JACS*, 125, 1293;
Herebian et al. (**2003**) *JACS*, 125, 10997
FN (**2003**) *J. Phys. Chem. Solids*, 65, 781

Numerical Comparison



Singlet-Triplet Gap

Difference Dedicated CI	:	-411 cm^{-1}
B3LYP	:	-434 cm^{-1}
BP	:	-1035 cm^{-1}

Conclusion:

- *Ab Initio* Methods Accurate, Reliable, (Beautiful ☺) but Expensive
- BS-DFT Can Be Used With Caution and Insight BUT Depends Rather Strongly on the Functional (GGA: ☹, Hybrid: ☺) and Can Have Substantial Errors

Zero-Field Splittings
And
g-Values

Relativistic Quantum Mechanics: 1 Electron

At the Nonrelativistic Level (HF or not!) Nothing can be Understood about EPR Spectroscopy but almost Everything about Chemistry!

1. *Need to Introduce the Electromagnetic Fields*
2. *Need to Introduce the Electron (and Nuclear) Spin in the Hamiltonian*
3. *Need to Consider the Additional Relativistic Interactions*

For a One Electron System this is Nicely Accomplished by the **Dirac Equation**:

External Potential

$$\begin{pmatrix} V & c(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}) \\ c(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}) & V - 2c^2 \end{pmatrix} \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix} = E \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix}$$

Electron Like States („Large Component“)

Two „Spin Components“ $\psi_L = \begin{pmatrix} \psi_L^{\alpha} \\ \psi_L^{\beta} \end{pmatrix}$

Positron Like States („Small Component“)

Two „Spin Components“ $\psi_S = \begin{pmatrix} \psi_S^{\alpha} \\ \psi_S^{\beta} \end{pmatrix}$

Generalized Momentum: $\boldsymbol{\pi} = \mathbf{p} - \mathbf{A}$

Introduces the Fields through their Vector Potential **A** ($\vec{\nabla}\mathbf{A} = 0$ **:Coulomb gauge)**

Pauli Matrices: $\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $\boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ $\boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

c = Speed of Light (~137 in atomic units)

Relativistic Quantum Mechanics: Many Electrons

Pragmatic Approach: Add the Nonrelativistic Electron-Electron Repulsion to the One Electron Dirac Equation (**Dirac-Coulomb Operator**)

Approximate Schemes:

1. Full Four Component Relativistic Born-Oppenheimer Calculations (Even Harder than the Nonrelativistic BO Theory).
2. Four Component Hartree-Fock Like Approximation (**Dirac-Fock Method**)
3. Decoupling of The Large and Small Component (**Two Components Methods**)
4. *Decoupling of the Spin Components and Introduction of Spin- and Field Dependent Terms via Perturbation Theory*

Types of Additional Terms to be Considered:

1. **Scalar Relativistic** (Kinematic) Term (do **not** Depend on Spin)
2. **Spin-Orbit Coupling**
3. Terms Involving the **External Fields** and/or the **Electron and Nuclear Spins**

Additional Terms due to Magnetic Fields and Relativity

(Noncomprehensive List)

Details: Neese, F.; Solomon, E.I. in: Miller, JS, Drillon, M. (Eds) *Magnetism Vol. IV*, Wiley-VCH, **2003**, pp 345-466

1. Scalar Relativistic Terms

a) Darwin Term $\pi/2\,\alpha^2 \sum_A \sum_i Z_A \delta(r_{iA})$

b) Mass-Velocity Term $-1/8\,\alpha^2 \sum_i \nabla_i^4$

- „Pauli Expansion“. Alternatives: ZORA, Douglas-Kroll-Hess,...
- Important in the Core Region

2. Spin-Orbit Coupling

a) One-Electron Part $1/2\,\alpha^2 \sum_A \sum_i Z_A r_{iA}^{-3} \mathbf{l}_i^A \mathbf{s}_i \qquad \mathbf{l}_i^A = (\mathbf{r}_i - \mathbf{R}_A) \times \mathbf{p}_i$

b) Two Electron Part $-1/2\,\alpha^2 \sum_i \mathbf{s}_i \sum_{j \neq i} r_{ij}^{-3} \{\mathbf{l}_i^j + 2\mathbf{l}_j^i\} \qquad \mathbf{l}_i^j = (\mathbf{r}_i - \mathbf{r}_j) \times \mathbf{p}_i$

- Breit-Pauli Form (Others Possible)
- !! Mixes Different Multiplicities !!
- !! Reintroduces Angular Momentum in Nondegenerate States !!
- Contributes to almost ALL EPR Properties (g,D,A)

~~$\lambda \hat{\mathbf{L}}\hat{\mathbf{S}}$~~ don‘t

3. Spin-Field Interaction Terms

a) Electron-Spin-Zeeman Term $1/2\,\alpha g_e \mathbf{B} \sum_i \hat{\mathbf{s}}_i$

b) Electron-Orbit-Zeeman Term $1/2\,\alpha \mathbf{B} \sum_i \hat{\mathbf{l}}_i$

c) Nuclear Zeeman Term $\beta_N \mathbf{B} \sum_A g_N^{(A)} \hat{\mathbf{I}}_A$

- g-Tensor
- Nuclear Shielding Tensor

4. Spin-Spin Terms

a) Electron-Spin-Spin Term $1/2\,\alpha^2 \sum_i \sum_{j \neq i} r_{ij}^{-5} \{r_{ij}^2 \mathbf{s}_i \mathbf{s}_j - 3(\mathbf{s}_i \mathbf{r}_{ij})(\mathbf{s}_j \mathbf{r}_{ij})\}$

b) Electron Spin-Nucleus Dipole/Dipole $1/2\,\alpha g_e \beta_N \sum_A g_N^{(A)} \sum_i r_{iA}^{-5} \{r_{iA}^2 \mathbf{s}_i \hat{\mathbf{I}}^{(A)} - (\mathbf{s}_i \mathbf{r}_{iA})(\hat{\mathbf{I}}^{(A)} \mathbf{r}_{iA})\}$

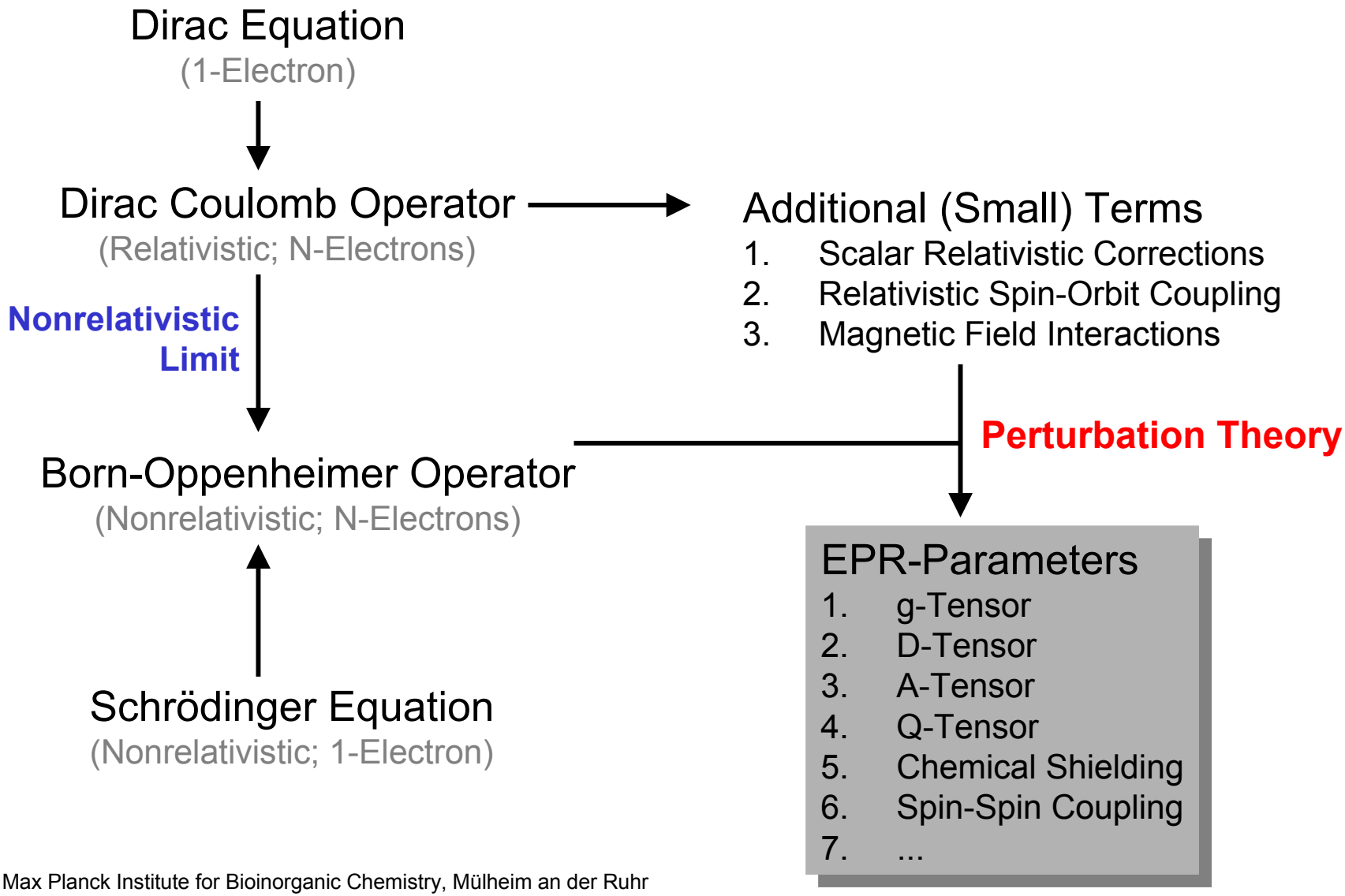
c) Electron Orbital-Nucleus Dipole $1/2\,\alpha \beta_N \sum_A g_N^{(A)} \sum_i r_{iA}^{-3} \mathbf{l}_i^A \hat{\mathbf{I}}^{(A)}$

d) Fermi Contact Term $4\pi/3\,\alpha g_e \beta_N \sum_A g_N^{(A)} \sum_i \mathbf{s}_i \hat{\mathbf{I}}^{(A)} \delta(r_{Ai})$

- Zero-Field Splitting
- Hyperfine Interaction

$\alpha = c^{-1}$ =Fine Structure Constant

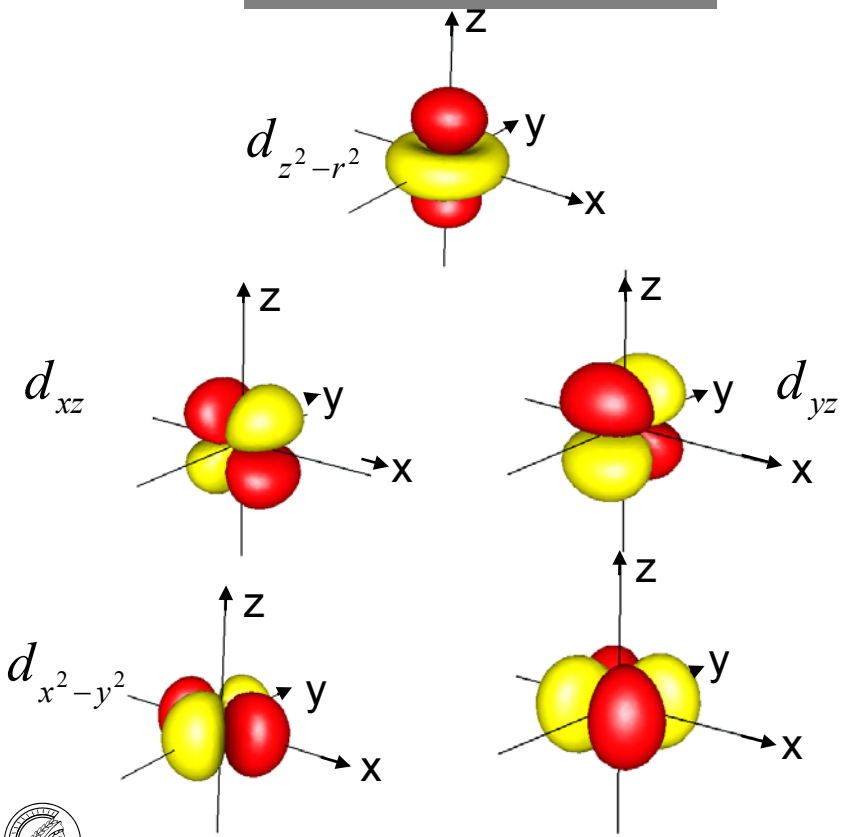
Summary


Dirac Equation
(1-Electron)
Dirac Coulomb Operator
(Relativistic; N-Electrons)
Additional (Small) Terms
1. Scalar Relativistic Corrections
2. Relativistic Spin-Orbit Coupling
3. Magnetic Field Interactions
Nonrelativistic Limit
Perturbation Theory
Born-Oppenheimer Operator
(Nonrelativistic; N-Electrons)
EPR-Parameters
1. g-Tensor
2. D-Tensor
3. A-Tensor
4. Q-Tensor
5. Chemical Shielding
6. Spin-Spin Coupling
7. ...
Schrödinger Equation
(Nonrelativistic; 1-Electron)

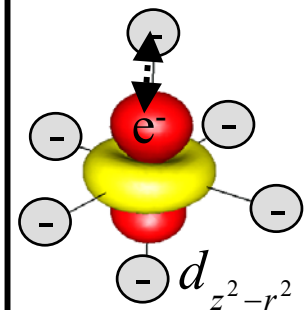
Ligand Field Theory

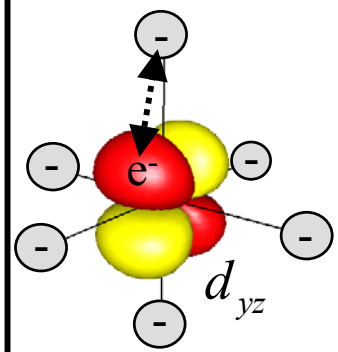
Ligand Field Theory may Be Viewed as a Simple but Logically Consistent and Qualitatively Correct Way to Construct the most Important Low-Lying Nonrelativistic Many Electron Wavefunctions

Shape of d-Orbitals



One-Electron in a Ligand Field

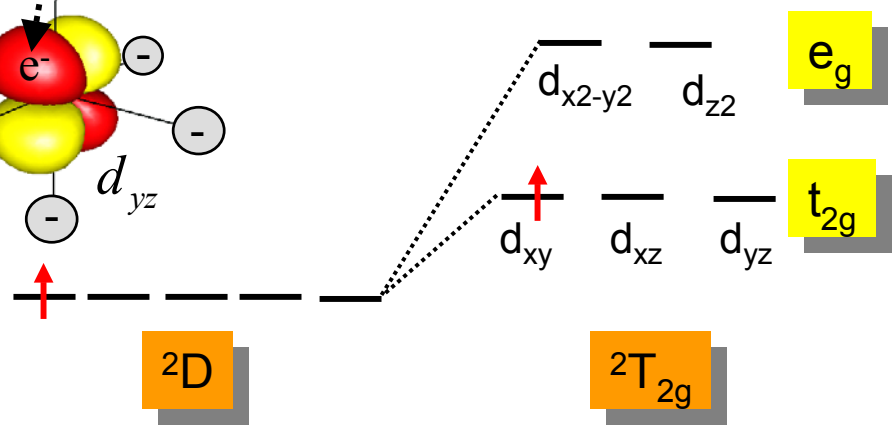




Nonspherical Electric Field Induces a Splitting of the Five d-Orbitals

↓

Very Sensitive Function of the Ligand Nature+Arrangement



Many Electron Ligand Field States

1. Distribute the *N* Electrons Among the Available Orbitals in all Possible Ways (**Configuration**).
2. Couple the Spins of the Unpaired Electrons to get a State of Well Defined Total Spin (**Multiplicity**).
3. Determine the Overall State Symmetry by Taking the Direct Product of the Irreps of all Partially Filled Shells (**Symmetry**).

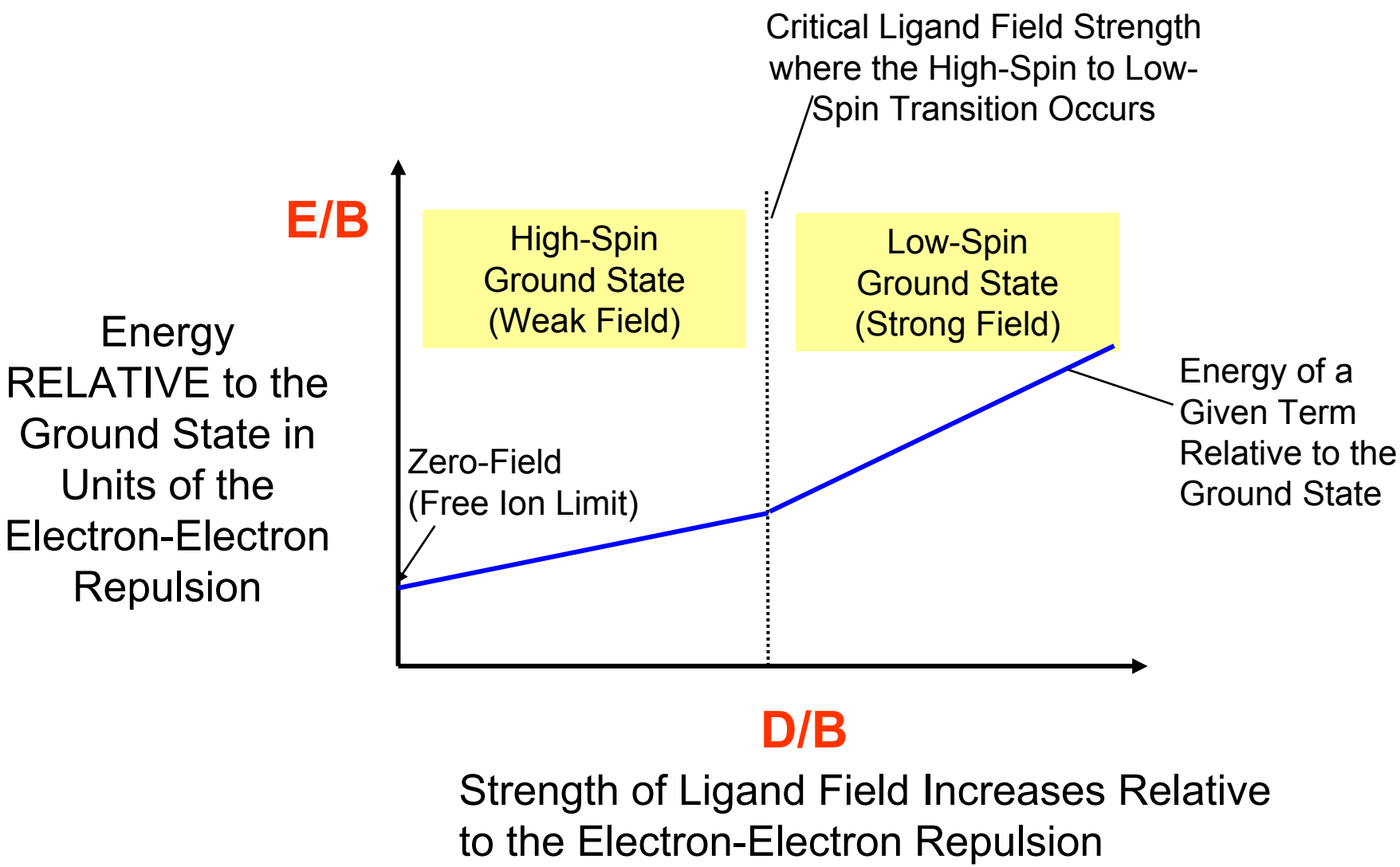
Configuration State Functions: $|\mathbf{n};\Gamma M_\Gamma;SM\mu\rangle$ Term Symbol: $d^{-2S+1}\Gamma$

d = 1,2,...

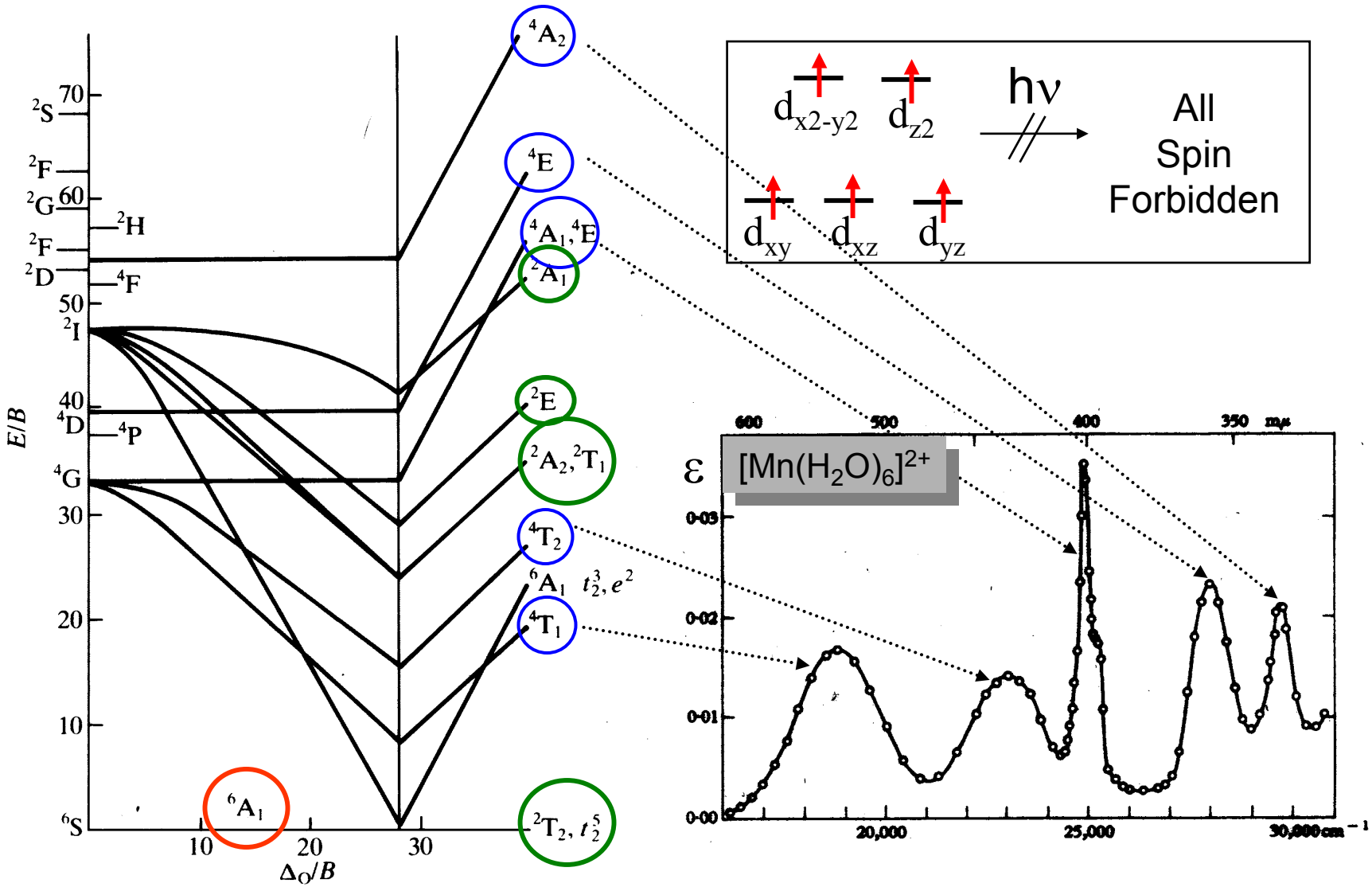
4. Use the Rules of Ligand Field Theory to Calculate the **Energy** of the Configuration State Function as a Function of the Ligand Field Parameters:
   1. **Ligand Field** (10Dq, Ds, Dt,...) or AOM (e_σ,e_π,e_δ,...) Parameters
   2. **Interelectronic Repulsion** Racah (A,B,C) or Slater-Condon (F0,F2,F4) Parameters
5. Possibly Allow the Interaction of Configuration State Functions of the Same Symmetry and Multiplicity (**Configuration Interaction**)
6. Possibly Allow the Interaction of the CI States Through the **Spin-Orbit-Coupling** Operator

Technical Details: Griffith, J.S. (**1964**) *The Theory of Transition Metal Ions.*, Camebridge University press, Camebridge

Tanabe-Sugano Diagrams



The d^5 Case


$^4A_2$
^4E
$^4A_1, ^4E$
$^2A_1$
^2E
$^2A_2, ^2T_1$
$^4T_2$
$^6A_1$ t_2^3, e^2
$^4T_1$
$^6A_1$
$^2T_2, t_2^5$
^2S 70
^2F
^2G 60
^2H
^2F
^2D
^4F
50
^2I
40
^4D
^4P
^4G
30
20
10
^6S
10
20
30
Δ_O/B
E/B
d_{x2-y2} d_{z2}
$h\nu$
All Spin Forbidden
d_{xy} d_{xz} d_{yz}
$[Mn(H_2O)_6]^{2+}$
ε
0·03
0·02
0·01
0·00
600
500
400
350 mμ
20,000
25,000
30,000 cm^{-1}

Perturbation Theory of SH Parameters

Divide the Complete Set of Many Electron States into Two Sets

1. „**Model Space**“: $|a;S_0M\rangle$ $M=S_0,S_0\text{-}1,\ldots,\text{-}S_0$

   The 2S+1 Component of the Orbitally Nondegenerate Ground State

2. „**Outer Space**“: $|b;S_bM\rangle$

   All Other States of Any Multiplicity and Symmetry

Goal: Build an „**Effective Hamiltonian**“ Which is Only Defined in the „a“ Space but Gives the Same Eigenvalues and Eigenvectors as the **Complete Hamiltonian** Including All Relativistic and Magnetic Field Interactions!

Perturbative Analysis to 2nd Order :

$$\langle aS_0M|H_{eff}|aS_0M'\rangle = \langle aS_0M|\hat{H}_1|aS_0M'\rangle - \sum_{b\neq 0,M''}(E_b-E_0)^{-1}\Big\{\langle aS_0M|\hat{H}_1|bS_bM''\rangle\langle aS_bM''|\hat{H}_1|aS_0M'\rangle + \langle aS_0M|\hat{H}_1|bS_bM''\rangle\langle bS_bM''|\hat{H}_1|aS_0M'\rangle\Big\}$$

$\hat{H}_1$ = Sum of ALL Relativistic and Magnetic Field Interactions

Insertion of the Explicit Forms and Term-by-Term Comparison yields Explicit Expressions for the Spin-Hamiltonian Parameters in Terms of Many Electron States and Their Energies

Straightforward but Sometimes Tedious

The g-Tensor

First Order Contributions:

$$g_{\mu\nu}^{(SZ)} = \delta_{\mu\nu} g_e$$

Isotropic Free Electron

$$g_{\mu\nu}^{(RMC)} = \delta_{\mu\nu} \frac{\alpha^2}{2} \frac{1}{S} \frac{g_e}{2} \left\langle aS_0S_0 \left| \sum_i \nabla_i^2 s_{zi} \right| aS_0S_0 \right\rangle$$

Relativistic Mass Correction (Small)

$$g_{\mu\nu}^{(GC)} = \frac{1}{S} \left\langle aS_0S_0 \left| \sum_{i,A} \xi(r_{iA}) \{ \mathbf{r}_{iA}\mathbf{r}_i - r_{iA,\mu} r_{i,\nu} \} s_{iz} \right| aS_0S_0 \right\rangle$$

Gauge Correction (Small)

Second Order Contribution:

$$g_{\mu\nu}^{(OZ/SOC)} = -\frac{1}{S} \sum_{b(S_b=S_0)} (E_b - E_0)_{-1} \left\{ \left\langle aS_0S_0 \left| \sum_i l_{i\mu} \right| bS_0S_0 \right\rangle \left\langle bS_0S_0 \left| \sum_{i,A} \xi(r_{iA}) l_{i\nu}^A s_{iz} \right| aS_0S_0 \right\rangle \right.$$

Orbital Zeeman/SOC

$$\left. + \left\langle aS_0S_0 \left| \sum_{i,A} \xi(r_{iA}) l_{i\mu}^A s_{iz} \right| bS_0S_0 \right\rangle \left\langle bS_0S_0 \left| \sum_i l_{i\nu} \right| aS_0S_0 \right\rangle \right\}$$

Usually Dominant

NOTES:
- Only Excited States of the Same Total Spin as the Ground State!
- Only Need to Know the „Principal Components“ with *M* = *S*!
- The Often Quoted Equation $g_{\mu\nu} = g_e - 2\lambda \sum_b (E_b - E_0)^{-1} \underbrace{\langle 0|L_\mu|b\rangle\langle b|L_\nu|0\rangle}_{\Lambda_{\mu\nu}^{(b)}}$

Is **not** Correct and Makes Only Limited Sense!

FN (**2001**) *Int. J. Quant. Chem.*, 83, 104

The D-Tensor

First Order Contribution: **Direct Electron-Electron Magnetic Dipole Interaction**

$$D_{\mu\nu}^{(SS)} = \frac{1}{2}\frac{\alpha^2}{S_0(2S_0-1)}\left\langle 0S_0S_0\left|\sum_i\sum_{j\neq i} r_{ij}^{-5}\left\{r_{ij}^2\delta_{\mu\nu} - 3(\mathbf{r}_{ij})_\mu(\mathbf{r}_{ij})_\nu\right\}\left\{2s_{zi}s_{zj} - s_{xi}s_{xj} - s_{yi}s_{yj}\right\}\right|aS_0S_0\right\rangle$$

Complicated!
Assumed Small for Transition Metals

Second Order Contribution: **Spin-Orbit Coupling**

Neese, F.; Solomon, E.I. (**1998**) *Inorg. Chem.*, 37, 6568

$$D_{\mu\nu}^{SOC-(0)} = -\frac{1}{S_0^2}\sum_{b(S_b=S)}\Delta_b^{-1}\left\langle aS_0S_0\left|\sum_{i,A}\xi(r_{iA})l_{i,\mu}^A s_{i,z}\right|bS_0S_0\right\rangle\left\langle bS_0S_0\left|\sum_{i,A}\xi(r_{iA})l_{i,\nu}^A s_{i,z}\right|aS_0S_0\right\rangle$$

$$D_{\mu\nu}^{SOC-(-1)} = -\frac{1}{S(2S-1)}\sum_{b(S_b=S-1)}\Delta_b^{-1}\left\langle aS_0S_0\left|\sum_{i,A}\xi(r_{iA})l_{i,\mu}^A s_{i,+1}\right|bS_0-1S_0-1\right\rangle\left\langle bS_0-1S_0-1\left|\sum_{i,A}\xi(r_{iA})l_{i,\nu}^A s_{i,-1}\right|aS_0S_0\right\rangle$$

$$D_{\mu\nu}^{SOC-(+1)} = -\frac{1}{(S_0+1)(2S_0+1)}\sum_{b(S_b=S+1)}\Delta_b^{-1}\left\langle aS_0S_0\left|\sum_{i,A}\xi(r_{iA})l_{i,\mu}^A s_{i,-1}\right|bS_0+1S_0+1\right\rangle\left\langle bS_0+1S_0+1\left|\sum_{i,A}\xi(r_{iA})l_{i,\nu}^A s_{i,+1}\right|aS_0S_0\right\rangle$$

NOTES:
- Excited States S_0 **and** $S_0 \pm 1$ Contribute!
- **No** Proportionality to the g-Tensor!
- **Not** Traceless!

(Review: FN (**2004**) Zero-Field Splitting. In: Kaupp, M.; Bühl, M.; Malkin, V. (Eds) *The Quantum Chemical Calculation of NMR and EPR Properties*. Wiley-VCH, in press

The g-Tensor in Ligand Field Theory

Only MOs of Dominantly Metal *d*-Character Considered: $\psi_i \approx \alpha d_i + \sqrt{1-\alpha^2}\, L_i$

Critical! **Metal** **Ligand**

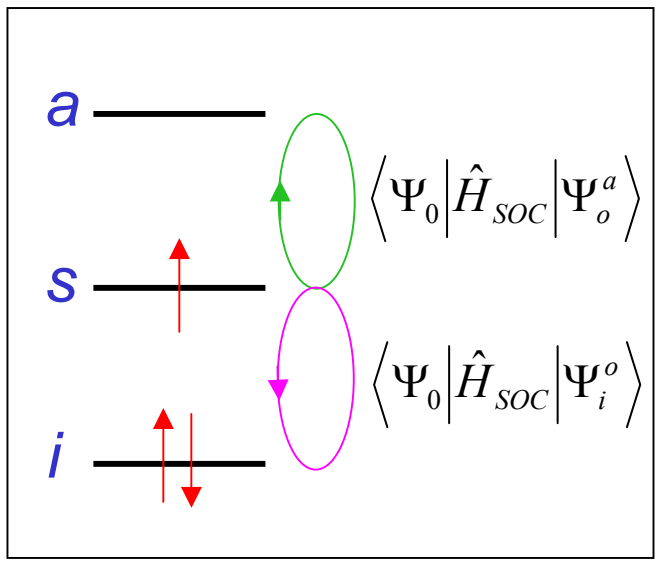
„Covalently Diluted“ Metal Orbitals with „Anisotropic Covalency“ ($\alpha_i \neq \alpha_j$)

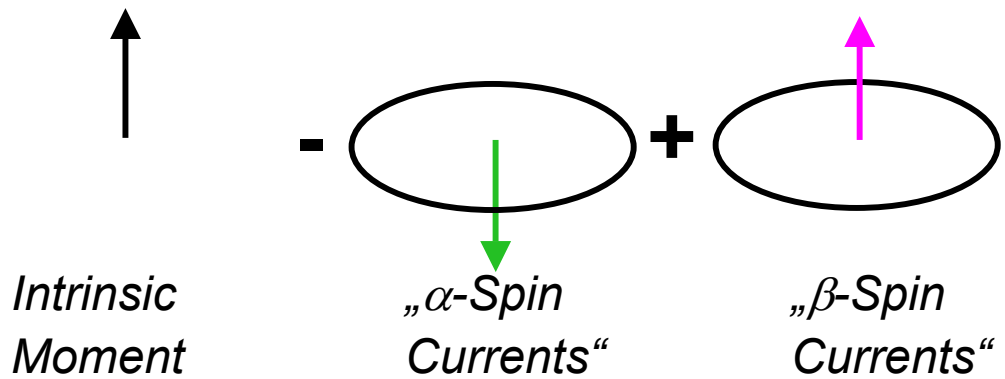
Neglect Ligand Part in All Matrix Elements $\left\langle \psi_i \middle| \hat{o} \middle| \psi_j \right\rangle \approx \alpha_i \alpha_j \left\langle d_i \middle| \hat{o} \middle| d_j \right\rangle$

Critical! See Review Article

$$g_{\mu\nu} \approx \delta_{\mu\nu} g_e + \frac{\zeta_{ion}}{S_0} \left\{ \sum_{i \to s} \Delta^{-1}_{i \to s} \alpha_i^2 \alpha_s^2 \left\langle d_i \middle| l_\mu^M \middle| d_s \right\rangle \left\langle d_s \middle| l_\nu^M \middle| d_i \right\rangle \ominus \sum_{s \to a} \Delta^{-1}_{s \to a} \alpha_s^2 \alpha_a^2 \left\langle d_s \middle| l_\mu^M \middle| d_a \right\rangle \left\langle d_a \middle| l_\nu^M \middle| d_s \right\rangle \right\}$$

DOMO→SOMO **SOMO→EMPTY**





Intrinsic Moment

„α-Spin Currents“

„β-Spin Currents“

The D-Tensor in Ligand Field Theory

Same Assumption as for the g-Tensor; Also Neglect Spin-Spin First Order Term

$$D_{\mu\nu}^{SOC-(0)} = -\frac{\zeta_{ion}^2}{4S_0^2}\left\{\sum_{i\to s}\Delta_{i\to s}^{-1}\alpha_i^2\alpha_j^2\left\langle d_i\left|l_\mu^M\right|d_s\right\rangle\left\langle d_s\left|l_\nu^M\right|d_i\right\rangle \oplus \sum_{s\to a}\Delta_{s\to a}^{-1}\alpha_i^2\alpha_j^2\left\langle d_s\left|l_\mu^M\right|d_a\right\rangle\left\langle d_a\left|l_\nu^M\right|d_s\right\rangle\right\}$$

DOMO→SOMO *No Sign Change* **SOMO→EMPTY**

Only IF: a) No Contributions from $\Delta S_0 \pm 1$
b) Either only DOMO→SOMO OR SOMO→EMPTY

$$D_{\mu\nu}^{SOC-(0)} \approx \pm\frac{\bar{\zeta}_{average}}{4S_0}\Delta g_{\mu\nu}$$

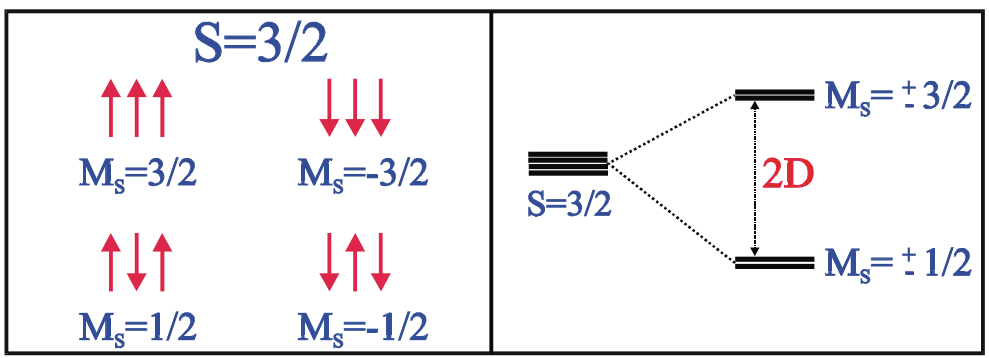
Contributions from Excited States with $S_0 \pm 1$ not as Simple → Detailed Attention

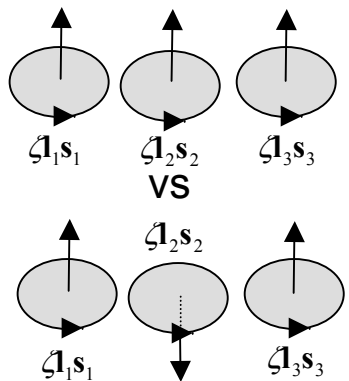
Convention: Principal Values of ***D*** are Ordered Such That

$$D = D_{zz} - \tfrac{1}{2}(D_{XX} + D_{YY})$$

$$E = \tfrac{1}{2}(D_{XX} - D_{YY})$$

and $0 \le E/D \le 1/3$





Angular Momentum Matrix Elements

l_x	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
d_{z^2}			$i\,3^{1/2}$		
d_{xz}					i
d_{yz}	$-i\,3^{1/2}$			$-i$	
$d_{x^2-y^2}$			i		
d_{xy}		$-i$			

l_y	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
d_{z^2}		$-i\,3^{1/2}$			
d_{xz}	$i\,3^{1/2}$			$-i$	
d_{yz}					$-i$
$d_{x^2-y^2}$		i			
d_{xy}			i		

l_z	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
d_{z^2}					
d_{xz}			$-i$		
d_{yz}		i			
$d_{x^2-y^2}$					$-2\,i$
d_{xy}				$2\,i$	

Use of These Tables
Let's You Calculate the Ligand Field Expressions for **g**, **D** and **A** as a Function of:

- The Excited State Energies

  (Experimental Input or Ligand Field and Interelectronic Repulsion Parameters)
- The Covalency Parameters

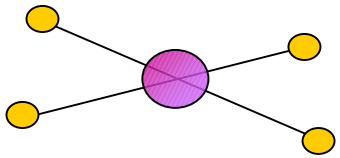
  (Result of the Analysis or MO Calculations but be careful – The Connection is not Clean and the Accuracy of HF and DFT is Often not High)
- The Free Ion SOC Constants

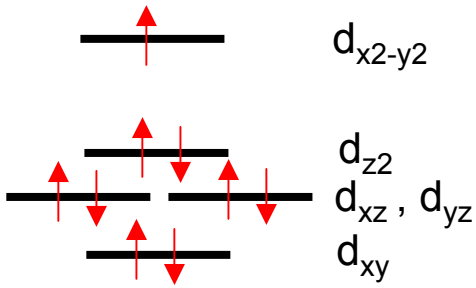
  (Usually taken from Tables)

Two Additional Parameters Arise for Hyperfine Interactions

- $g_e g_N \beta_e \beta_N \langle r^{-3} \rangle_d$ from Tables
- A_{iso} from Fit to Experiment

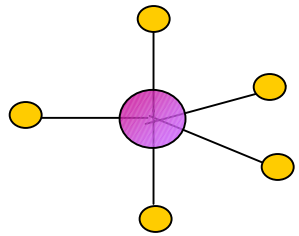
The g-Tensor of d^9 Complexes (S=1/2)

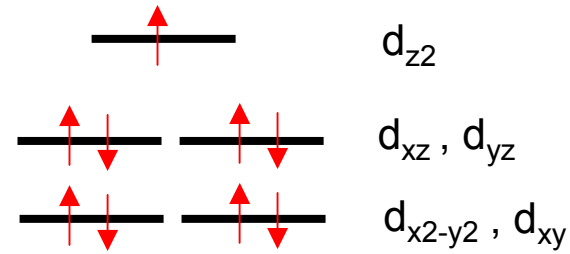




$$g_{zz} = g_e + \frac{8\zeta_{Cu}\alpha^2_{x^2-y^2}\alpha^2_{xy}}{\Delta_{xy\rightarrow x^2-y^2}}$$

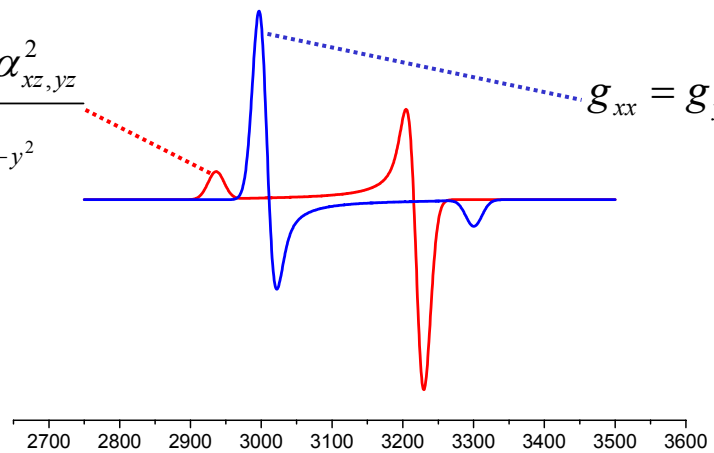
$$g_{xx} = g_{yy} = g_e + \frac{2\zeta_{Cu}\alpha^2_{x^2-y^2}\alpha^2_{xz,yz}}{\Delta_{xz,yz\rightarrow x^2-y^2}}$$





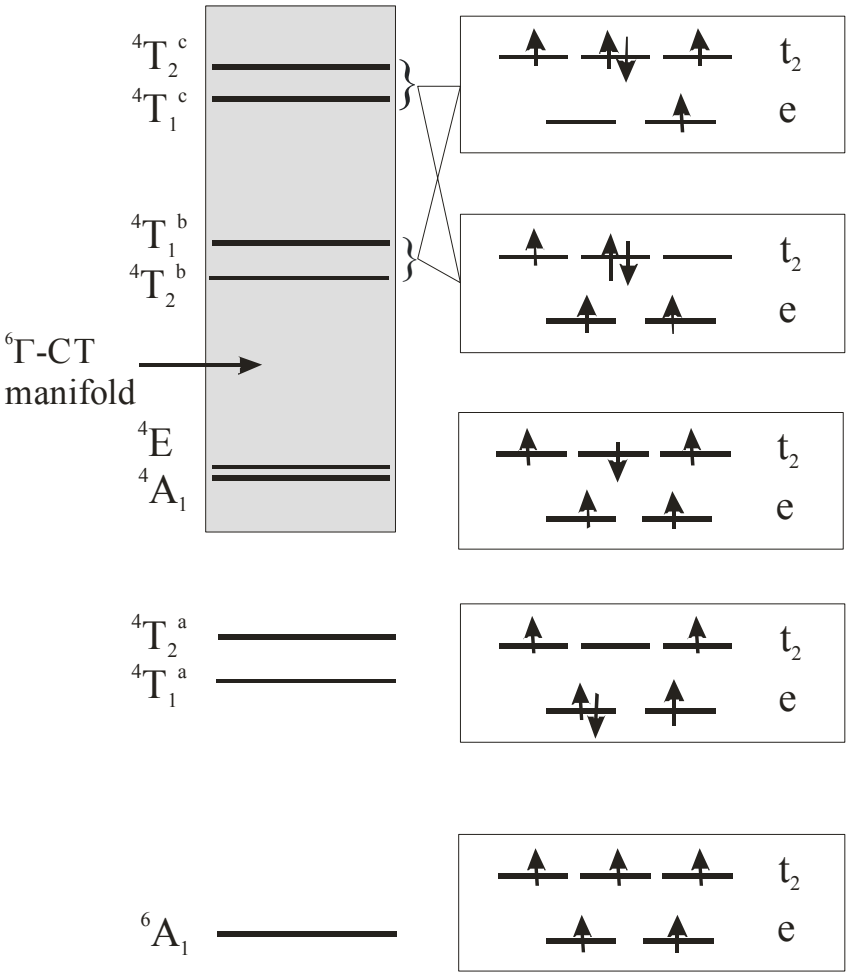
$$g_{zz} = g_e$$

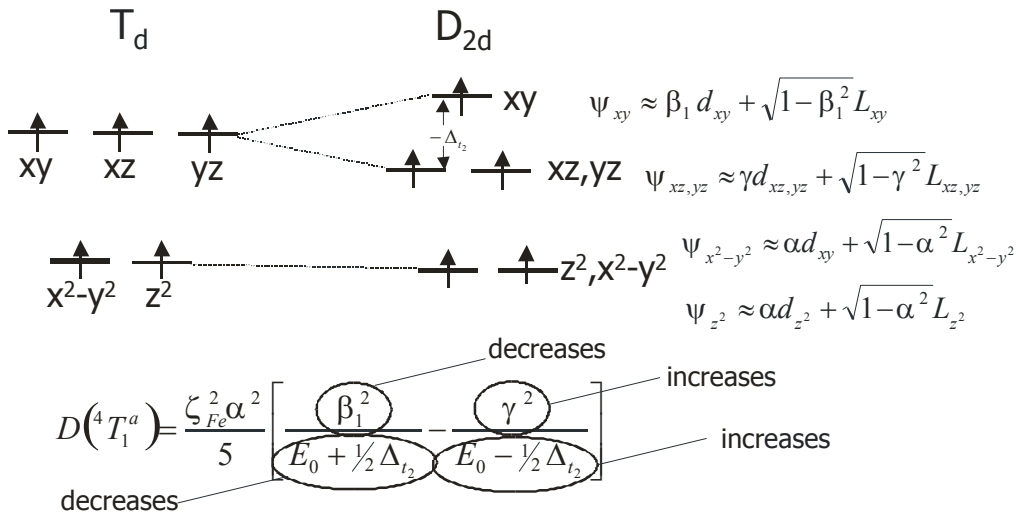
$$g_{xx} = g_{yy} = g_e + \frac{6\zeta_{Cu}\alpha^2_{z^2}\alpha^2_{xz,yz}}{\Delta_{xz,yz\rightarrow x^2-y^2}}$$



Key Message:
g-Values React Sensitively to Geometry

ZFS of Tetrahedral d^5 Complexes (S=5/2)



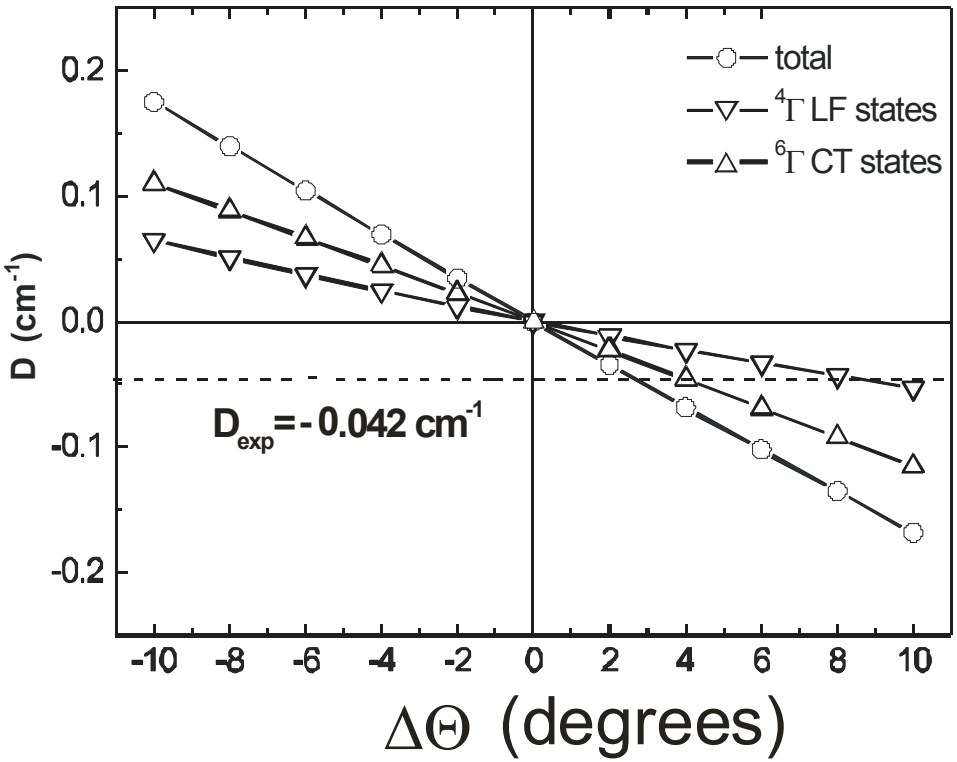


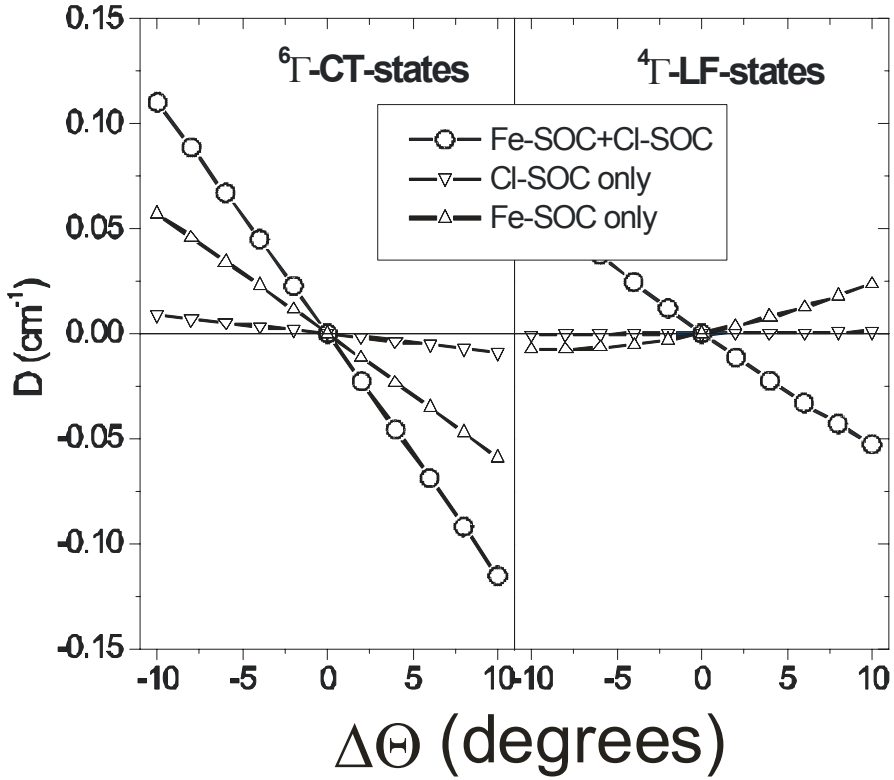
Key Messages:

1) Anisotropic Covalency can be a Key Determinant of the ZFS
2) Spin-Flip Contributions can be Dominant

Neese, F.; Solomon, E.I. (**1998**) *Inorg. Chem.*, 37, 6568

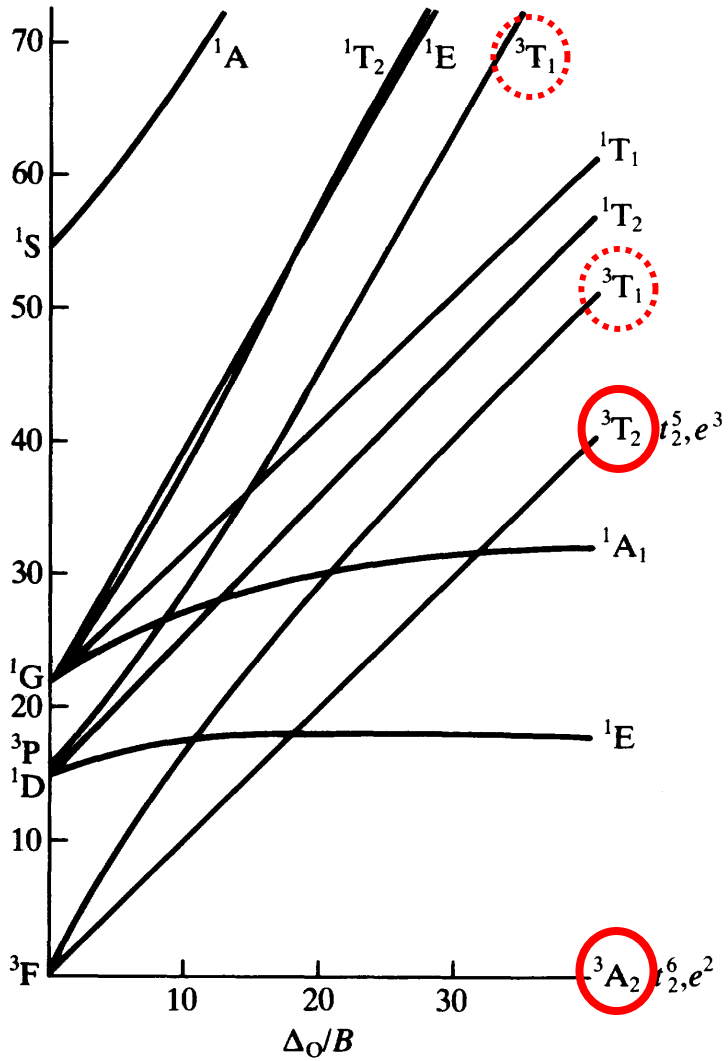
d-d versus CT States in $FeCl_4^-$

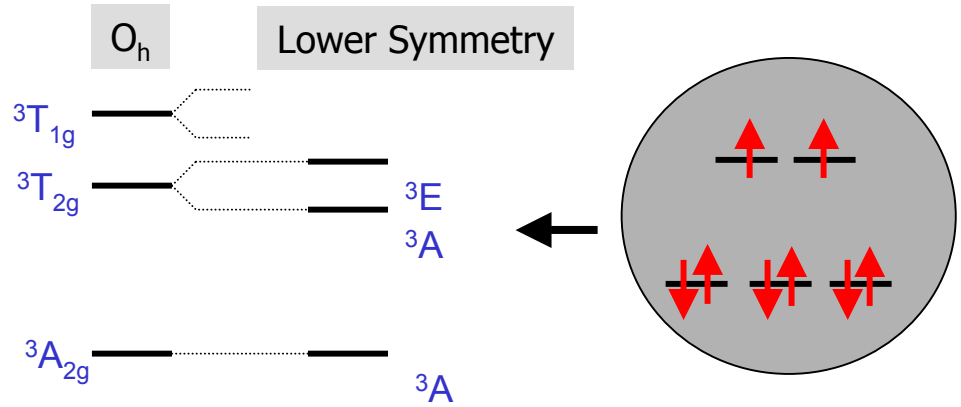




Neese, F.; Solomon, E.I. (**1998**) *Inorg. Chem.*, 37, 6568

g- and D-Values in Octahedral d^8 (S=1)



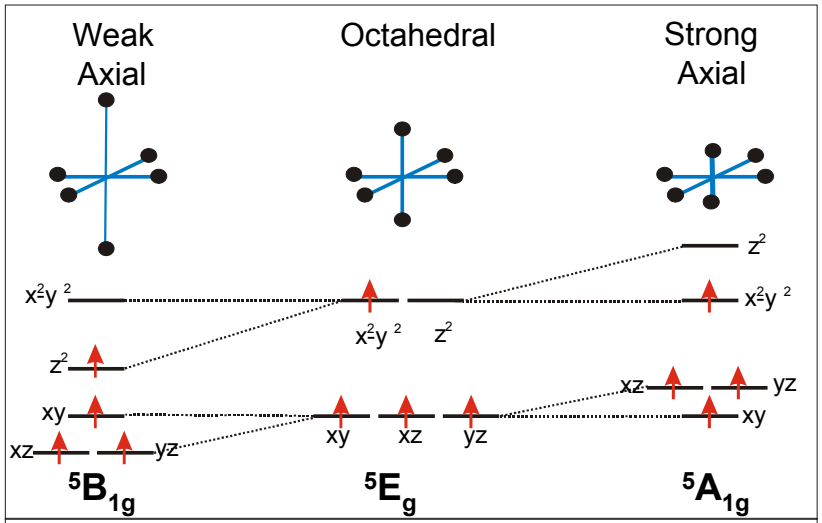


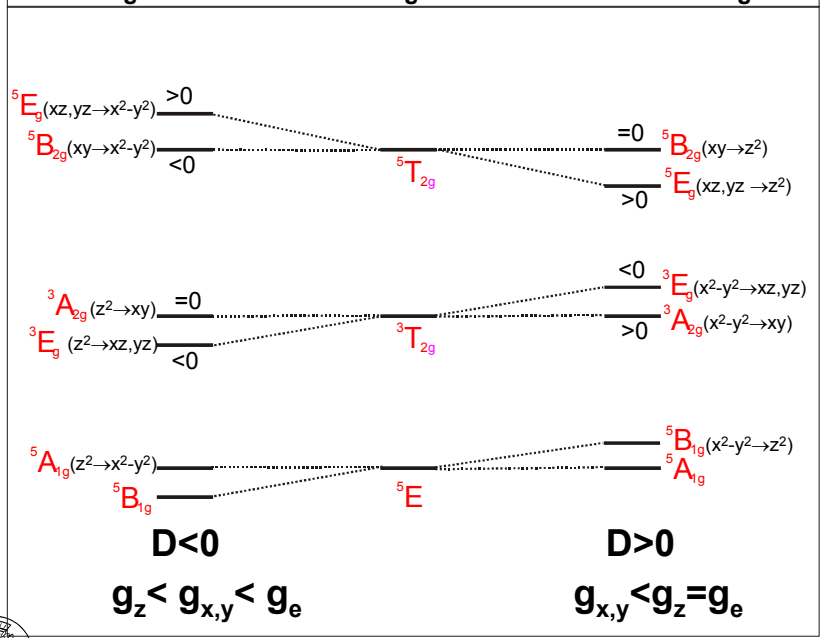
Contributions from Triplets

$$D \approx \frac{\zeta_{ion}^2}{4}\left[\frac{4\alpha_{xy}^2\alpha_{x^2-y^2}^2}{E(^4A)} - \frac{1}{4}\frac{\alpha_{xz,yz}^2(3\alpha_{z^2}+\alpha_{x^2-y^2})^2}{E(^4E)}\right]$$

$$\approx (\zeta_{ion}/4)\left[\Delta g_{zz} - \tfrac{1}{2}(\Delta g_{xx}+\Delta g_{yy})\right]$$

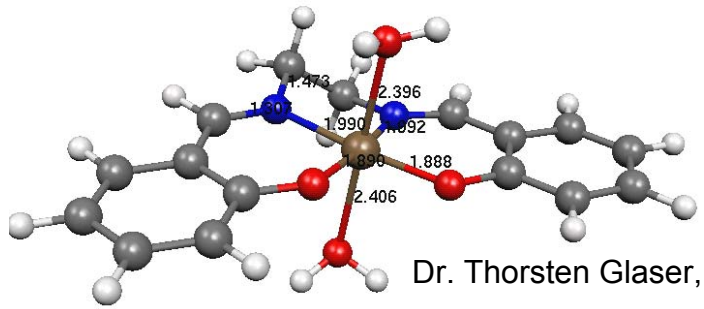
g- and D-Values in d^4 (S=2)





Usually the Complete *D* is Attributed to the Lowest Spin Quintet:

However, the Triplets are at Least Equally Important:



Dr. Thorsten Glaser, Münster

	Mn	Cr
g_1	1.994	1.984
g_2	2.001	1.988
g_3	2.001	1.992
D (cm^{-1})	-2.0	-0.4
E/D	0.03	0.33
Contr. to D (S=2; 3/2)	-0.3	-0.2
Contr. to D (S=1; 1/2)	-1.7	-0.2

Quantum Chemistry

Problem:

- Theory is Formulated in Terms of an **Infinite Number** of Many Electron States
  - ➢ General but Intellectually Very Inefficient Way to Deal with Small Perturbations
- Most Succesful Quantum Chemical Methods (MPn, CC, DFT, ...) Only Apply to the **Ground State**

  (Generally: Lowest State of a Given Symmetry)

➢ *Alternative to Sum-Over-States is Needed*

➢ ***Response Theory***

Study the Total Energy of the Ground State in the Presence of Multiple Small Perturbations $\lambda_1 h_{\lambda 1}$, $\lambda_2 h_{\lambda 2}$, $\lambda_3 h_{\lambda 3}$,... (Any of the Operators Listed Before)

$$E_0 \rightarrow E_0(\lambda_1,\lambda_2,\lambda_3,\ldots)$$

Response Theory (ctd.)

Series Expansion:

$$E_0(\lambda_1,\lambda_2,\ldots) = E_0(0,0,\ldots) + \sum_n \lambda_n \left.\frac{\partial E_0}{\partial \lambda_n}\right|_{\boldsymbol{\lambda}=0} + \frac{1}{2}\sum_n \lambda_n \lambda_m \left.\frac{\partial^2 E_0}{\partial \lambda_n \partial \lambda_m}\right|_{\boldsymbol{\lambda}=0} + \ldots$$

Define Properties: $\left.\frac{\partial E_0}{\partial \lambda_n}\right|_{\boldsymbol{\lambda}=0}$ First Order

$\left.\frac{\partial^2 E_0}{\partial \lambda_n \partial \lambda_m}\right|_{\boldsymbol{\lambda}=0}$ Second Order

$\lambda_1 =$ Electric Field

Examples:

$\lambda_1 =$	Electric Field			Dipole Moment
$\lambda_1 = \lambda_2 =$	Electric Field			Polarizability
$\lambda_1 =$	Magnetic Field	$\lambda_2 =$	Electron Spin	EPR g-Tensor
$\lambda_1 =$	Magnetic Field	$\lambda_2 =$	Nuclear Spin	NMR Chemical Shielding Tensor
$\lambda_1 =$	Electron Spin	$\lambda_2 =$	Nuclear Spin	Hyperfine Coupling

Elegant and General but Derivatives May be Very Hard to Calculate!

g-Tensor: DFT and HF

- g-Values can be Defined by: $g_{rs} = \frac{\partial^2 E}{\partial B_r \partial S_s}$
- Four Contributions Arise: $g_{rs} = g_e \delta_{rs} + \Delta g^{RMC} \delta_{rs} + \Delta g_{rs}^{GC} + \Delta g_{rs}^{OZ/SOC}$
- In the CPKS Approach the Kohn-Sham Molecular Orbitals are Calculated in the Presence of a Magnetic Field **B**

$$\psi_j^\sigma = \psi_j^{\sigma(0)} + i\vec{B}\psi_j^{\sigma(1)} + \ldots = \psi_j^{\sigma(0)} + i\vec{B}\sum_{b\in\sigma} U_{jb}^\sigma \psi_b^{\sigma(0)} + \ldots$$

- The UKS-CPKS Equations Become:

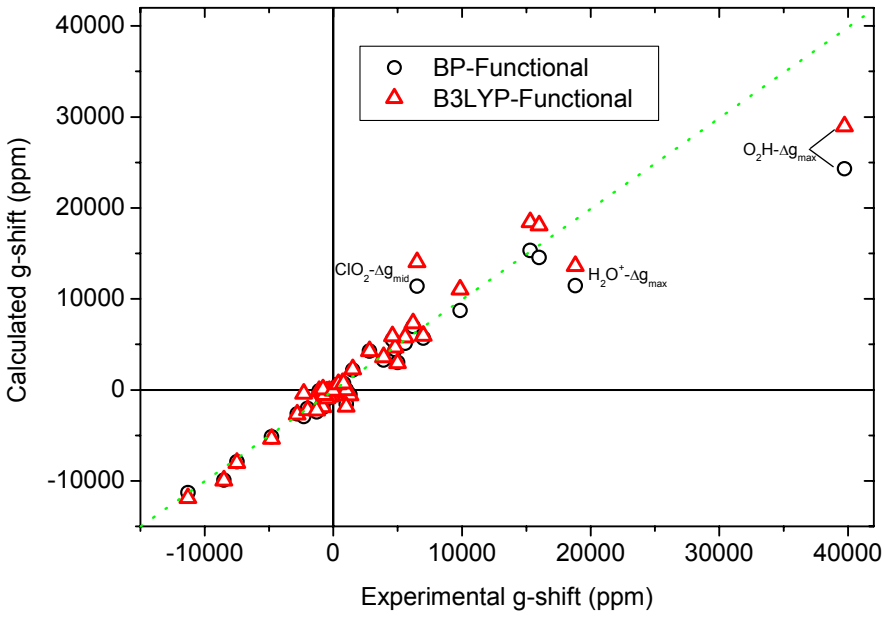
$$\begin{pmatrix} \mathbf{A}^{\alpha\alpha} & 0 \\ 0 & \mathbf{A}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{U}^\alpha \\ \mathbf{U}^\beta \end{pmatrix} = -\begin{pmatrix} \mathbf{V}^\alpha \\ \mathbf{V}^\beta \end{pmatrix} \qquad \text{with: } V_{ia}^\sigma = \left\langle \psi_i^\sigma \middle| \mathbf{l} \middle| \psi_a^\sigma \right\rangle$$

- Gives: $\Delta g_{rs}^{OZ/SOC} = -\frac{1}{\beta S} \sum_{\sigma=\alpha,\beta} (-1)^{\delta_{\sigma\beta}} \sum_{i,a\in\sigma} \mathrm{Im}\left(U_{ia}^{\sigma;r}\right) \mathrm{Im}\left(\left\langle \psi_i^{\sigma(0)} \middle| \sum_A \xi(r_A) \vec{l}_{A,s} \middle| \psi_a^{\sigma(0)} \right\rangle\right)$

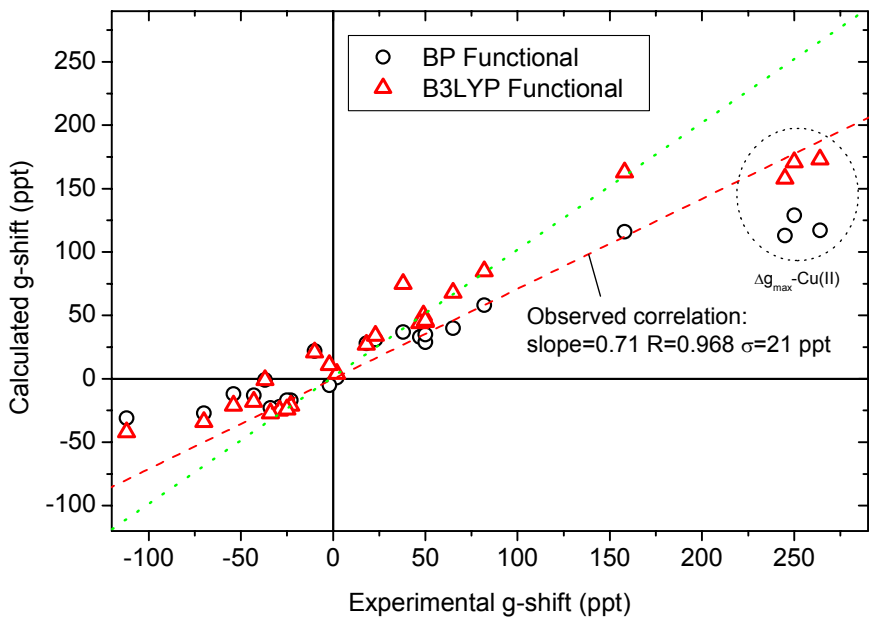
FN. (**2001**) *J. Chem. Phys.*, 115, 11080
Hyperfine Treatment see:
FN (**2003**) *J. Chem. Phys.* 3939
FN (**2001**) *J. Phys. Chem. A*, 105, 4290

DFT Results: g-Values

Small Radicals



Transition Metals

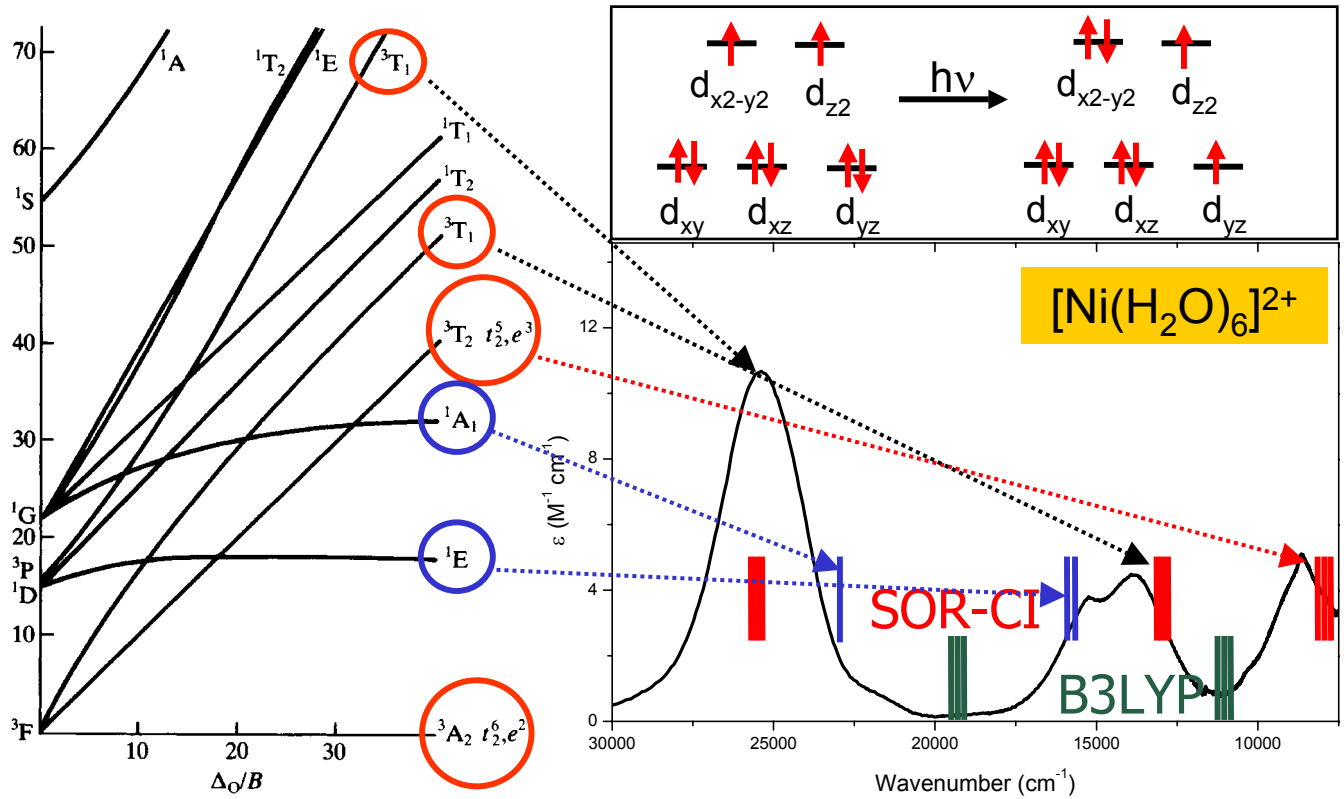


- Reasonable but Still Some Problems Especially for Metals
- Zero-Field Splittings Maybe Approached Similarly but there are Even Some Conceptual Problems

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

Spectroscopy ORiented Configuration Interaction

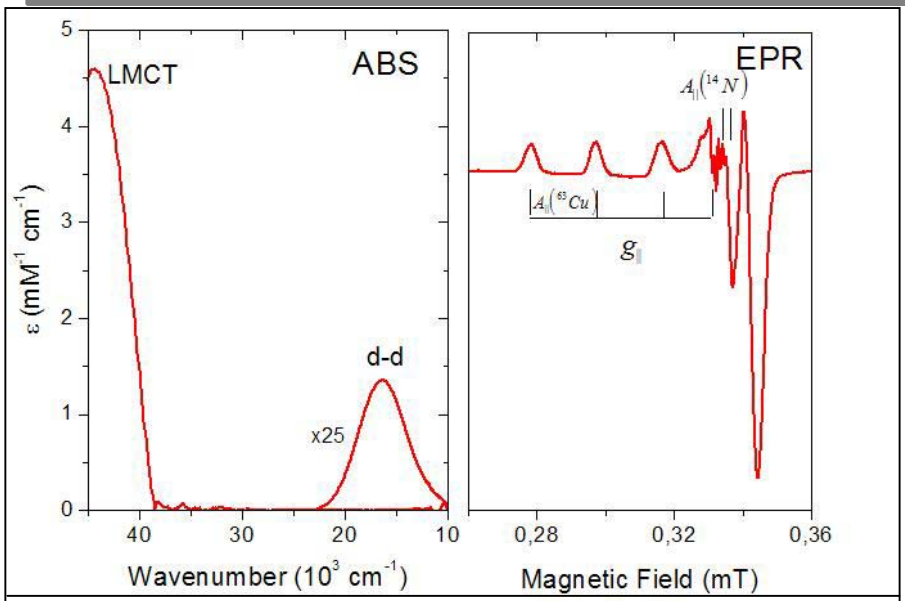
General *ab Initio* Method For Calculating Excited States and SOS Based Properties. Designed for *Energy Differences*

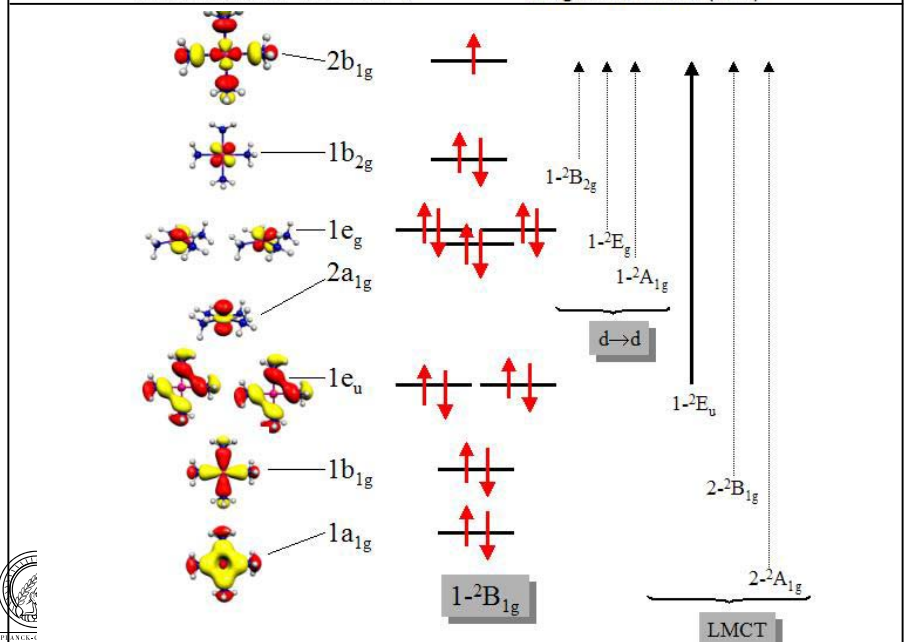


Accurate Description of d-d Multiplets Should give Good EPR Parameter Predictions

FN (**2003**) *J. Chem. Phys.*, 119, 9428
FN (**2003**) *Chem. Phys. Lett.*, 380/5-6, 721

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





	Exp	SORCI	B3LYP
g-Shifts	0.241	0.248	0.142
	0.047	0.058	0.040
^{63}Cu-HFC's (MHz)	-596	-591	-611
	-71?	1	-34
^{14}N-HFC's (MHz)	39	37	49
	31	26	34
ΔE(d-d) (eV)	2.03	2.09	2.69
	2.08	2.37	2.55
	2.18	2.55	2.72
ΔE(CT) (eV)	5.58	5.38	5.22

FN (**2004**) *submitted*