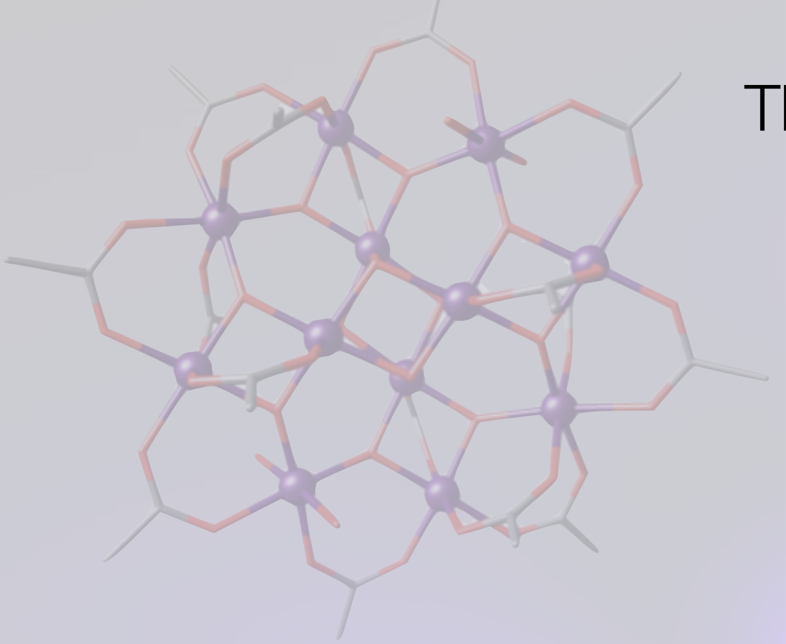
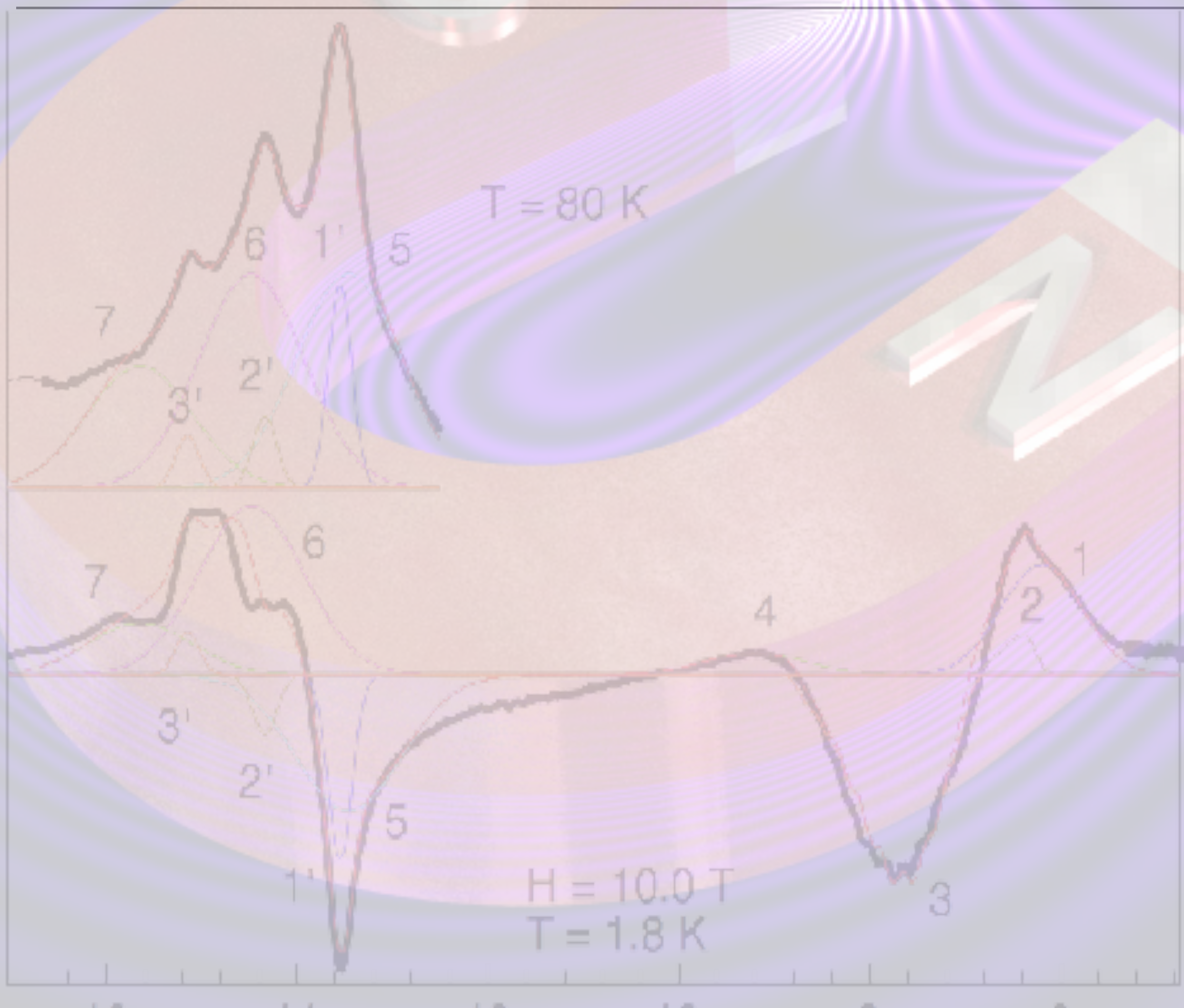
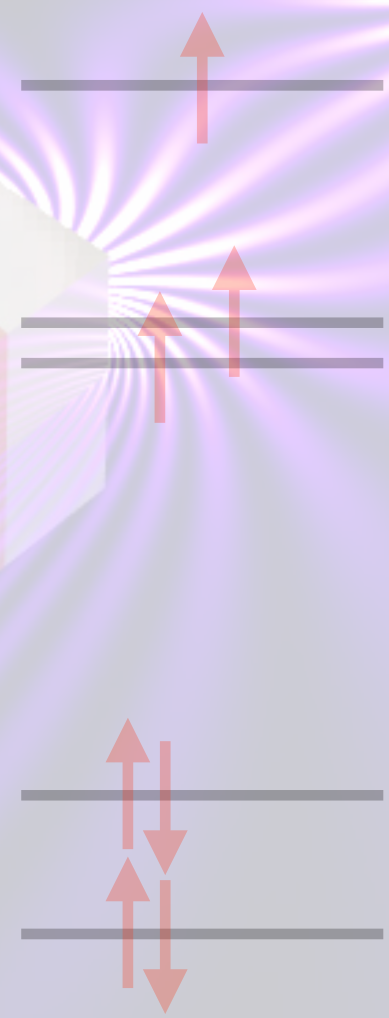


The Bioinorganic Workshop/Summer Symposium

in Molecular Biology 2018

Introduction to Coordination Chemistry and Ligand Field Theory





Frank Neese

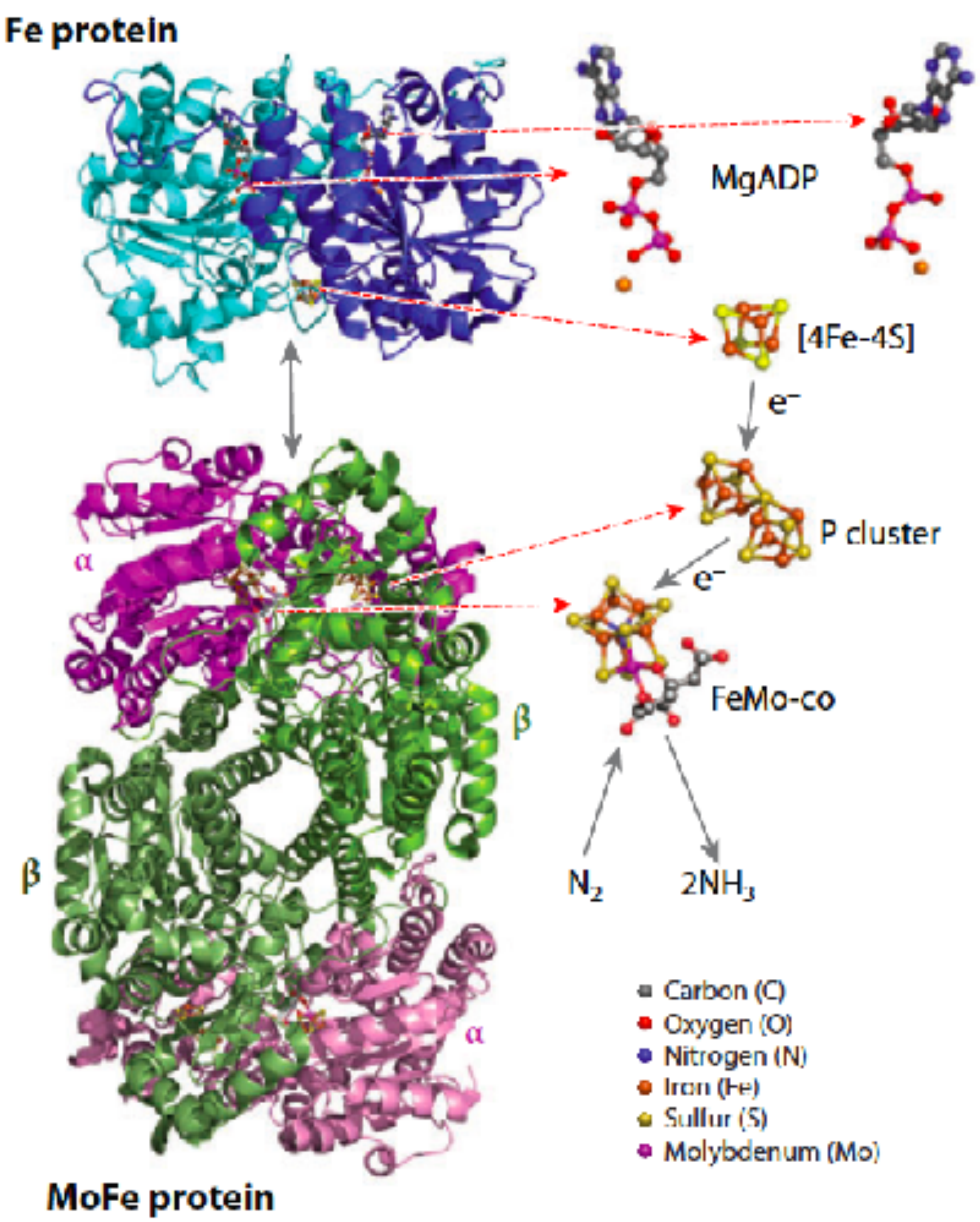
MAX-PLANCK-GESELLSCHAFT

MPI für Kohlenforschung

Kaiser-Wilhelm Platz 1

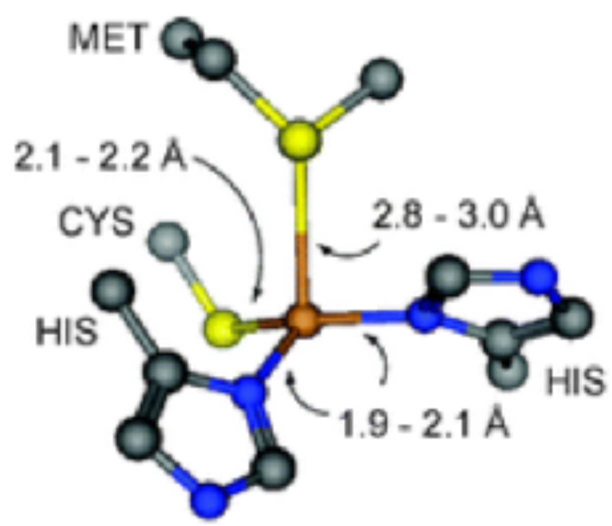
Mülheim an der Ruhr

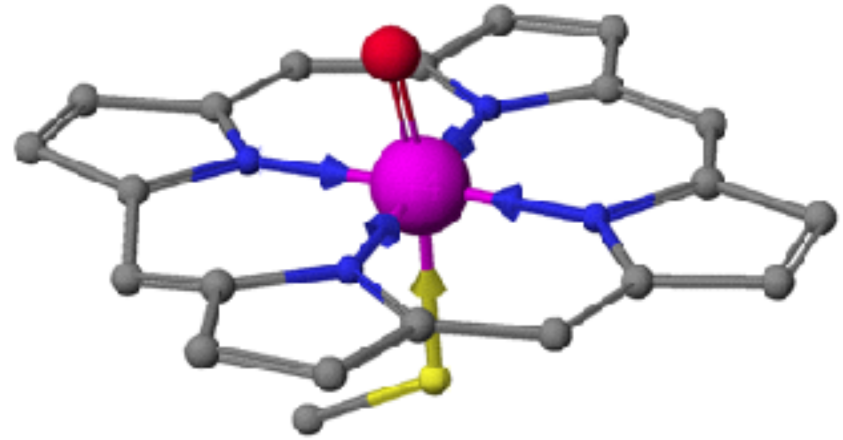
Transition Metal Sites in Enzymes

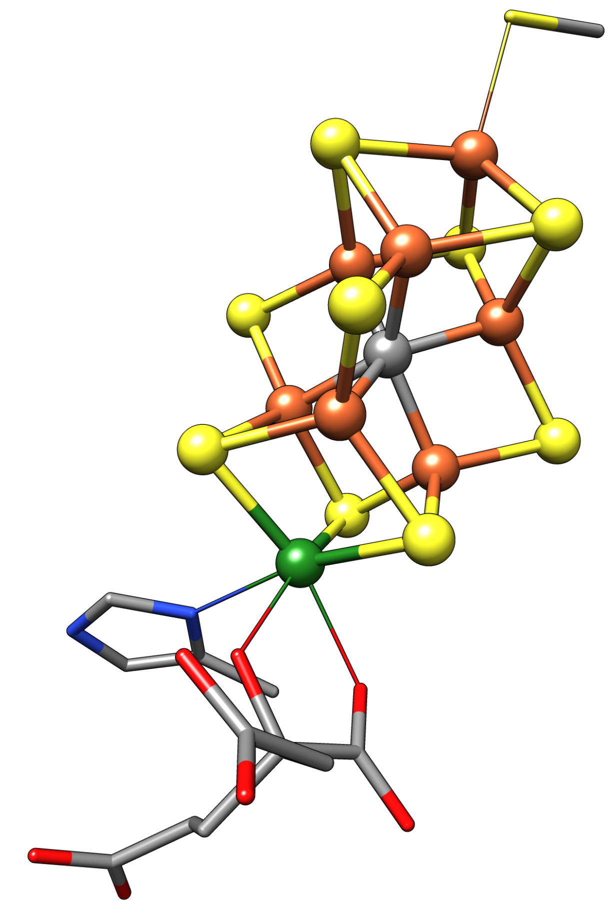


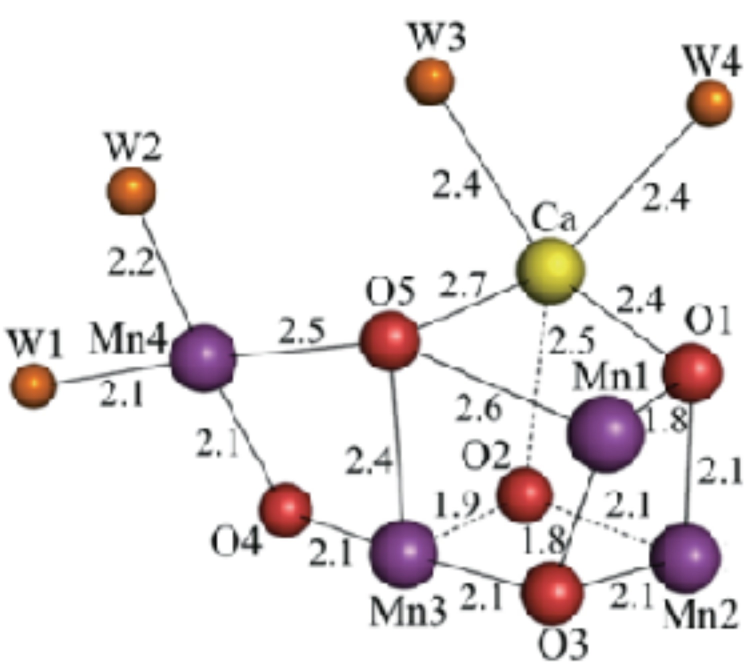
- ~1/3 of all enzymes contain metal cofactors
- These cofactors are the site of redox processes, substrate binding, reactivity
- A crystal structure does not tell the whole story...
- Spectroscopy provides a route to understanding changes that occur at the active sites during electron transfer and catalytic processes

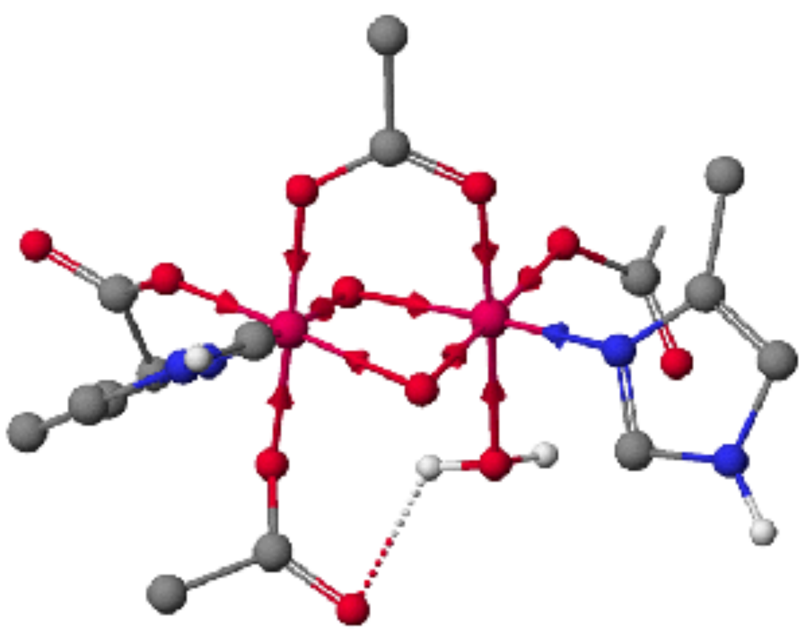
Active Sites in Biology - A Chemist's View





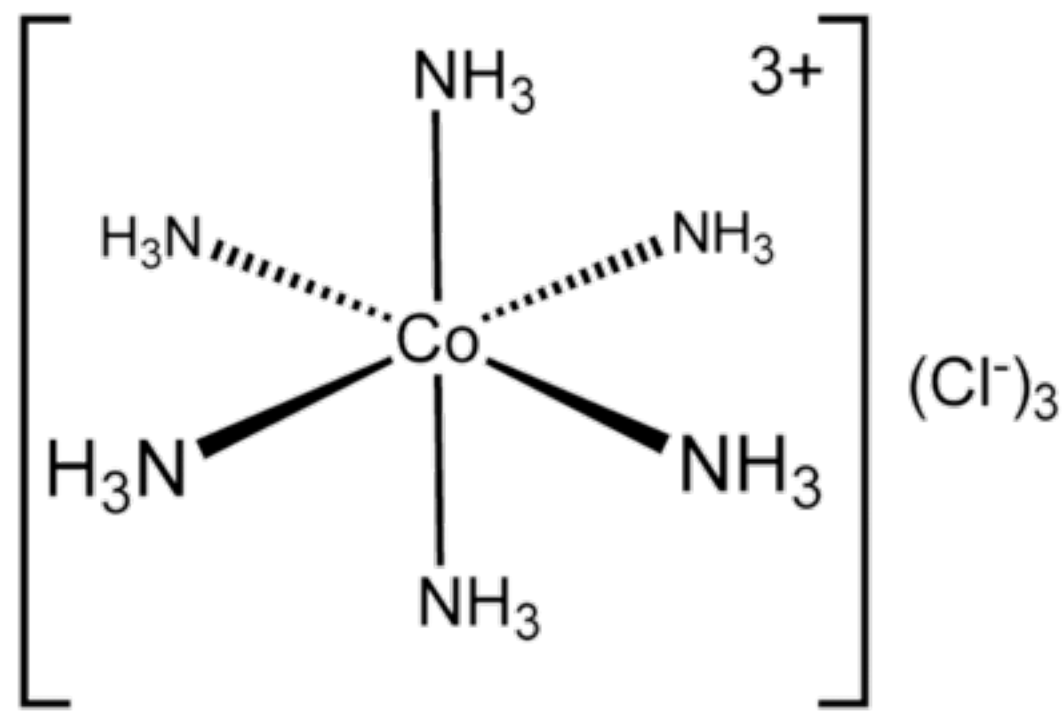






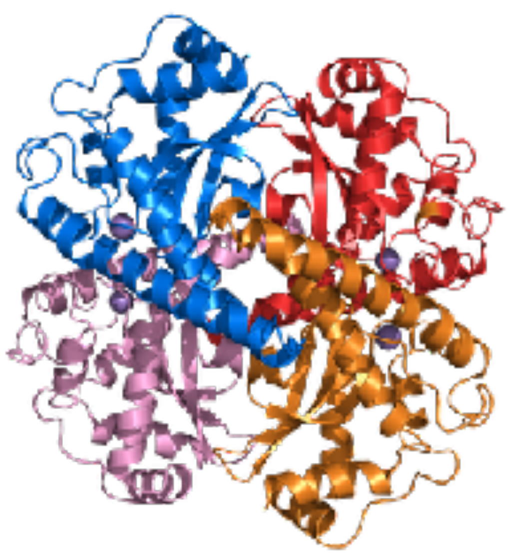
how do these unique coordination environments enable different functions?

Alfred Werner (1866-1919)

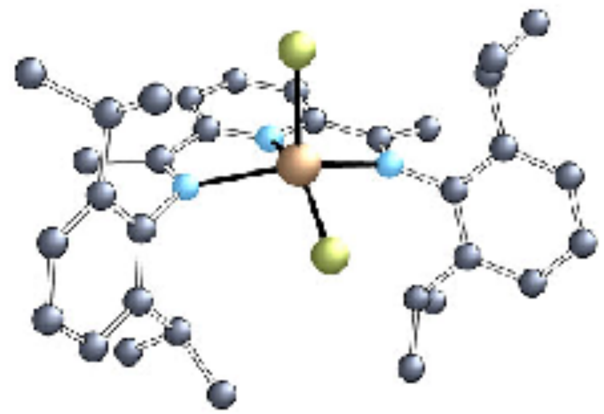


The Magic of d- and f-Block Elements

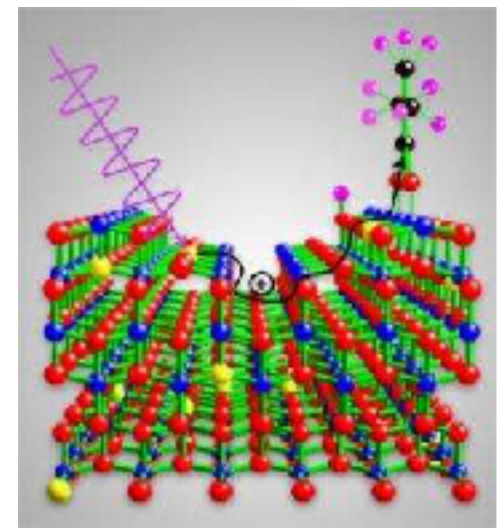
Metalloenzymes



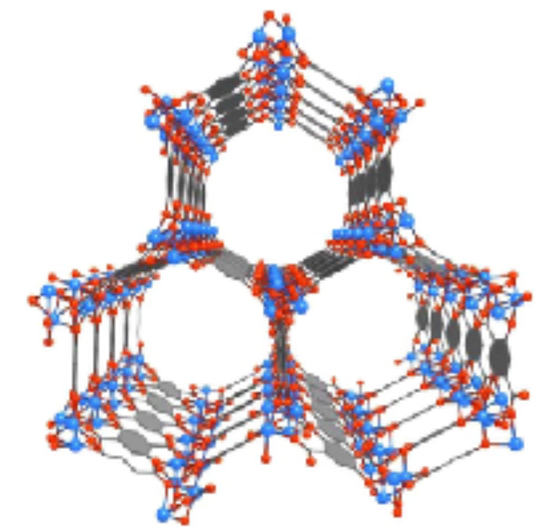
Homogeneous catalysts



Trans. Metal Oxides

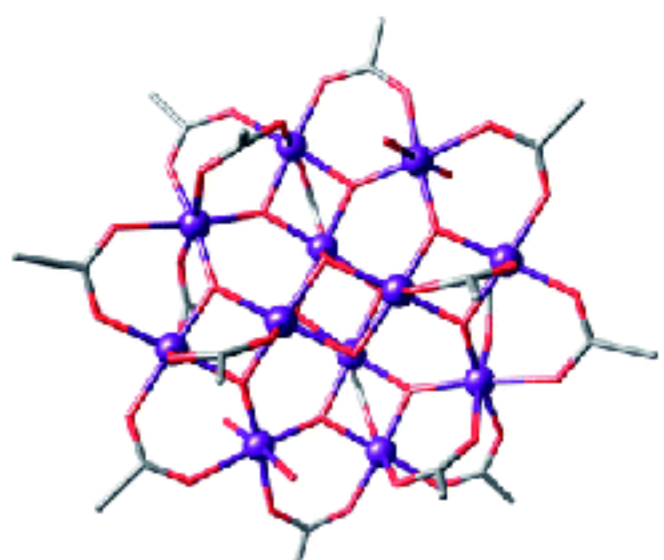


MOFs

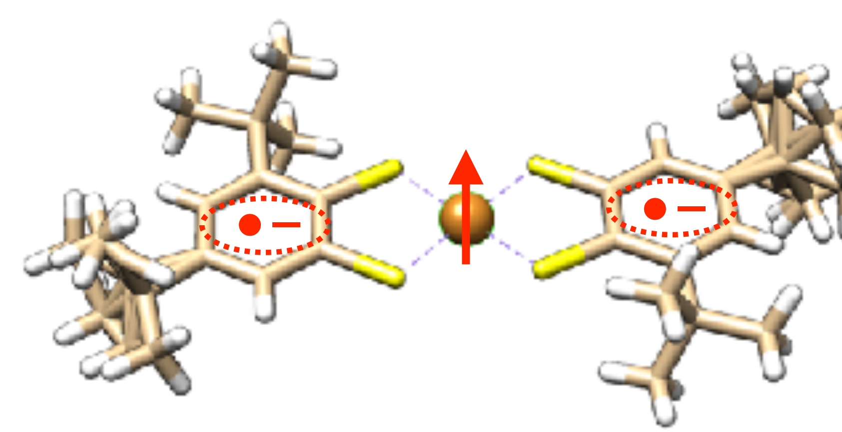


Rare-Earth Luminescence

Single-Molecule Magnets



Metal-Radicals

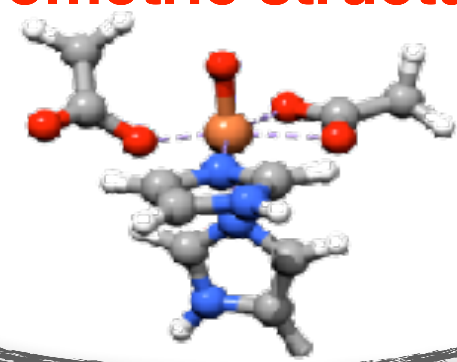


„The only source of knowledge is experiment. The rest is poetry, imagination“

(Max Planck)

Ligand Field Theory as the Guide

geometric structure

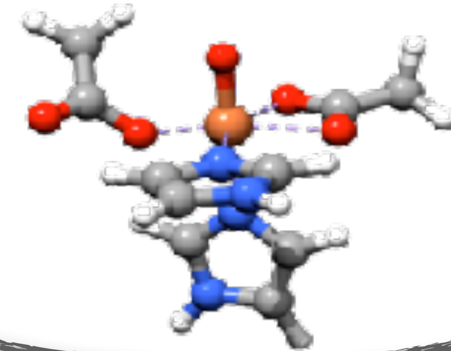


- Nature of ligand
- d^N count
- Local geometry

LFT

Ligand Field Theory as the Guide

geometric structure



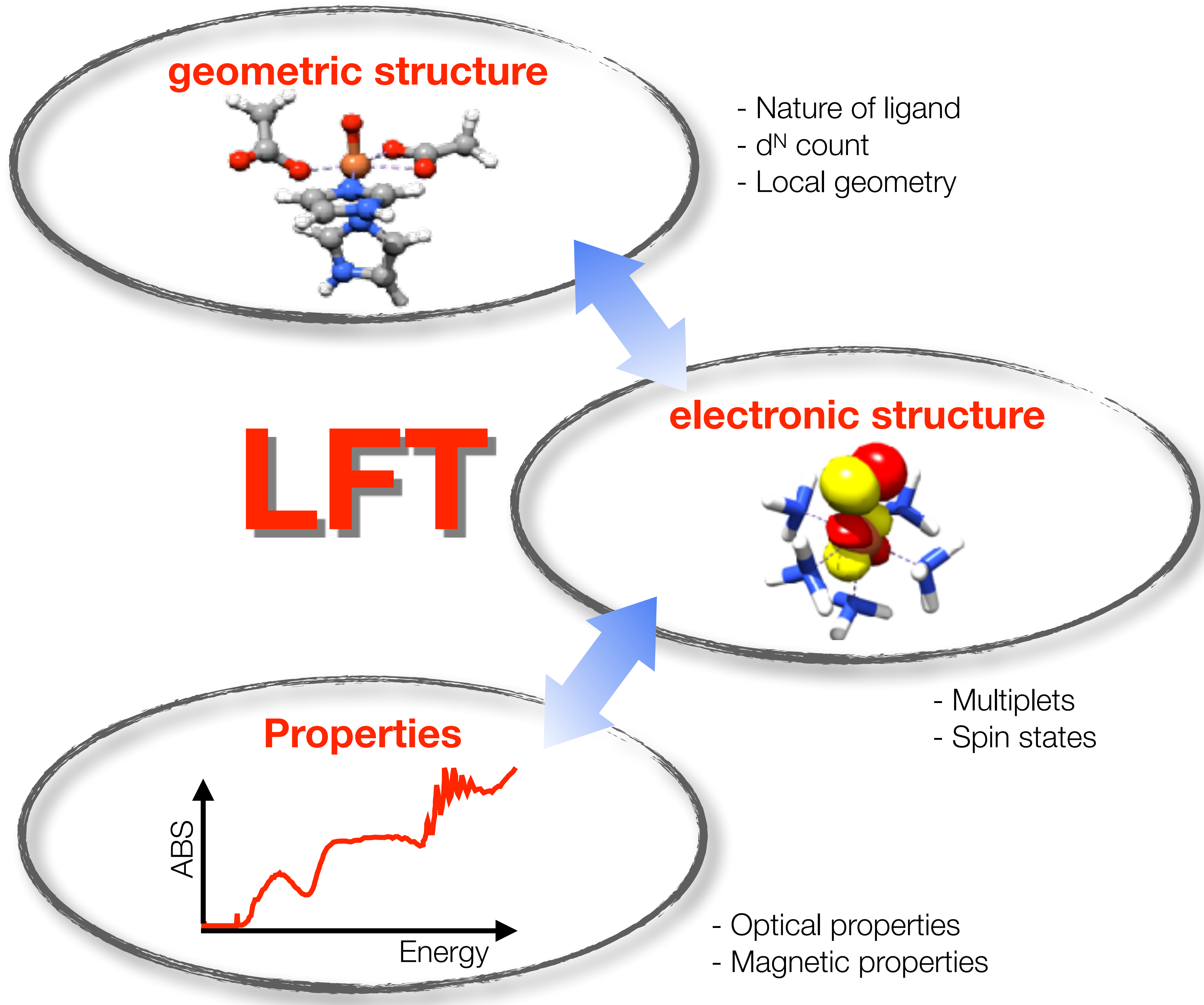
- Nature of ligand
- d^N count
- Local geometry

LFT

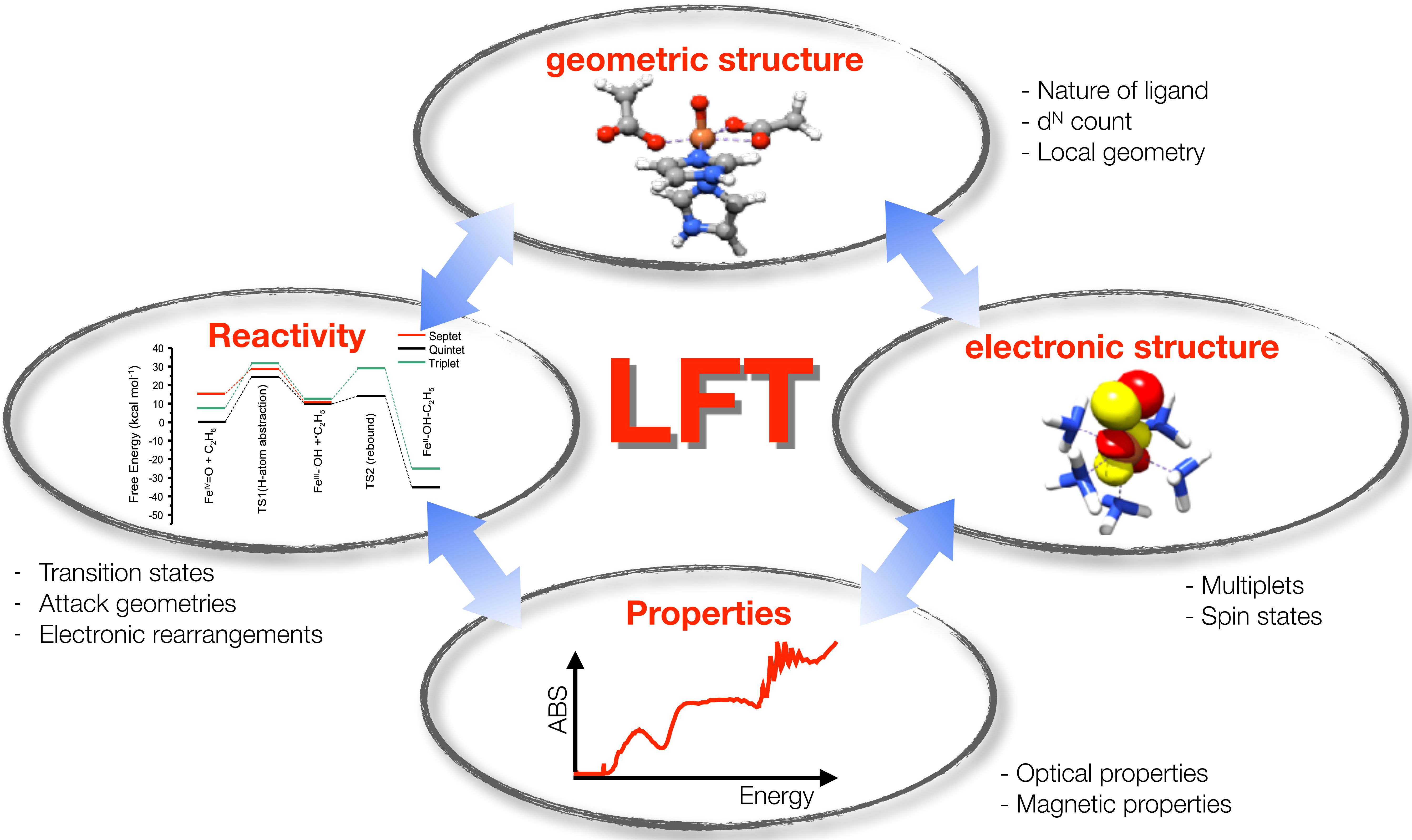
electronic structure

- Multiplets
- Spin states

Ligand Field Theory as the Guide



Ligand Field Theory as the Guide



What is Ligand Field Theory ?

★ **Ligand Field Theory is:**

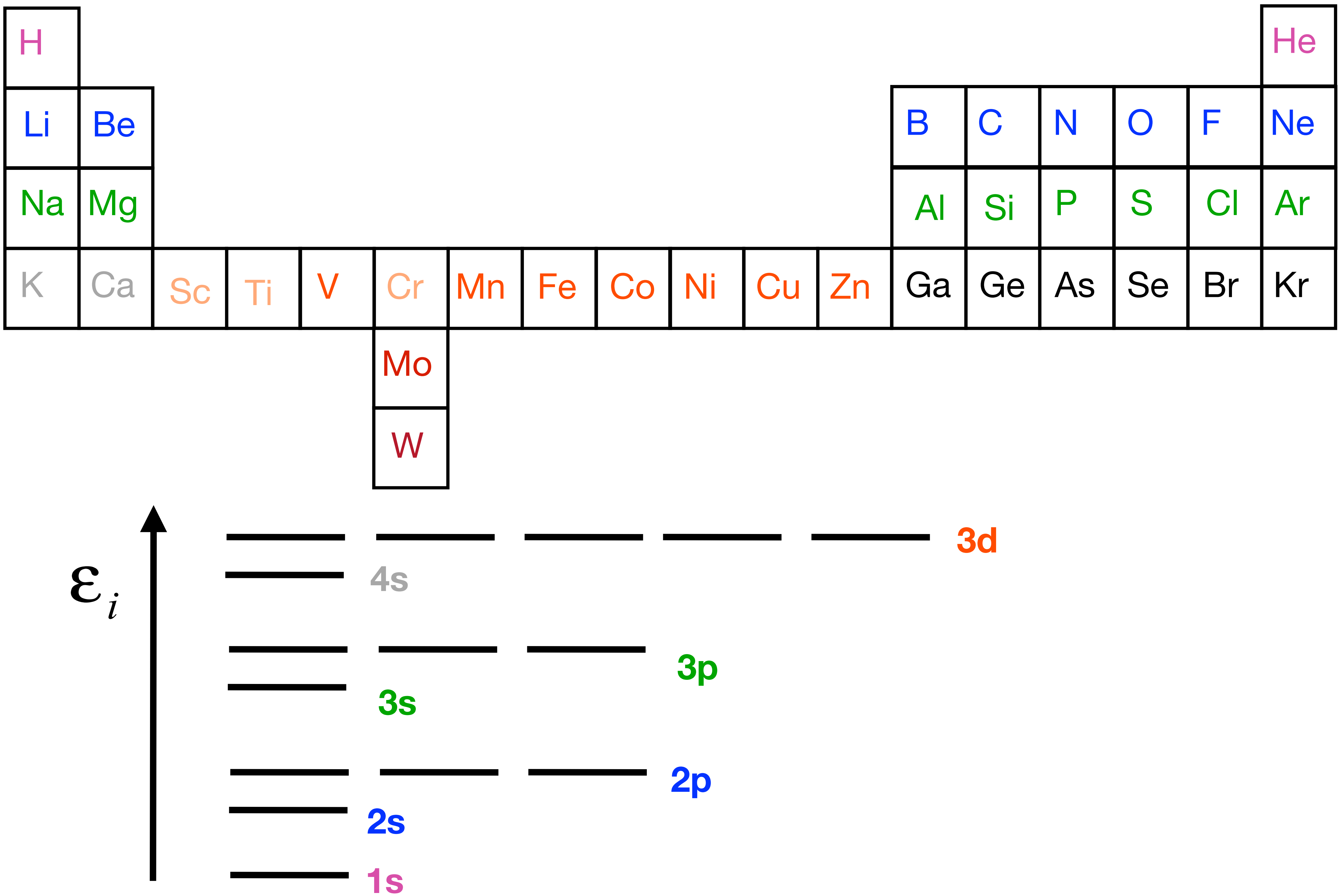
- A semi-empirical theory that applies to a **CLASS** of substances (transition metal complexes).
- A **LANGUAGE** in which a vast number of experimental facts can be rationalized and discussed.
- A **MODEL** that applies only to a restricted part of reality.

★ **Ligand Field Theory is NOT:**

- An ***ab initio* theory** that lets one predict the properties of a compound ‚from scratch'
- A physically rigorous treatment of transition metal electronic structure

Hans Primas (1928-2014)

Many Electron Atoms and the ‚Aufbau‘ Principle



States of Atoms and Molecules

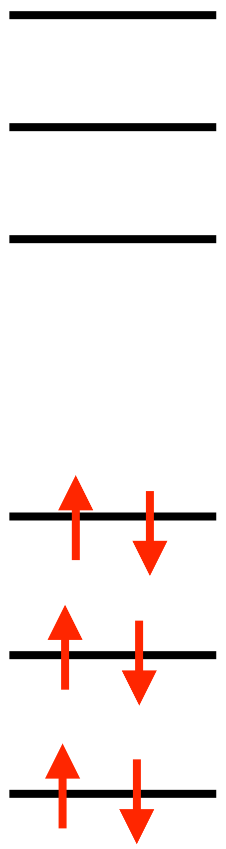
★ Atoms and Molecule exist in electronic **STATES**

★ A **STATE** of an atom or molecule may be characterized by four criteria:

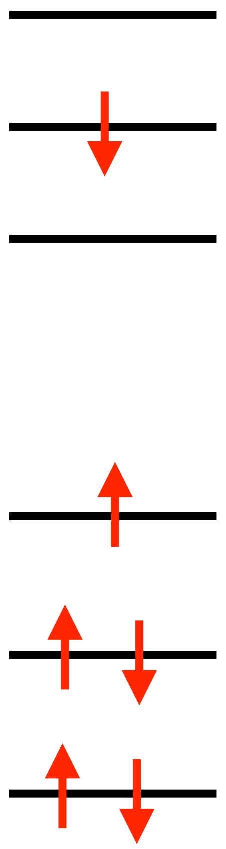
1. The distribution of the electrons among the available orbitals (the electron **CONFIGURATION**) (A set of occupation numbers)
2. The overall **SYMMETRY** of the STATE (Γ Quantum Number)
3. The **TOTAL SPIN** of the STATE (S-Quantum Number)
4. The **PROJECTION** of the Spin onto the Z-axis (M_S Quantum Number)

$$|\mathbf{n}(SM)(\Gamma M_\Gamma)>$$

An Example

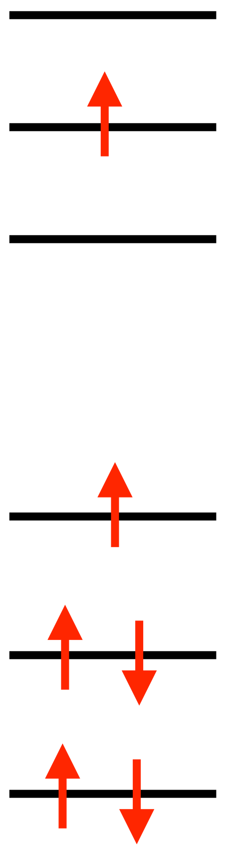


An Example



One Singlet

An Example



One Singlet

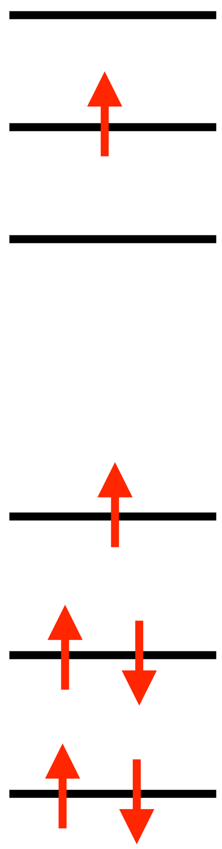
One Triplet

An Example

One Singlet

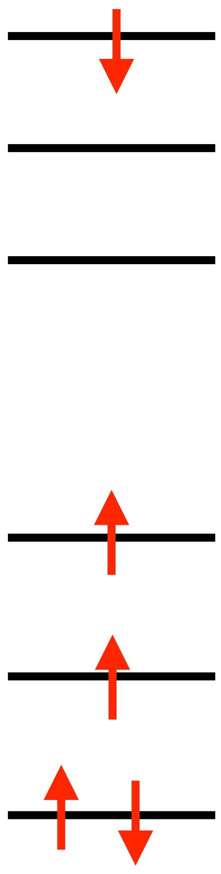
One Triplet

An Example



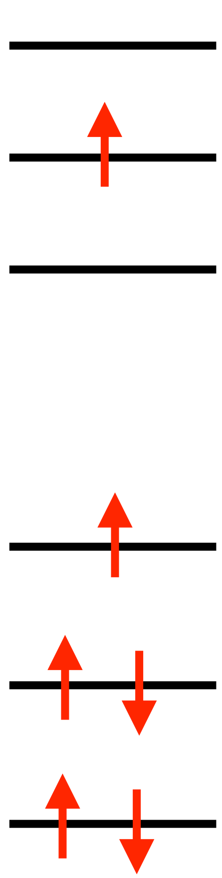
One Singlet

One Triplet



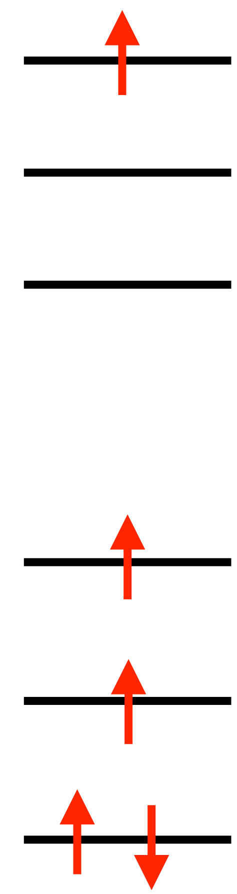
One Doublet

An Example



One Singlet

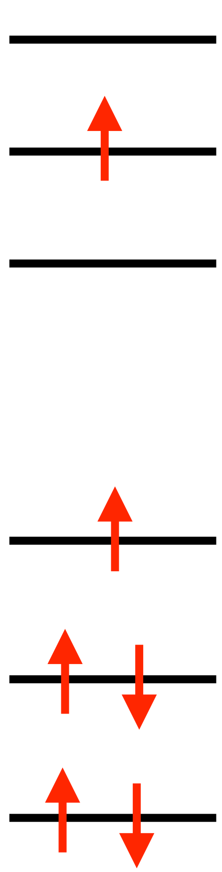
One Triplet



One Doublet

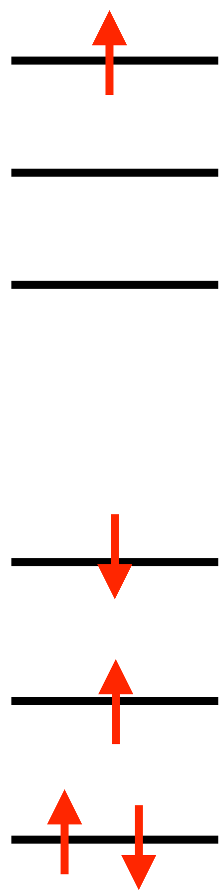
One Quartet

An Example



One Singlet

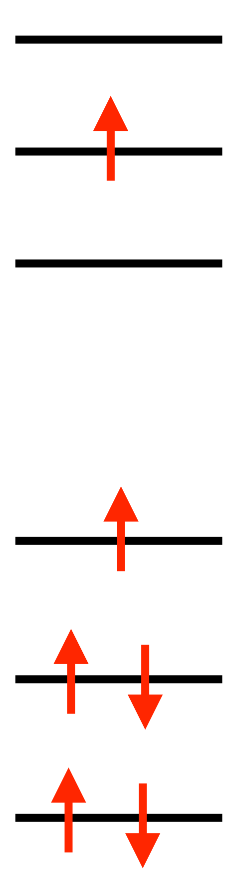
One Triplet



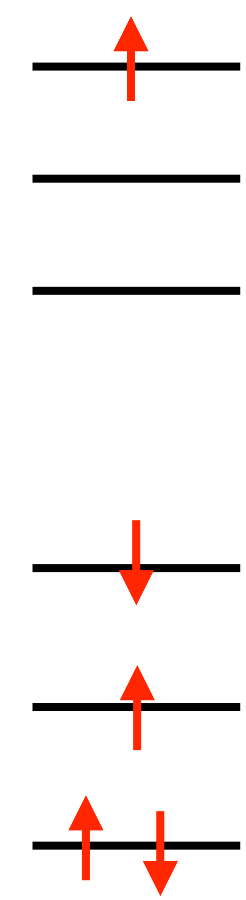
TWO Doublets

One Quartet

An Example



Configurations with several unpaired electrons generate several states



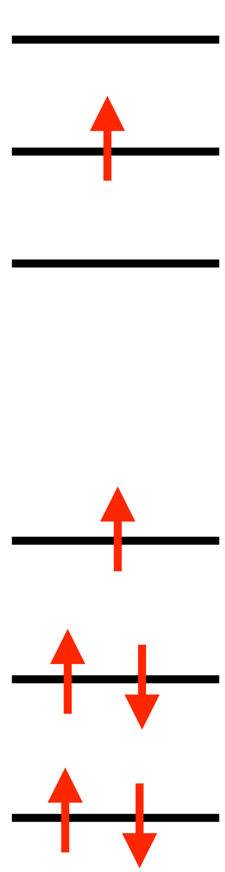
One Singlet

One Triplet

TWO Doublets

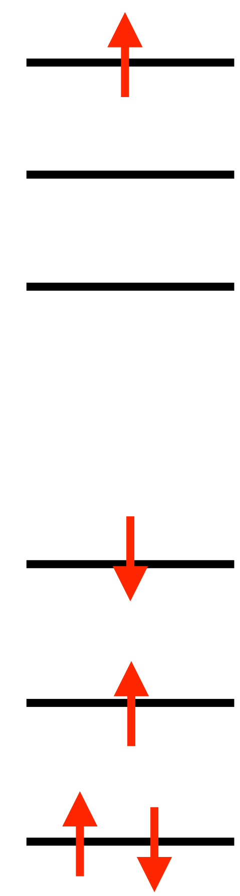
One Quartet

An Example



Configurations with several unpaired electrons generate several states

Only STATES are observable, ORBITALS are NOT!



One Singlet

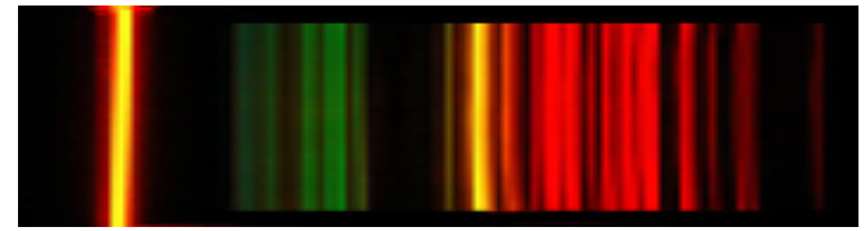
One Triplet

TWO Doublets

One Quartet

Atoms: Atomic „Russel-Saunders“ Terms

Atomic Term Symbol: ^{2S+1}L



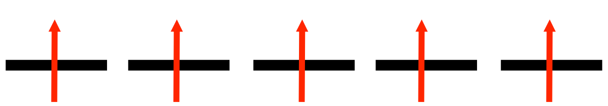
Rules:

- A L-Term is 2L+1 fold orbitally degenerate and (2S+1)(2L+1) fold degenerate in total
- L=0,1,2,3,4... terms are given the symbols S,P,D,F,G,...
- Terms of a given configuration with higher S are lower in energy (Hund I)
- Terms with given configuration and equal spin have the higher L lower in energy (Hund II)

Examples for d^N Configurations:

2S+1=2;
5 equivalent ways to put one e^- into five degenerate orbitals

$\Rightarrow$ ^2D (Ti^{3+}; V^{4+})



2S+1=6;
1 equivalent ways to put five e^- with parallel spin in five orbitals

$\Rightarrow$ ^6S (Mn^{2+};Fe^{3+})

2S+1=3;
10 Ways to put two e^- with parallel spin in five orbitals

$\Rightarrow$ $^3F+^3P$ (V^{3+}; Cr^{4+})

Note: „holes“ create the same terms as „electrons“

Molecules: Symmetry and Group Theory

★ A Molecule can be classified according to the operations that turn the molecule into itself (=symmetry operations), i.e rotations, improper rotations, inversion, reflection.

★ The precise mathematical formulation is part of „group theory“

★ The results is that states can be classified according to their „irreducible representation“ („symmetry quantum number“)

Rules for naming „irreducible representations“:

- Small Letters : Reserved for **orbitals** (One-electron level)
- Capital Letters : Reserved for **states** (Many electron level)
- T,t : Triply degenerate level
- E,e : Doubly degenerate level
- A,B : Non-degenerate Levels

(Mulliken notation)

Term-Symbol: $\boxed{{}^{2S+1}\Gamma}$

2S+1 : „Multiplicity“ = Spin Degeneracy

Γ : „Irreducible Representation“

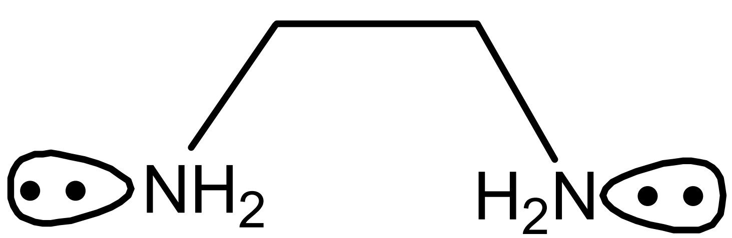
Principles of Ligand Field Theory

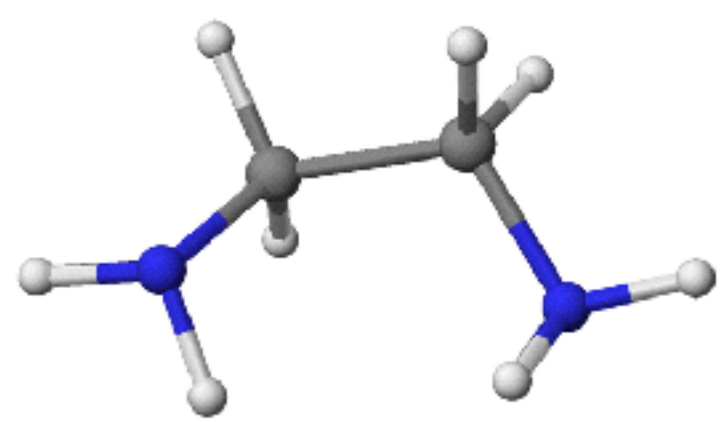
R-L| M

δ-   δ+

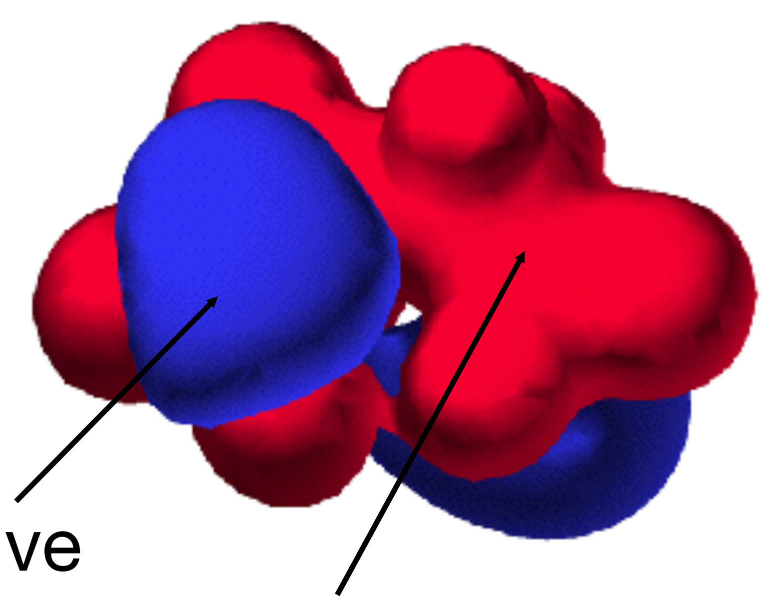
Strong Attraction

Example:



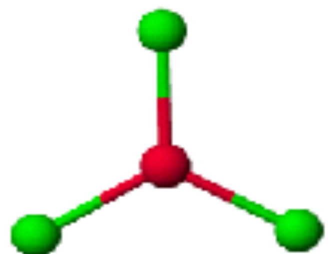


Electrostatic Potential



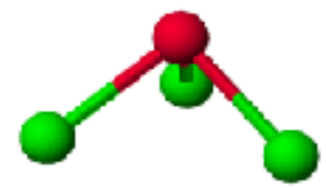
Complex Geometries

3



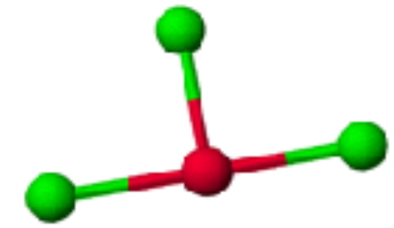
Trigonal

D_{3h}



Trigonal Pyramidal

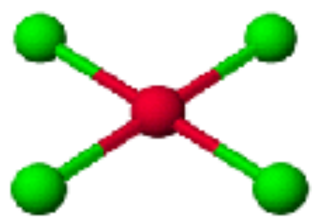
D_{3h}



T-Shaped

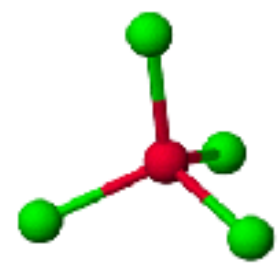
C_{2v}

4



Quadratic Planar

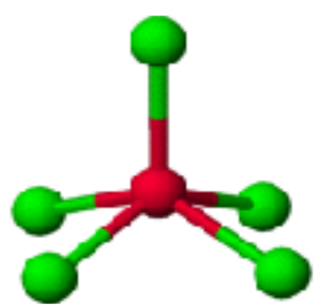
D_{4h}



Tetrahedral

T_d

5



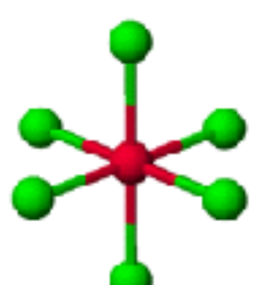
Quadratic Pyramidal

C_{4v}

Trigonal Bipyramidal

D_{3h}

6



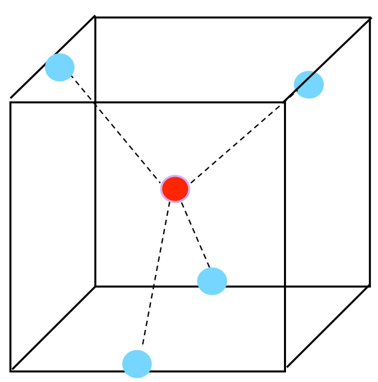
Octahedral

O_h

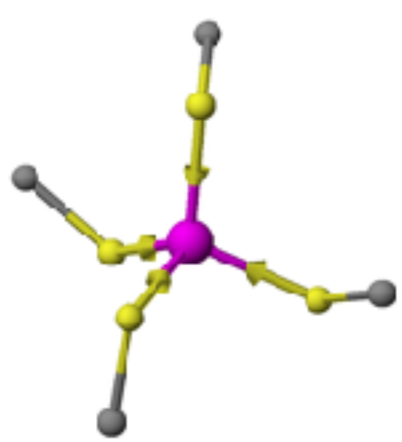
Coordination Geometries

- Approximate Symmetries Observed in Enzyme Active Sites -

Tetrahedral

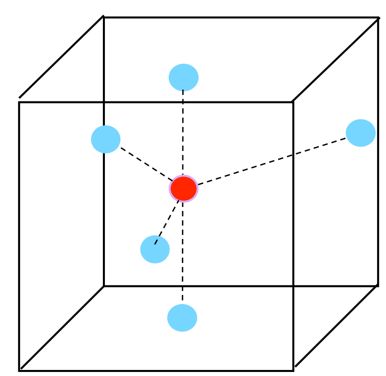


T_d

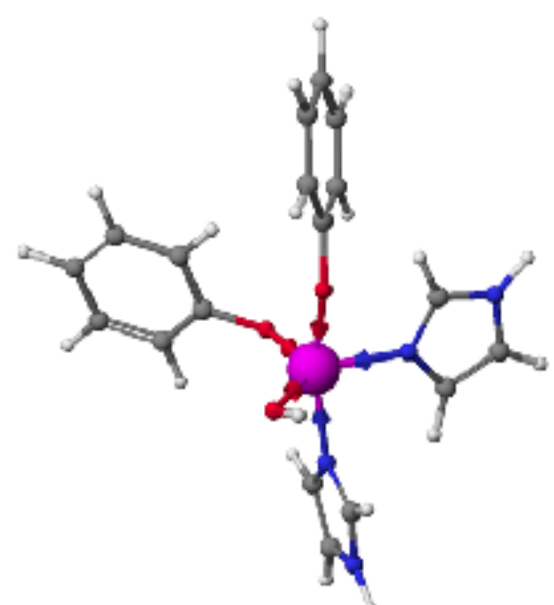


Rubredoxin

Trigonal Bipyramidal

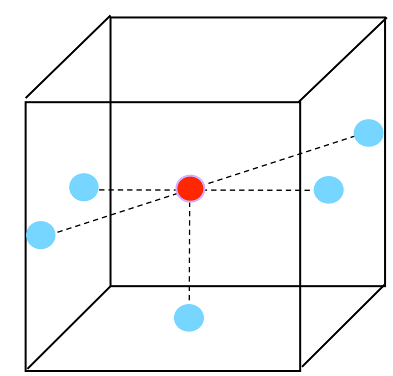


D_{3h}

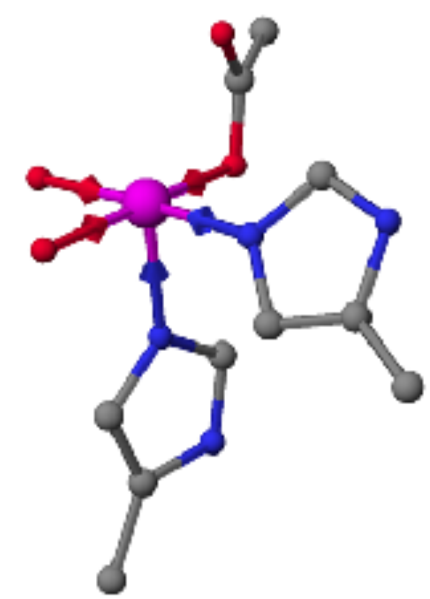


3,4-PCD

Tetragonal Pyramidal

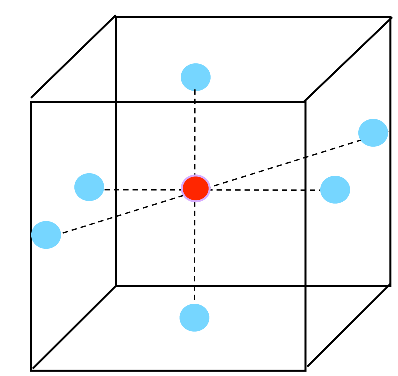


C_{4v}

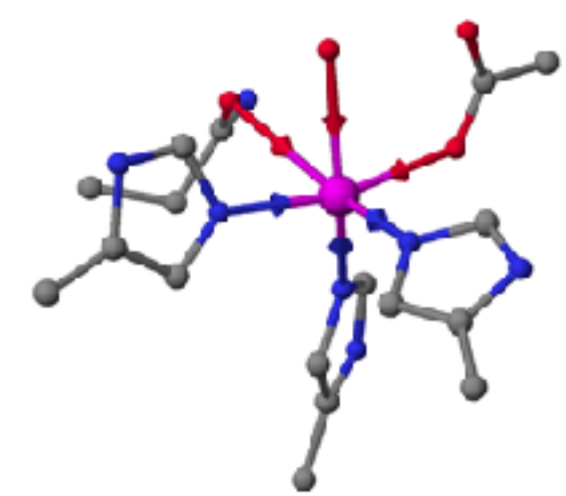


Tyrosine Hydroxylase

Octahedral

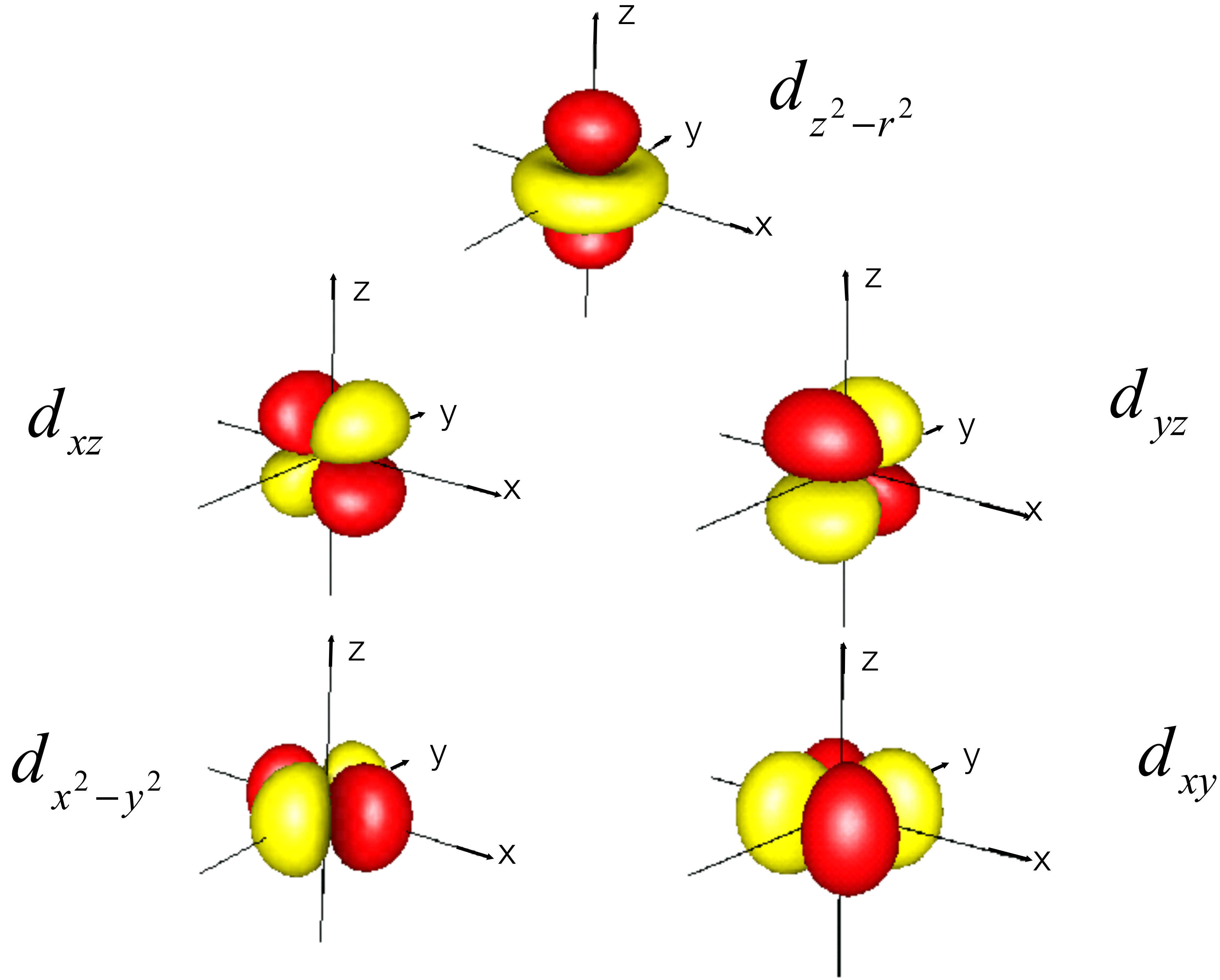


O_h

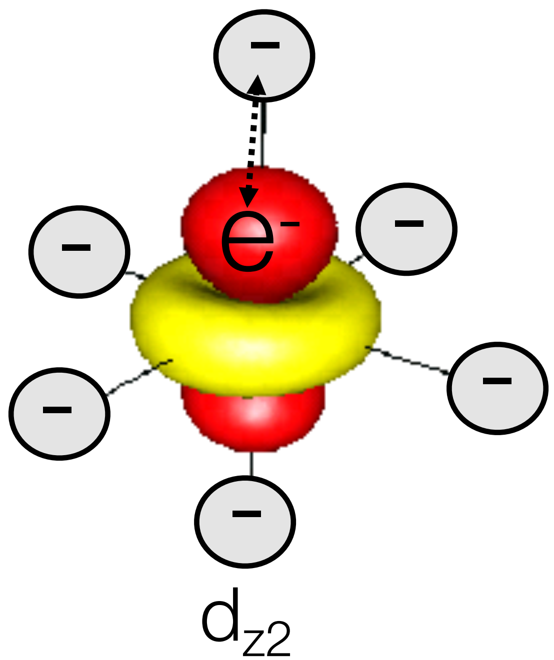


Lipoxygenase

The Shape of Orbitals



A Single d-Electron in an Octahedral Field



The Negatively Charged Ligands Produce an Electric Field+Potential

⇩

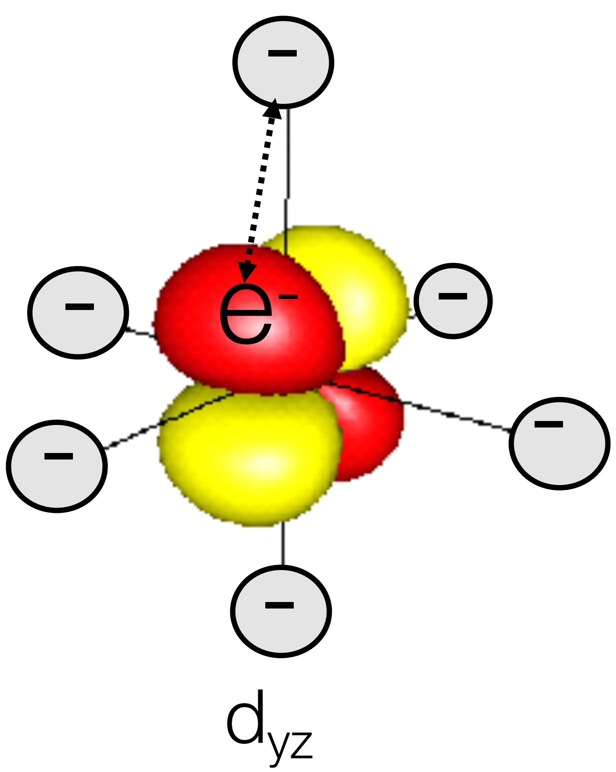
The Field Interacts with the d-Electrons on the Metal (Repulsion)

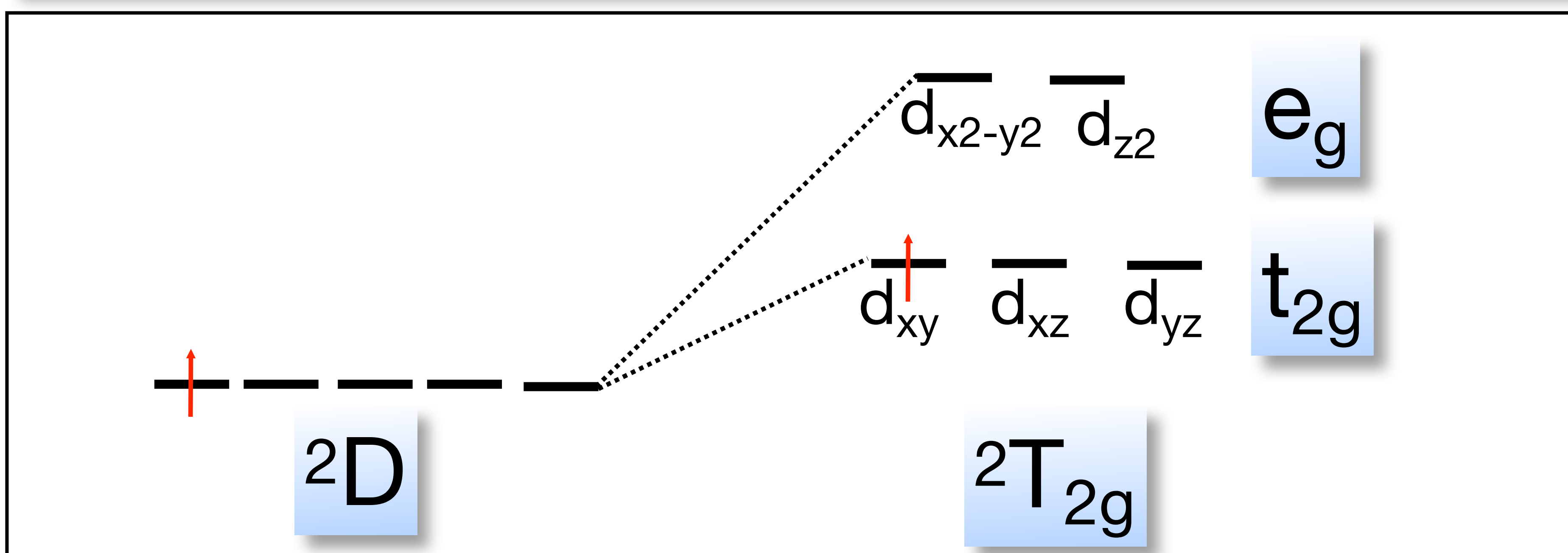
⇩

The Interaction is NOT Equal for All Five d-Orbitals

⇩

1. The Spherical Symmetry of the Free Ions is Lifted
2. The d-Orbitals Split in Energy
3. The Splitting Pattern Depends on the Arrangement of the Ligands





Making Ligand Field Theory Quantitative?

Hans Bethe
1906-2005

Charge Distribution of Ligand Charges: $\rho(\mathbf{R})=\sum_{i=1}^{N_L} q_i \delta\left(\mathbf{R}-\mathbf{R}_{L_i}\right)$

Ligand field potential: $V_{LF}(\mathbf{r})=\int \frac{\rho(\mathbf{R})}{|\mathbf{R}-\mathbf{r}|} d\mathbf{R}$ $\quad$ q_i=charges

Expansion of inverse distance: $\frac{1}{|\mathbf{R}-\mathbf{r}|}=\sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} \sum_{m=-l}^{l} S_{lm}(\mathbf{R}) S_{lm}(\mathbf{r})$

S_l^m=real spherical harmonics
$r_{<,>}$ Smaller/Larger or r and R

Insertion into the potential: $V_{LF}(\mathbf{r})=\sum_{l=0}^{\infty} r^l \sum_{m=-l}^{l} S_{lm}(\mathbf{r}) A_{lm}$

„Geometry factors“: $A_{lm}=\sum_{i=1}^{N_L} \frac{4\pi}{2l+1} \frac{q_i}{R_{L_i}^{l+1}} S_{lm}\left(\mathbf{R}_{L_i}\right)$

Ligand-field matrix elements: $\left\langle d_i \middle| V_{LF} \middle| d_j \right\rangle=-\sum_{l=0}^{\infty}\left\langle r^l\right\rangle \sum_{m=-l}^{l} A_{lm} \left(\begin{array}{cc|c} l_i & l_j & l \\ m_i & m_j & m \end{array}\right)$

$\left(\begin{array}{cc|c} l_i & l_j & l \\ m_i & m_j & m \end{array}\right)$ =Gaunt Integral (tabulated)

Ligand-field splitting in O_h: $\boxed{\left\langle d_{e_g} \middle| V_{LF} \middle| d_{e_g} \right\rangle-\left\langle d_{t_{2g}} \middle| V_{LF} \middle| d_{t_{2g}} \right\rangle \equiv 10Dq=\frac{5}{3} \frac{q}{R^5}\left\langle d \middle| r^4 \middle| d \right\rangle}$

Don‘t evaluate these integrals analytically, plug in and compare to experiment! LFT is not an ab initio theory (the numbers that you will get are ultimately absurd!). What we want is a parameterized model and thus we want to leave 10Dq as a fit parameter. The ligand field model just tells us how many and which parameters we need what their relationship is

Making Ligand Field Theory Quantitative?

Hans Bethe
6-2005

Charge Distribution of Ligand Charges: $\rho(\mathbf{R})=\sum_{i=1}^{N_L} q_i\delta\left(\mathbf{R}-\mathbf{R}_{L_i}\right)$

Ligand

Expan … l harmonics
… r or r and R

Inserti

„Geon

Ligand … $l_j \; l$ … $m_j \; m$

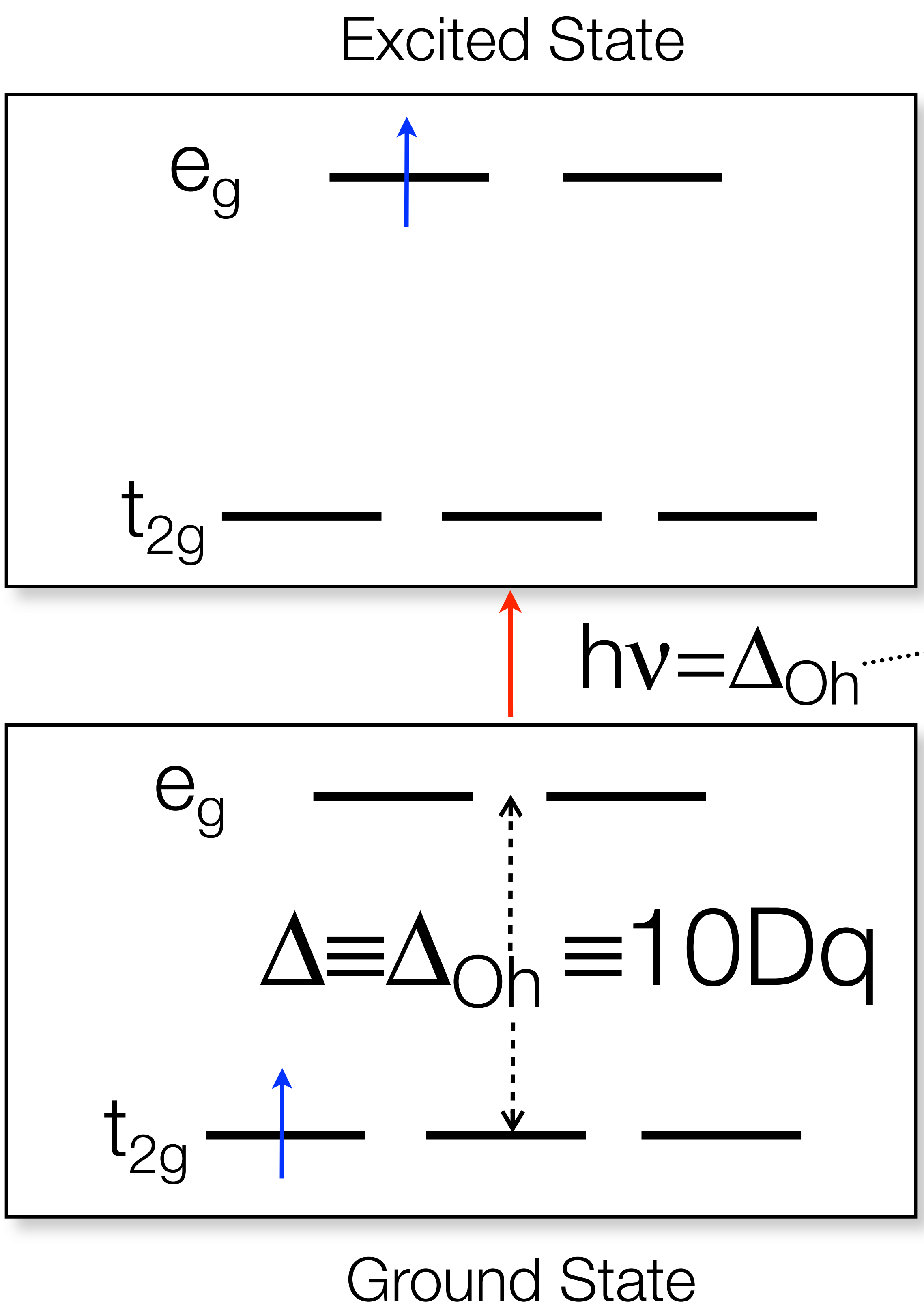
Ligand … t Integral
… ated)

THUS

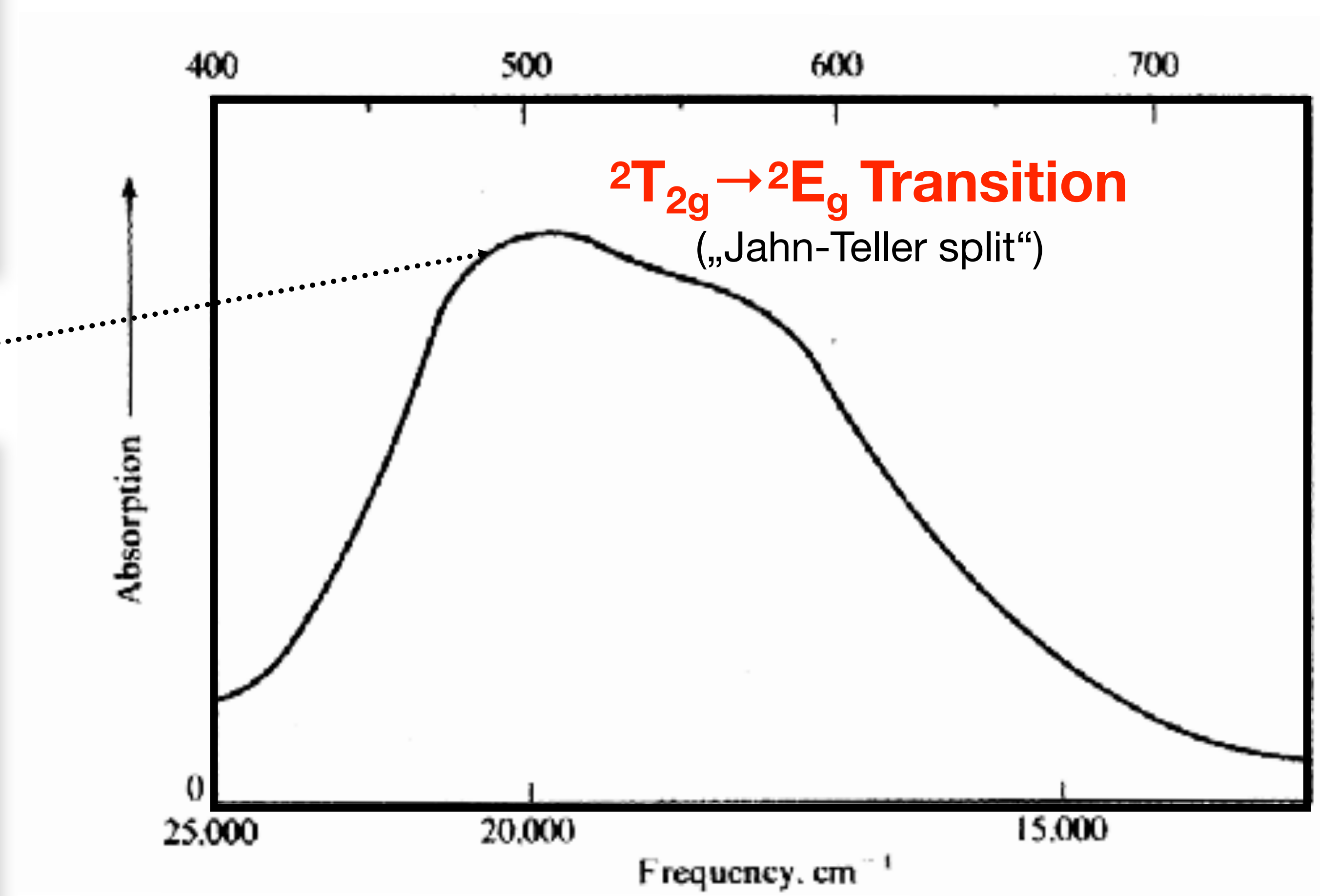
- **LFT taken literally is unphysical**
- **LFT Parameters are not theoretically defined**
- **Fitting to experimental data is mandatory to determine them**

Don‘t evaluate these integrals analytically, plug in and compare to experiment! LFT is not an ab initio theory (the numbers that you will get are ultimately absurd!). What we want is a parameterized model and thus we want to leave 10Dq as a fit parameter. The ligand field model just tells us how many and which parameters we need what their relationship is

Optical Measurement of Δ: d-d Transitions



$[Ti(H_2O)_6]^{3+}$



The Spectrochemical Series

A „Chemical“ Spectrochemical Series

$I^- < S^{2-} < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^- < CO \sim NO < NO^+$

Δ SMALL

Δ LARGE

A „Biochemical“ Spectrochemical Series (A. Thomson)

Asp/Glu < Cys < Tyr < Met < His < Lys < His^-

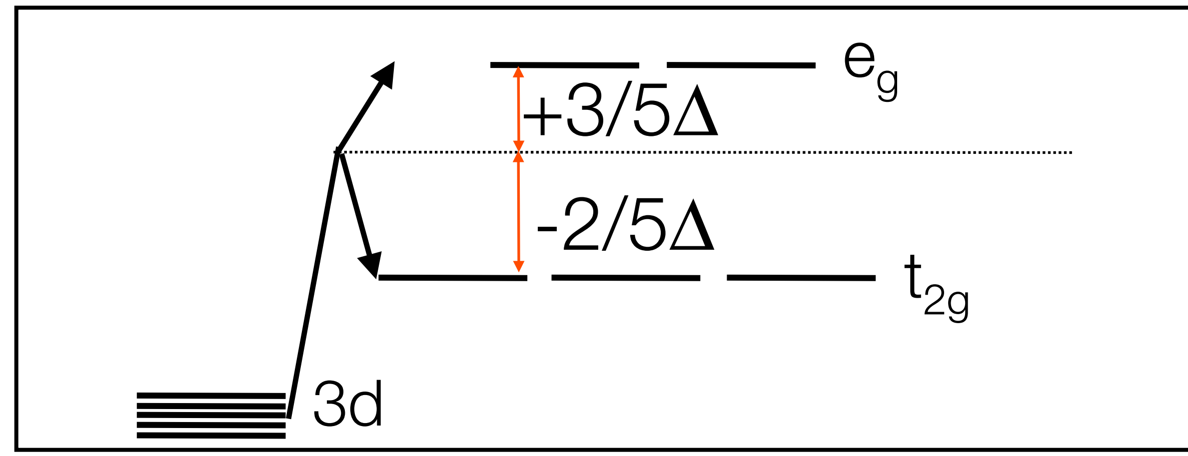
Δ SMALL

Δ LARGE

Ligand Field Stabilization Energies

Central Idea:

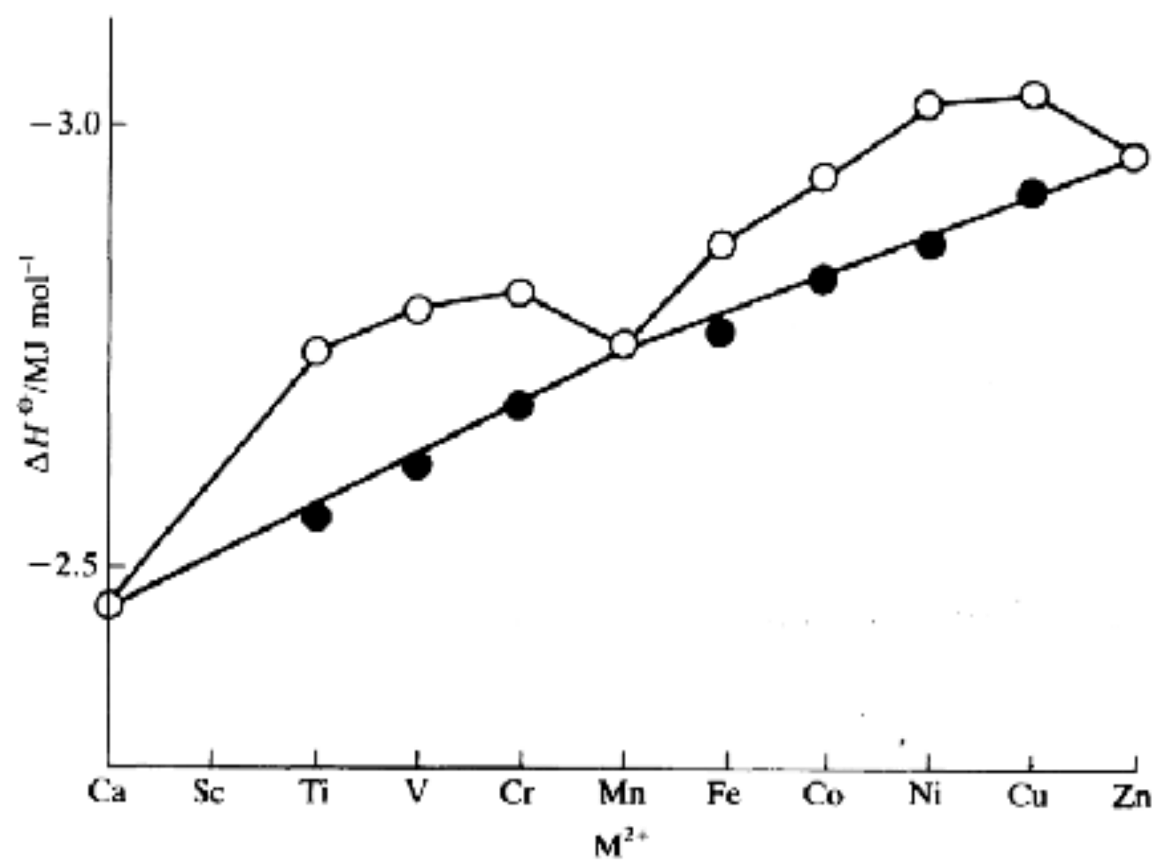
- ➡ Occupation of t_{2g} orbitals stabilizes the complex while occupation of e_g orbitals destabilizes it.
- ➡ Ligand Field Stabilization Energy (LSFE)



d^N	LSFE
1	$-2/5\Delta$
2	$-4/5\Delta$
3	$-6/5\Delta$
4	$-3/5\Delta$
5	**0**
6	$-2/5\Delta$
7	$-4/5\Delta$
8	$-6/5\Delta$
9	$-3/5\Delta$
10	**0**

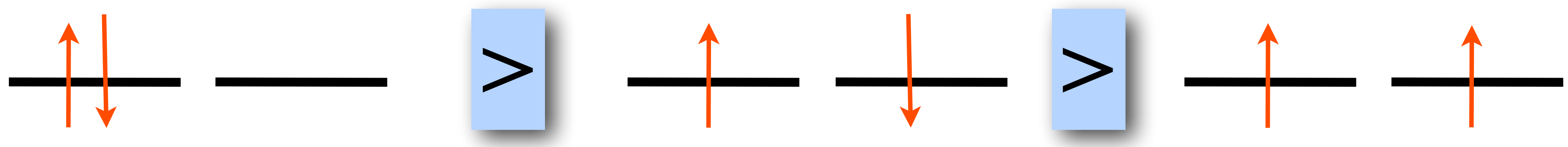
Experimental Test:

- ➡ Hydration energies of hexaquo M^{2+}



Many Electrons in a Ligand Field: Electron Repulsion

BASIC TRUTH: Electrons REPEL Each Other



Rules:

- Electrons in the SAME orbital repel each other most strongly.
- Electrons of oppsite spin repel each other more strongly than electrons of the same spin.

Consequences:

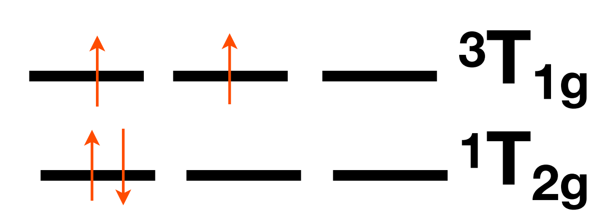
- In degenerate orbitals electrons enter first with the same spin in different orbitals (→Hund‘s Rules in atoms!)
- A given configuration produces several states with different energies

Ligand Field Theory:

- Electron repulsion can be taken care of by 2 PARAMETERS: B (~1000 cm^{-1}) and C
  - C/B~4

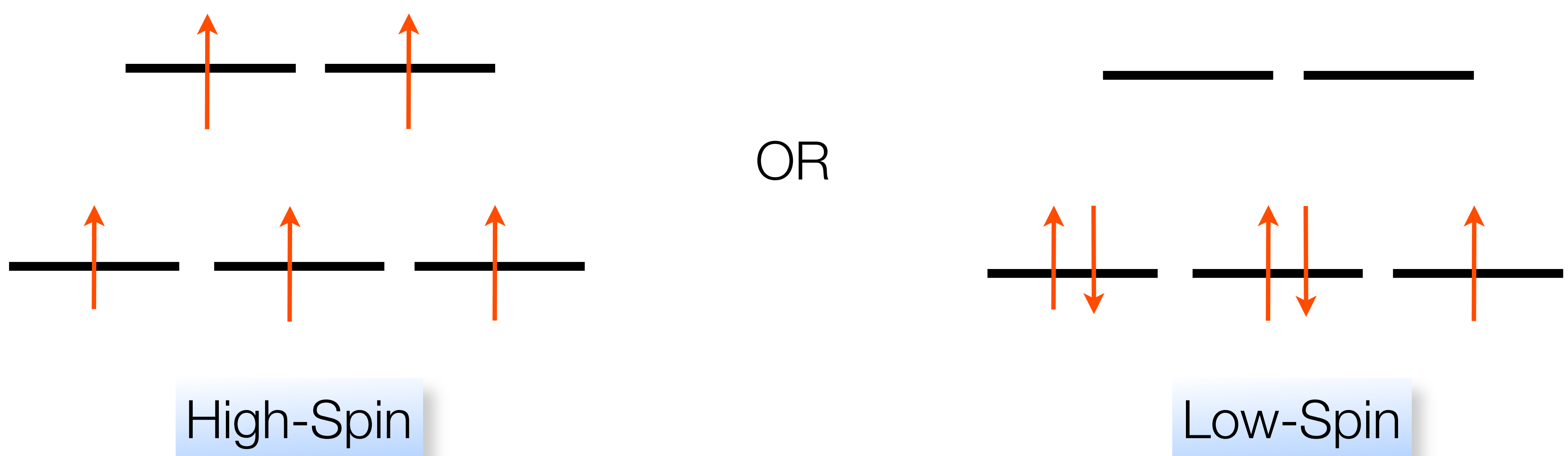
Example:

- d^2-Configuration: $\Delta E(^1T_{2g}-^3T_{1g})$ ~ 6B+2C ~ 14,000 cm^{-1}

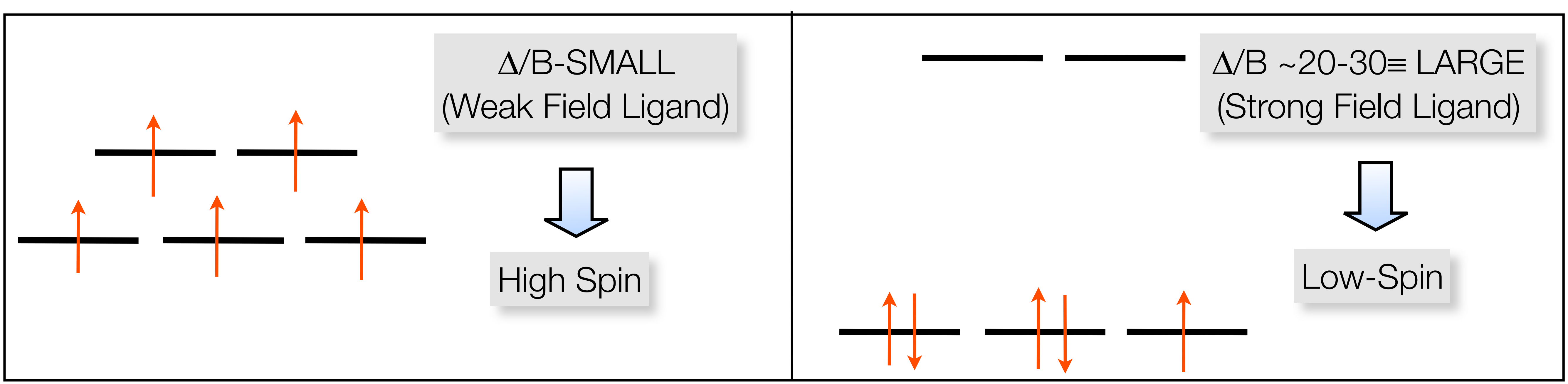


High-Spin and Low-Spin Complexes

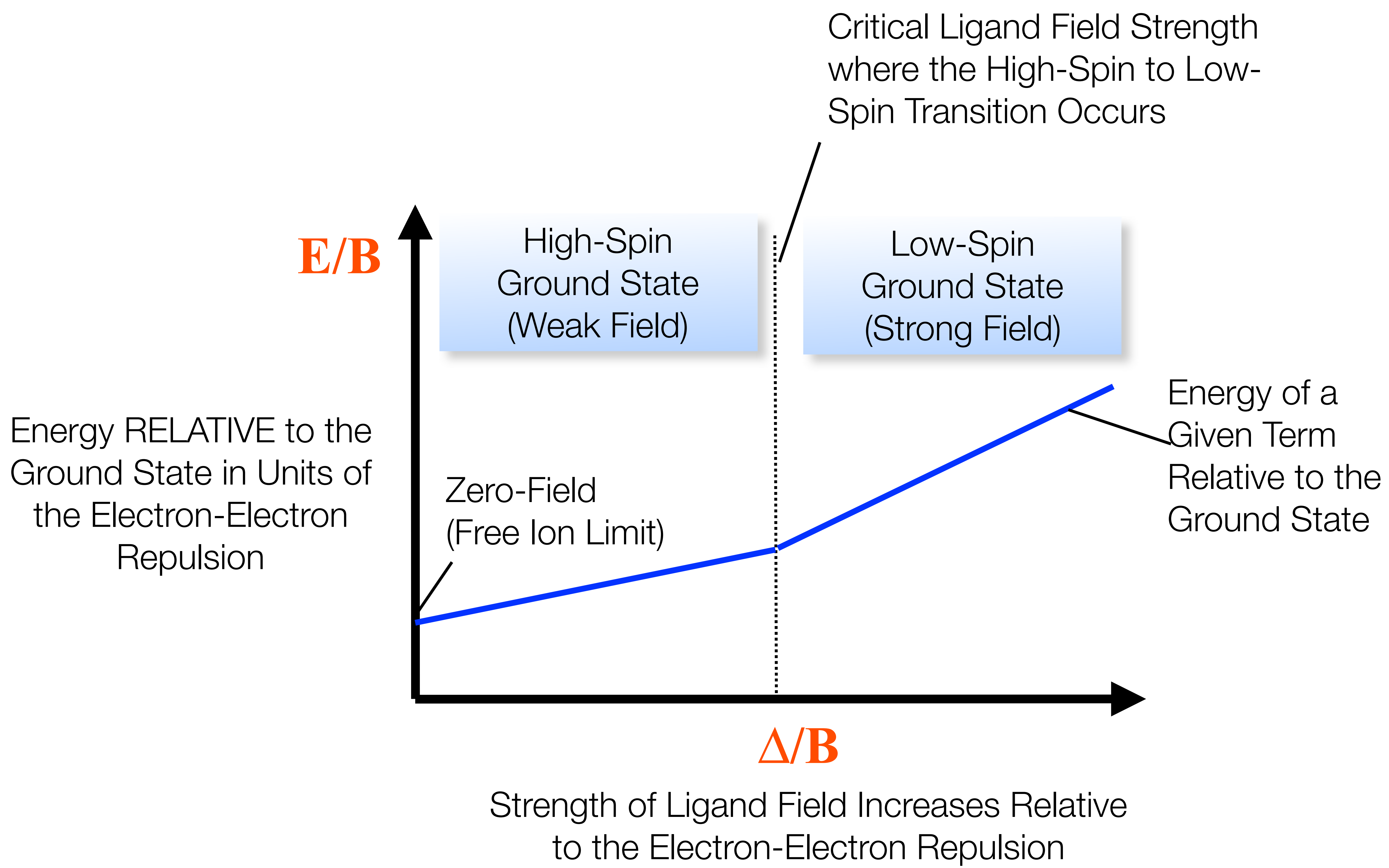
QUESTION: What determines the electron configuration?



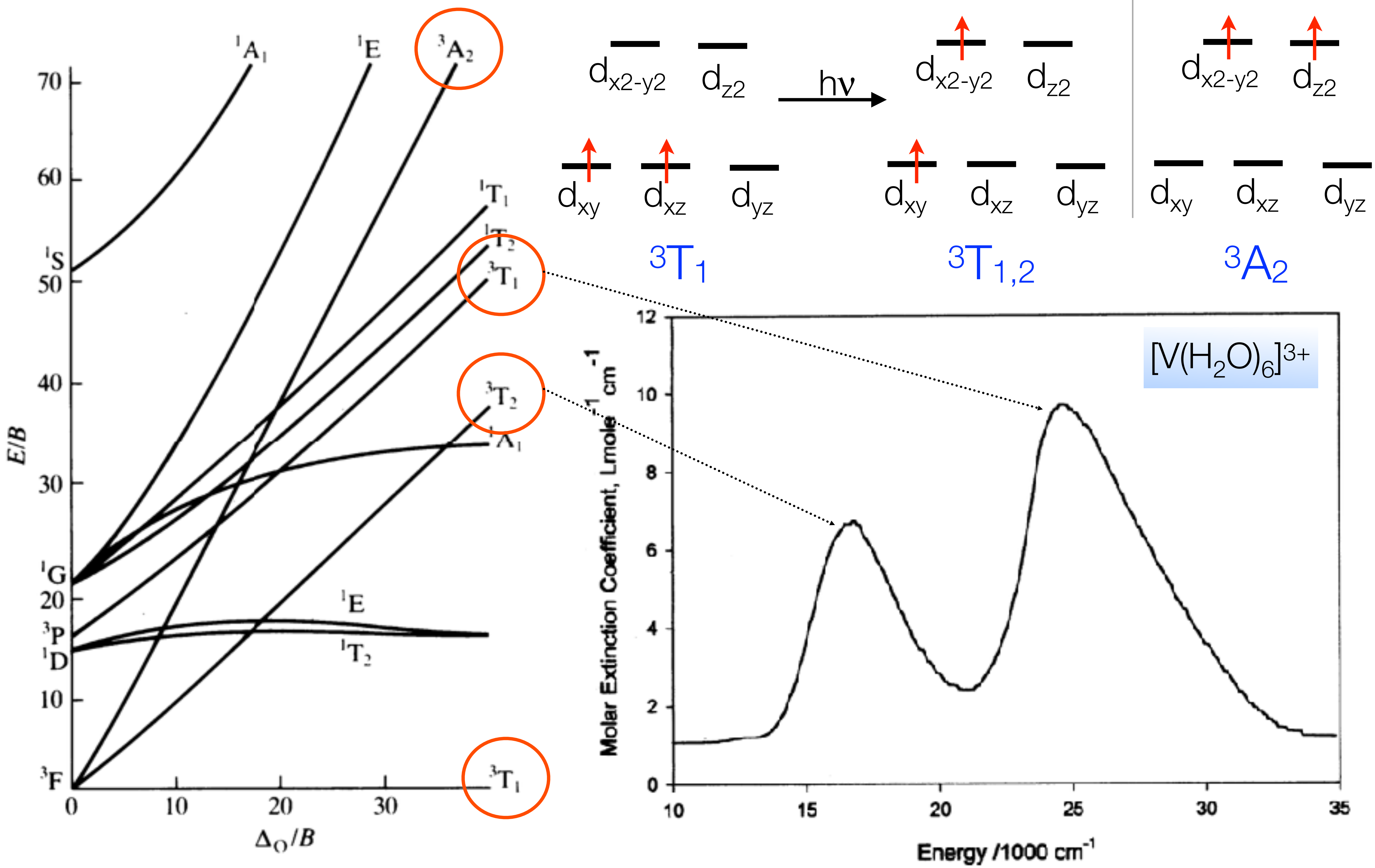
ANSWER: The balance of ligand field splitting and electron repulsion (‚**Spin-Pairing Energy**‘ P=f(B))



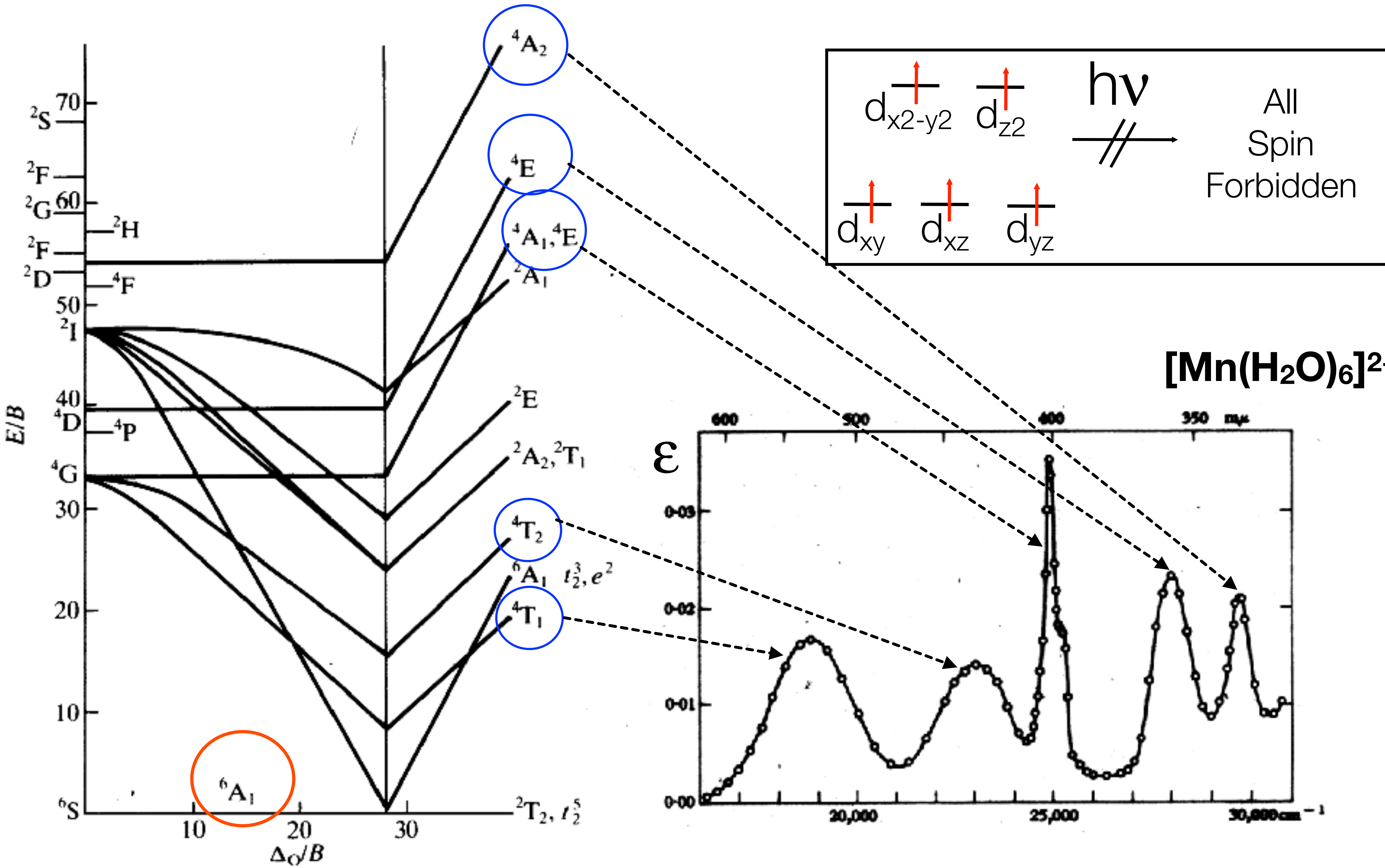
Inside Ligand Field Theory:Tanabe-Sugano Diagrams



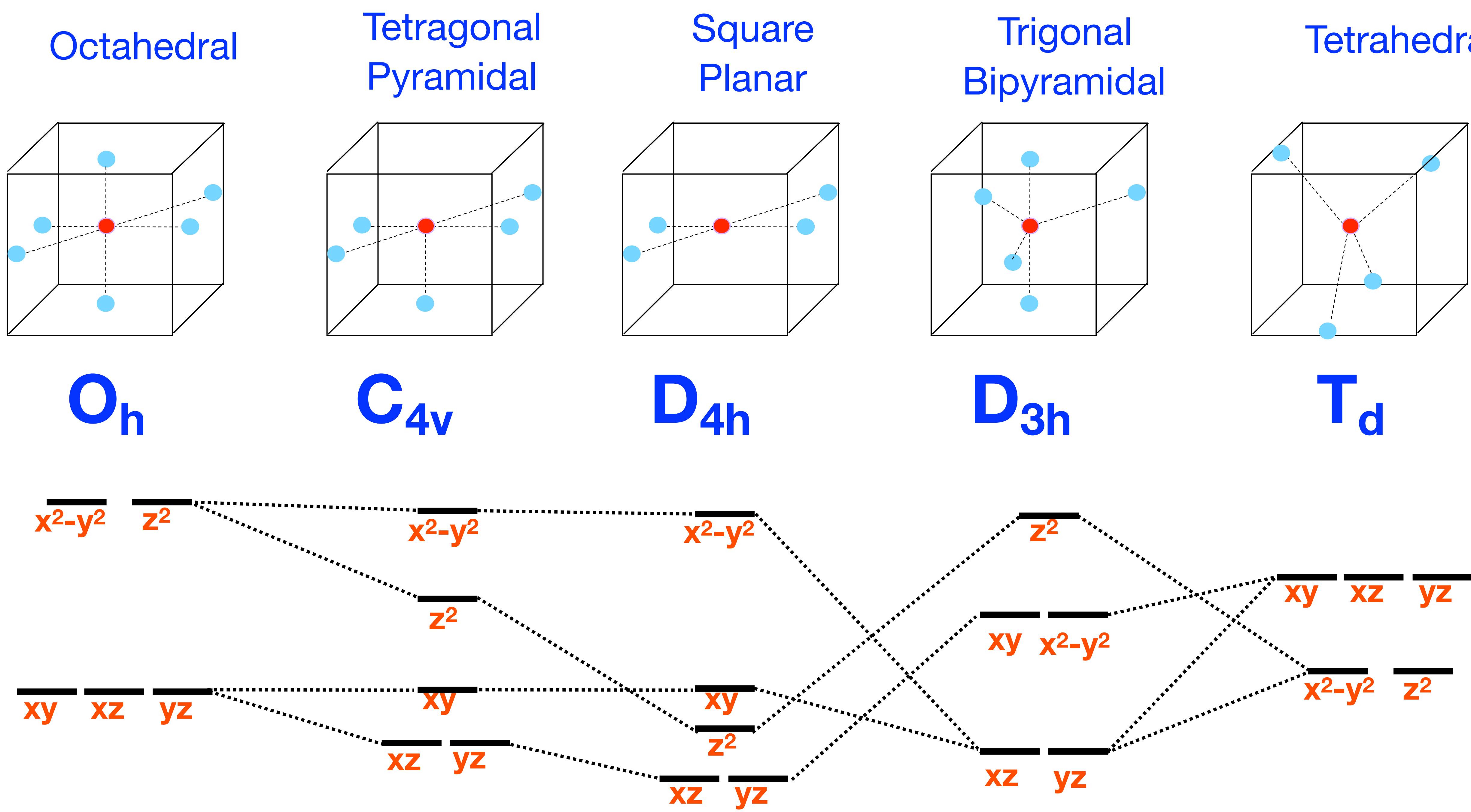
Optical Properties: d-d Spectra of d^2 Ions



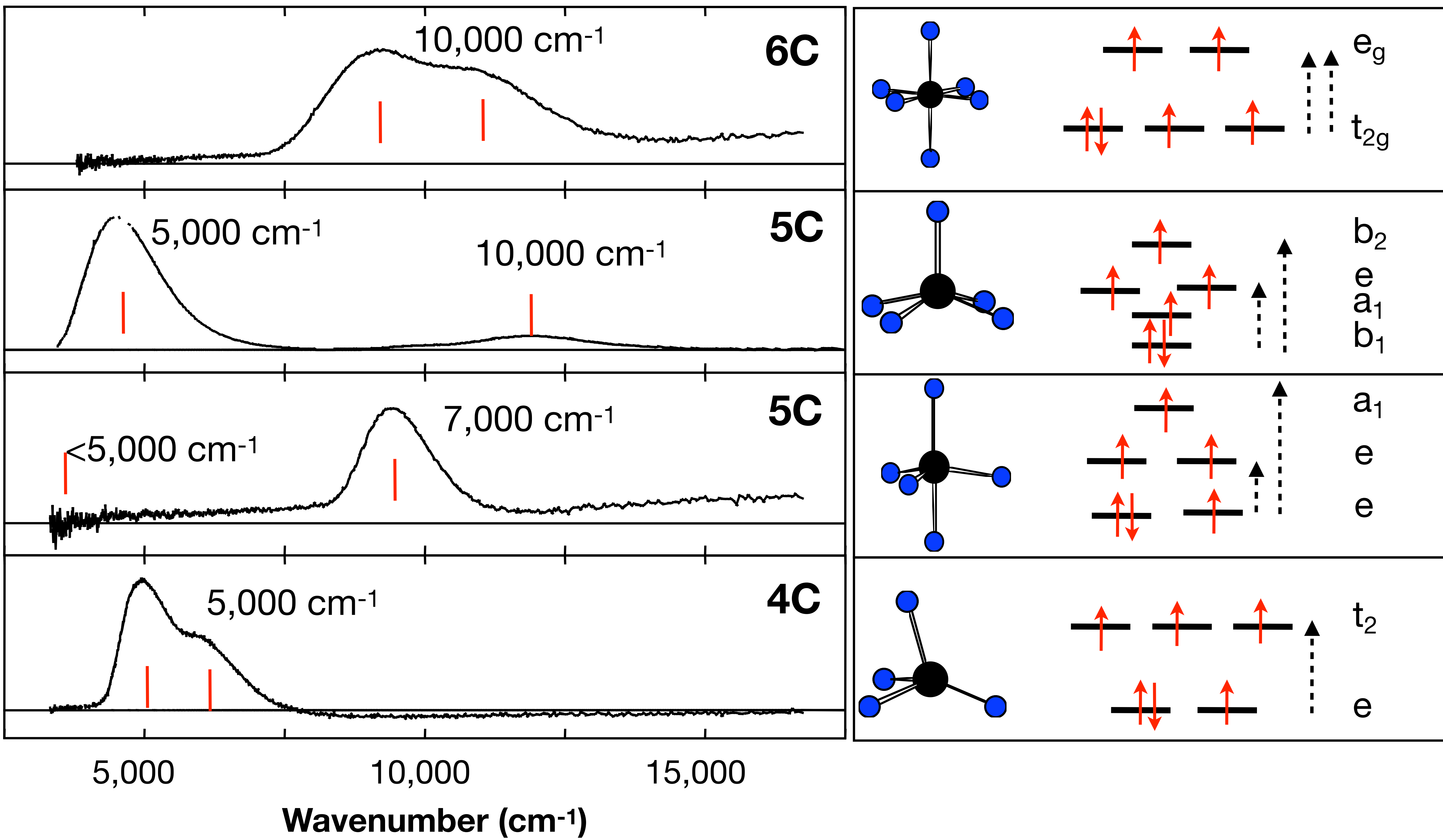
d-d Spectra of d5 Ions (Fe^{III}, Mn^{II})



Ligand Field Splittings in Different Coordination Geometries

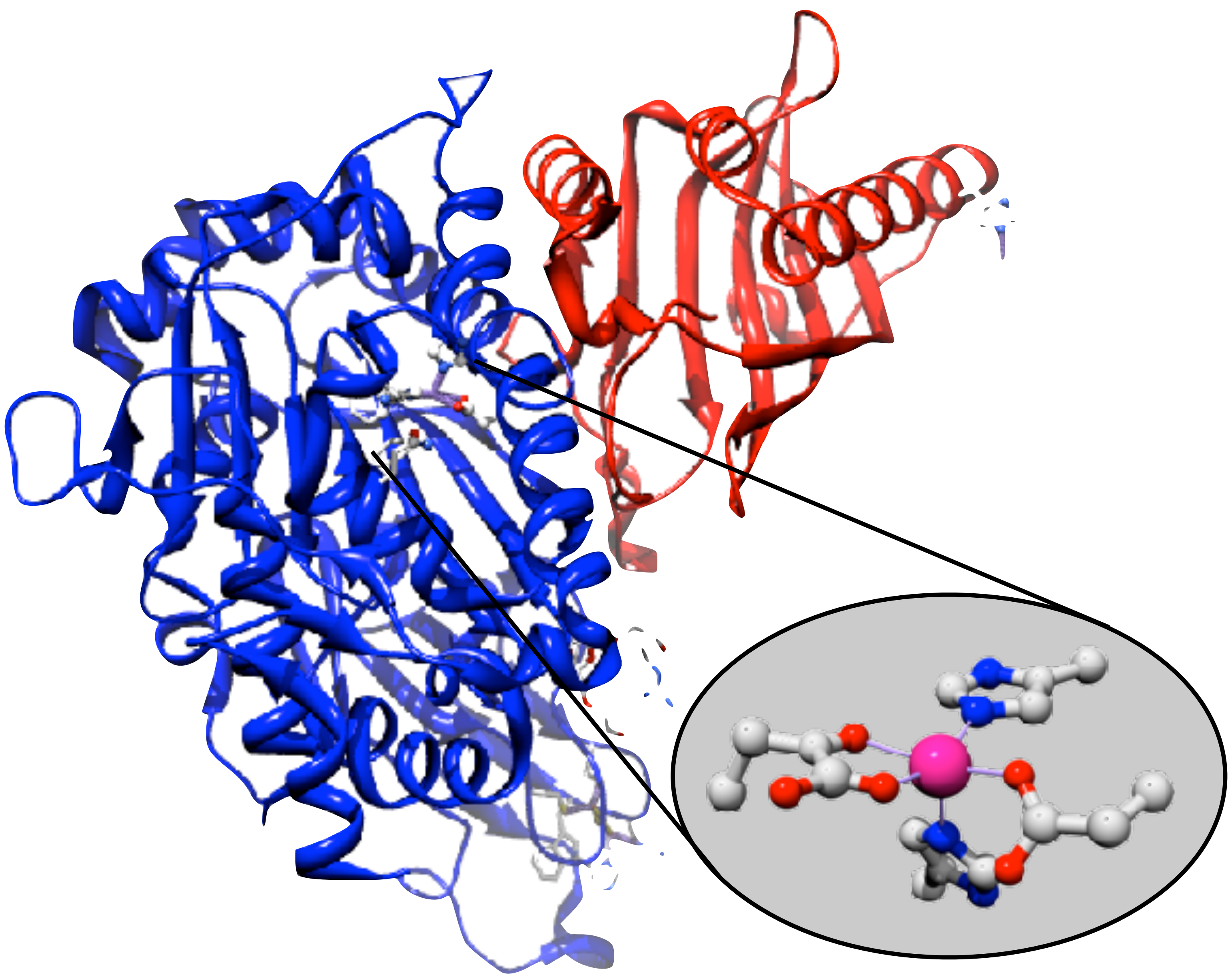


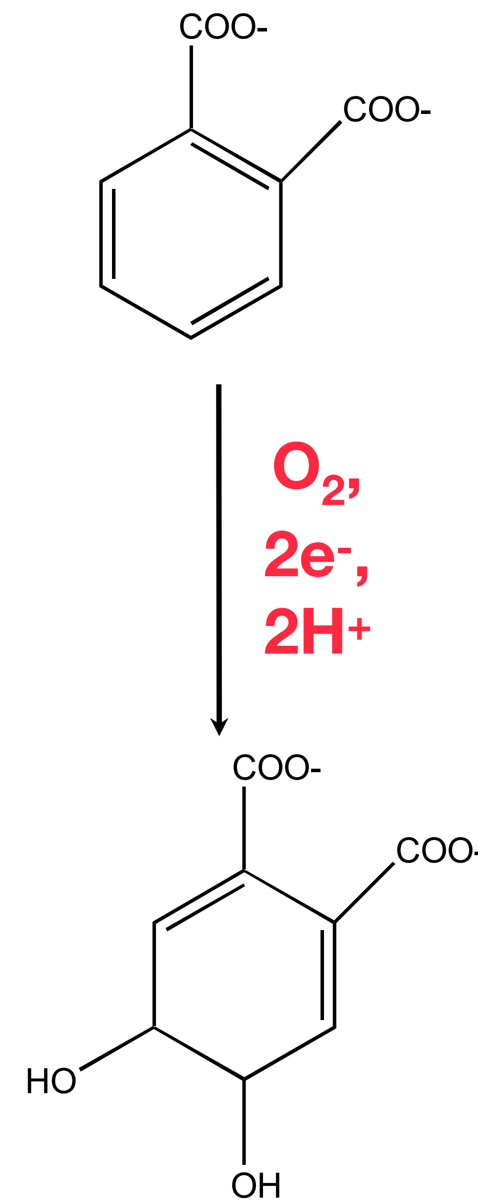
Coordnation Geometry and d-d Spectra: HS-Fe(II)



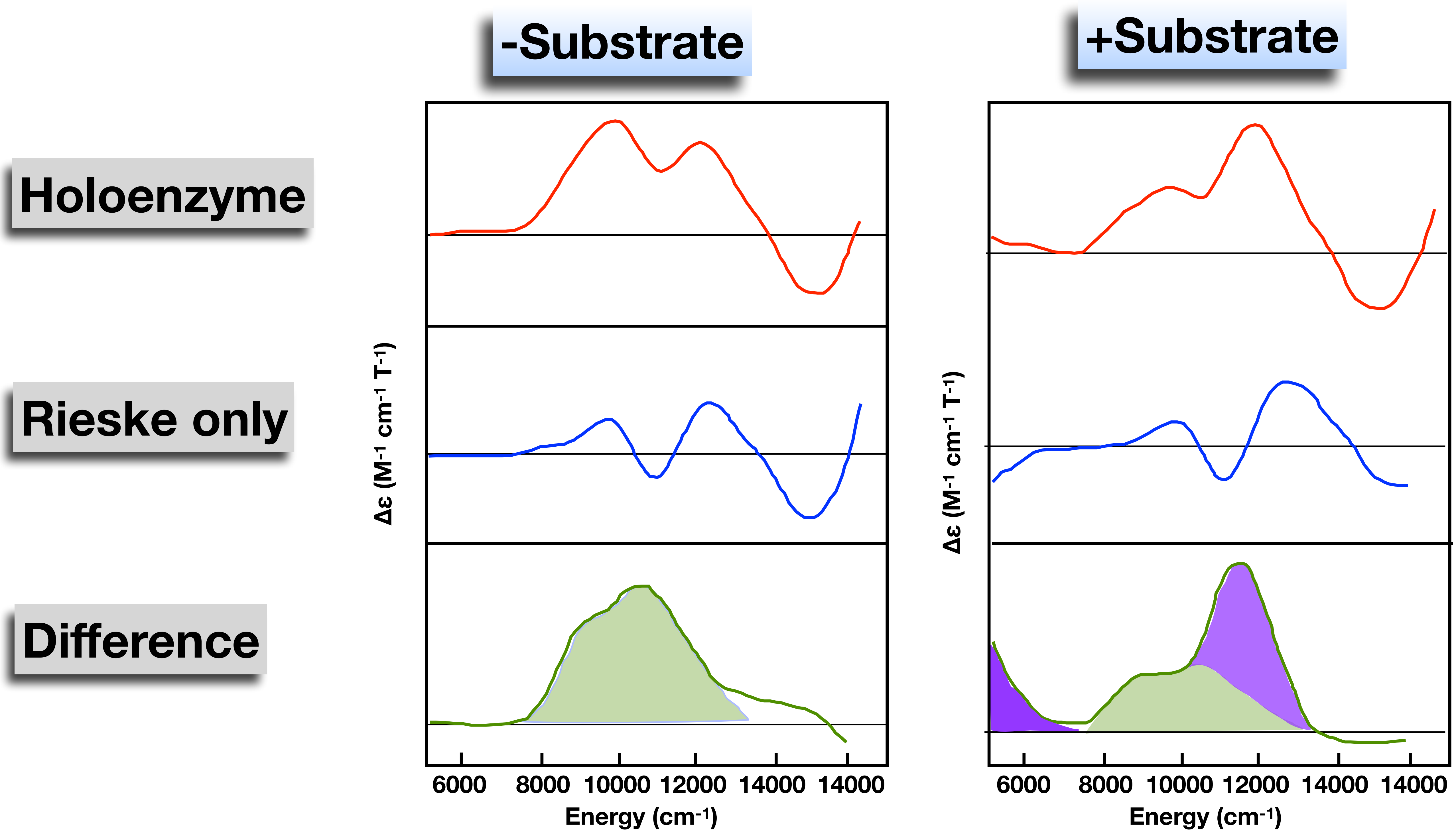
Studying Enzyme Mechanisms

Rieske-Dioxygenases



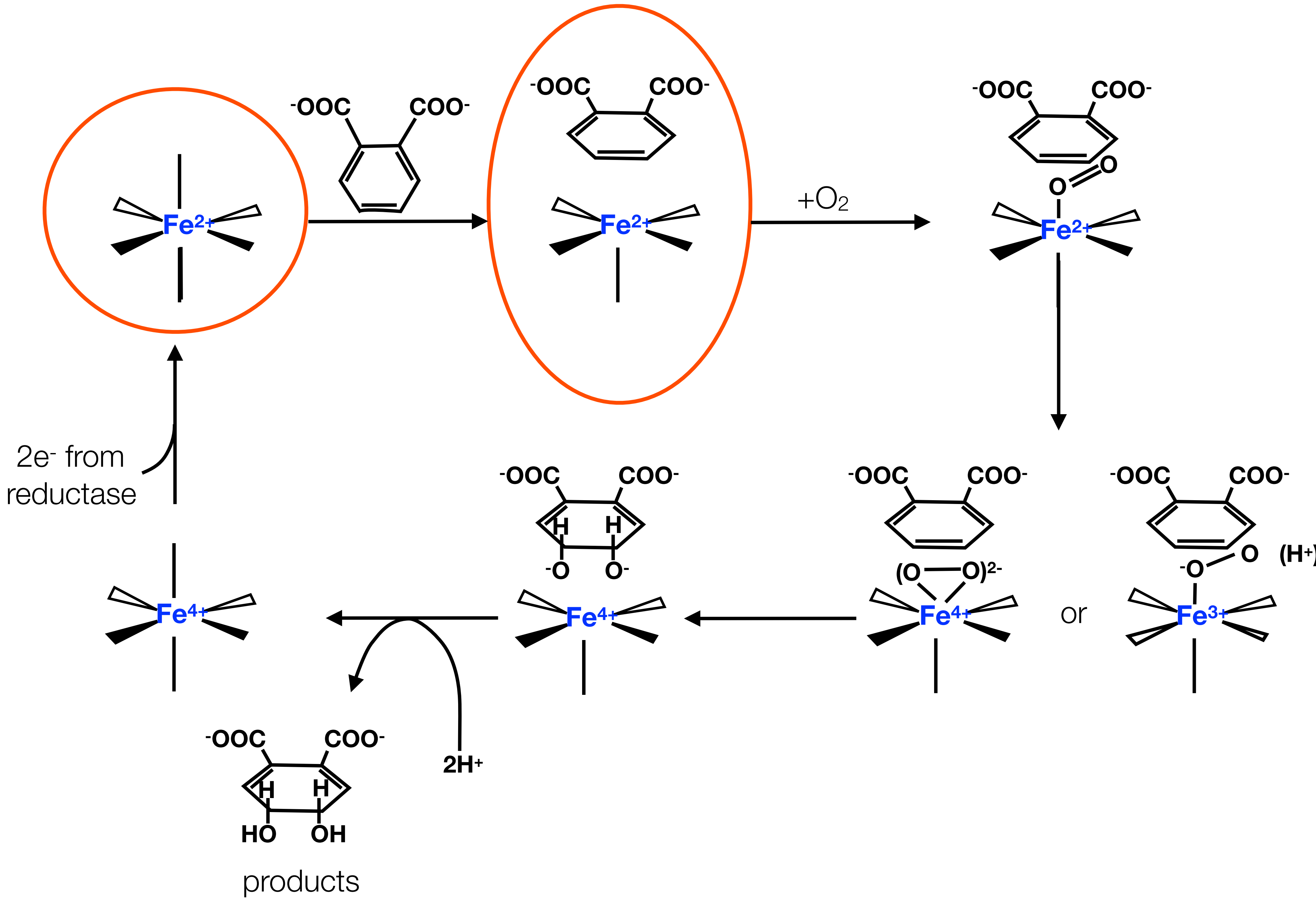


Active Site Geometry from d-d Spectra

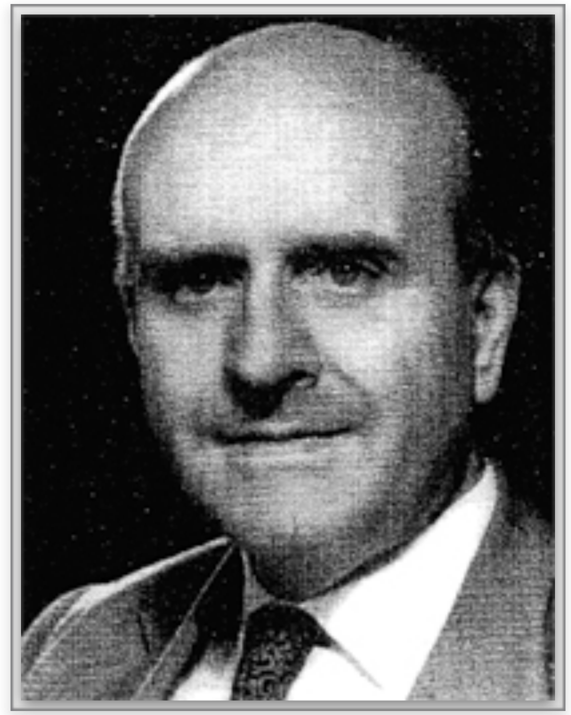


Solomon et al., (**2000**) *Chem. Rev.*, 100, 235-349

Mechanistic Ideas from Ligand Field Studies

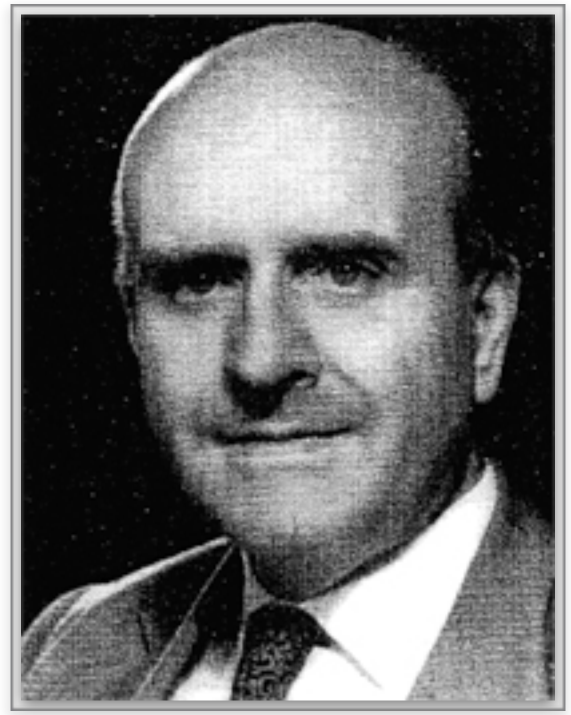


Solomon et al., (**2000**) *Chem. Rev.*, 100, 235-349



Christian Klixbüll Jörgensen

(1931-2001)



Christian Klixbüll Jörgensen

(1931-2001)

„Personally, I do not believe much of the electrostatic romantics, many of my colleagues talked about“

(C.K. Jörgensen, **1966** *Recent Progress in Ligand Field Theory*)

Failures of CFT…

J. OWEN
K. W. H. STEVENS

NATURE May 9, 1953 VOL. 171

Crystal of $[Ir(IV)Cl_6]^{4-}$ d^5 S=1/2 exhibited an EPR spectrum with complex hyperfine (no spectrum actually shown in orig. publication)

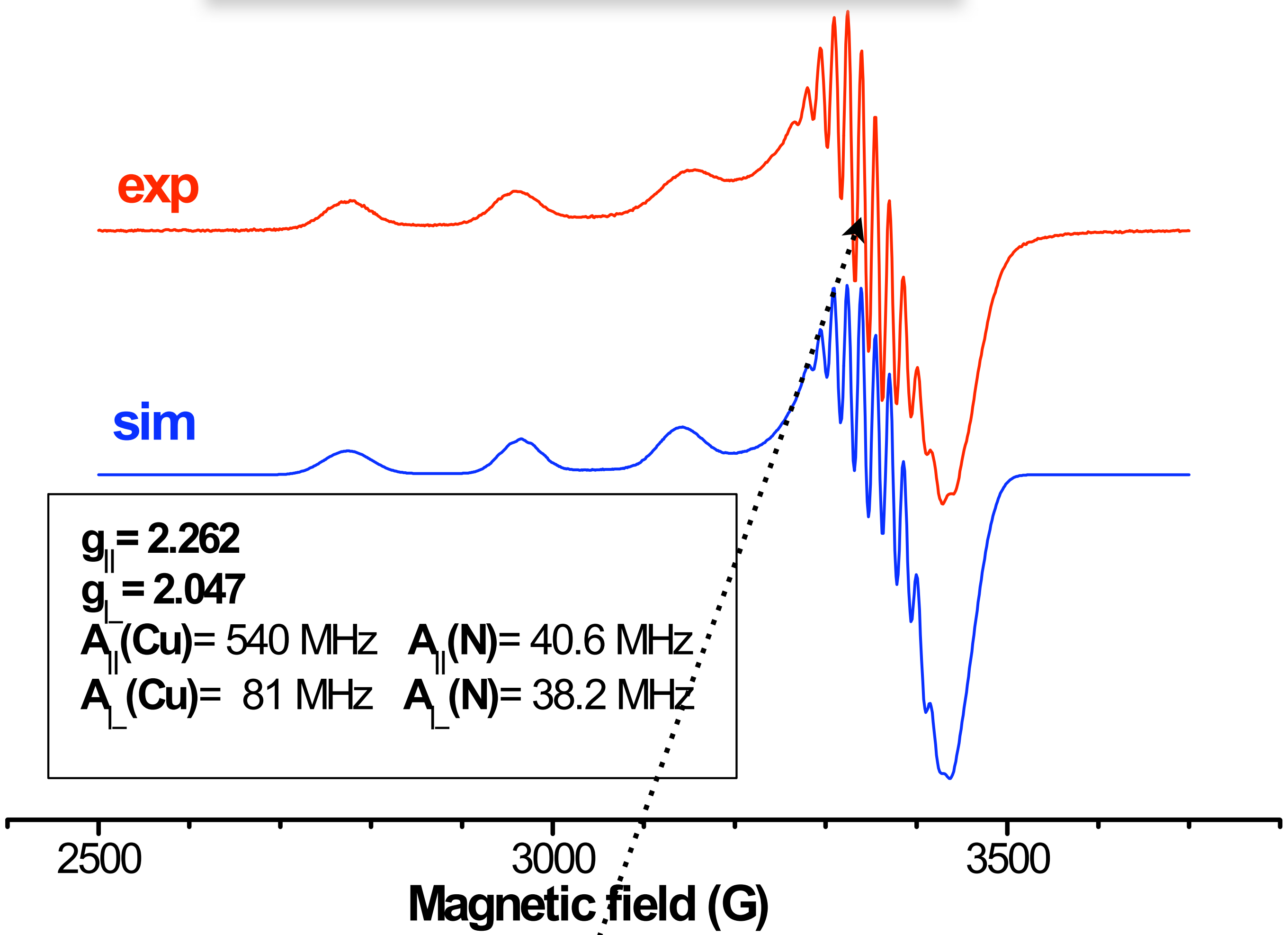
For Ir (I=3/2) 4 lines are expected, but many more observed. Must be due to additional hyperfine splitting due to I=3/2 chlorines ligands….

The experimental evidence in ammonium chloroiridate suggests that the magnetic hole is described by admixtures of $3p_\pi$ (Cl) orbitals with $5d_{xy}$, d_{yz}, d_{zx} (Ir) orbitals. This can also be pictured as a mechanism whereby for part of the time an electron is transferred from Cl^- to Ir^{4+}, cancelling the unpaired spin on the iridium, and leaving an unpaired spin on a chlorine atom.

Van Vleck's theory. From the measured size of the hyperfine structure, and from the observed value, $g = 1{\cdot}8$, we have tentatively estimated that the electron hole is on a particular chlorine atom for about 3 per cent of the time, and on some chlorine atom for about 18 per cent. The paramagnetic resonance method thus gives a direct and quantitative measure of π-bonding, or, crudely, of the whereabouts of the electron hole.

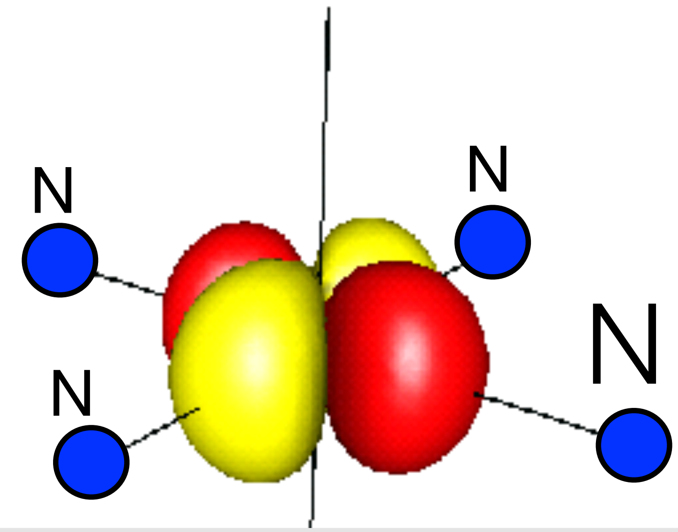
Experimental Proof of the Inadequacy of LFT

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



Clearly Observed Coupling Between The Unpaired Electron and the Nuclear Spin of Four ^{14}N Nitrogens (I=1)

Ligand Field Picture



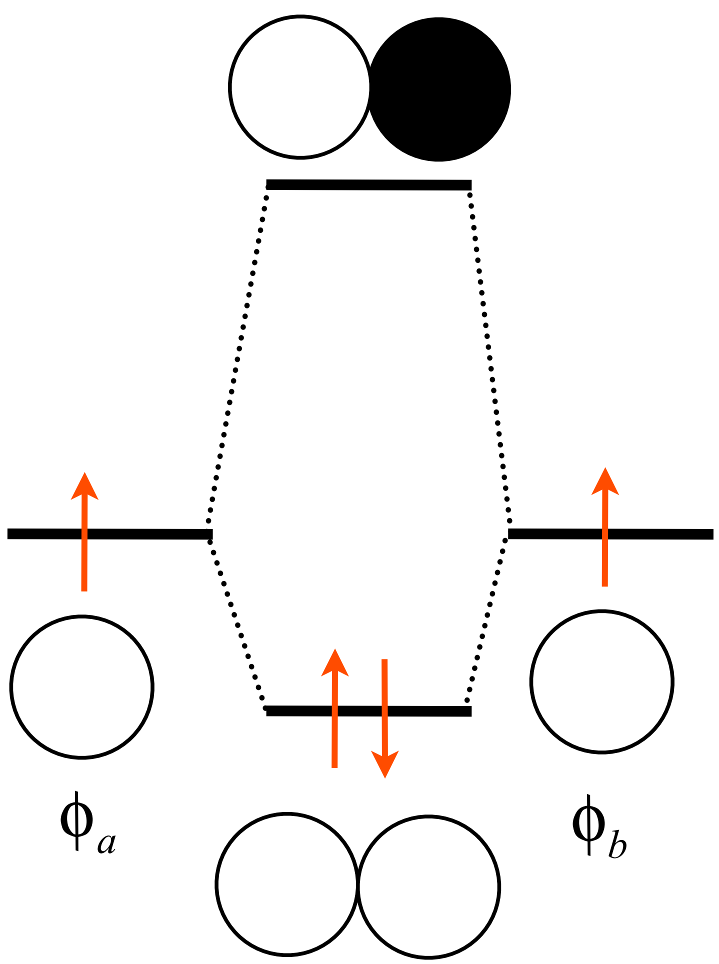
Wavefunction of the Unpaired Electron Exclusively Localized on the Metal

No Coupling Expected

Need a Refined Theory that Includes the Ligands Explicitly

Description of Bonds in MO Theory

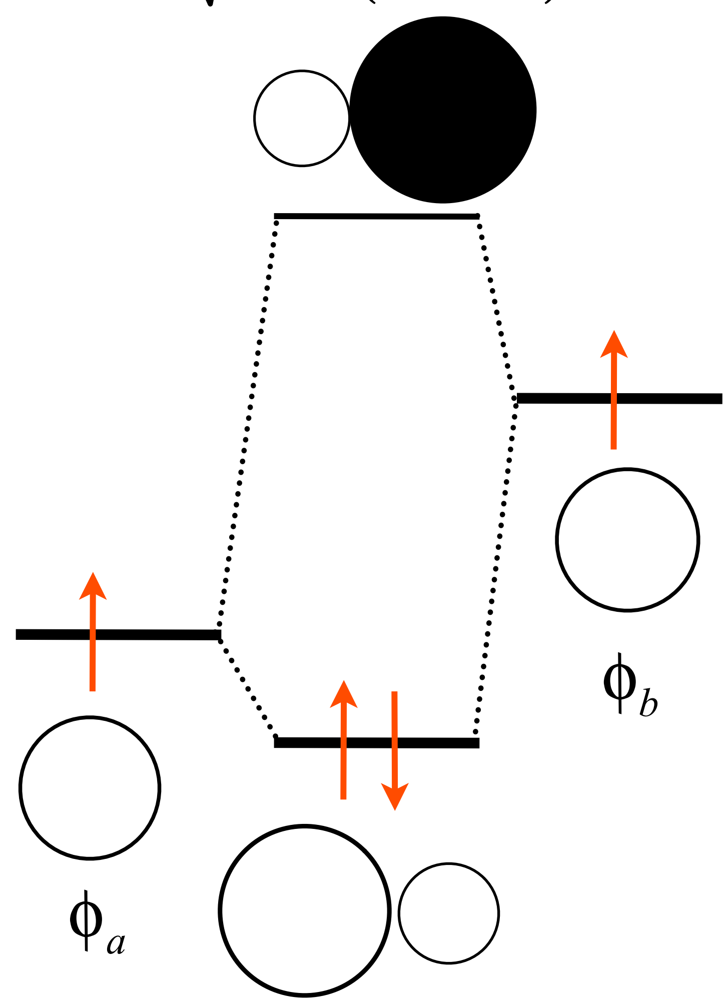
$$\frac{\phi_a - \phi_b}{\sqrt{2(1-S)}}$$



$$\frac{\phi_a + \phi_b}{\sqrt{2(1+S)}}$$

Homopolar Bond

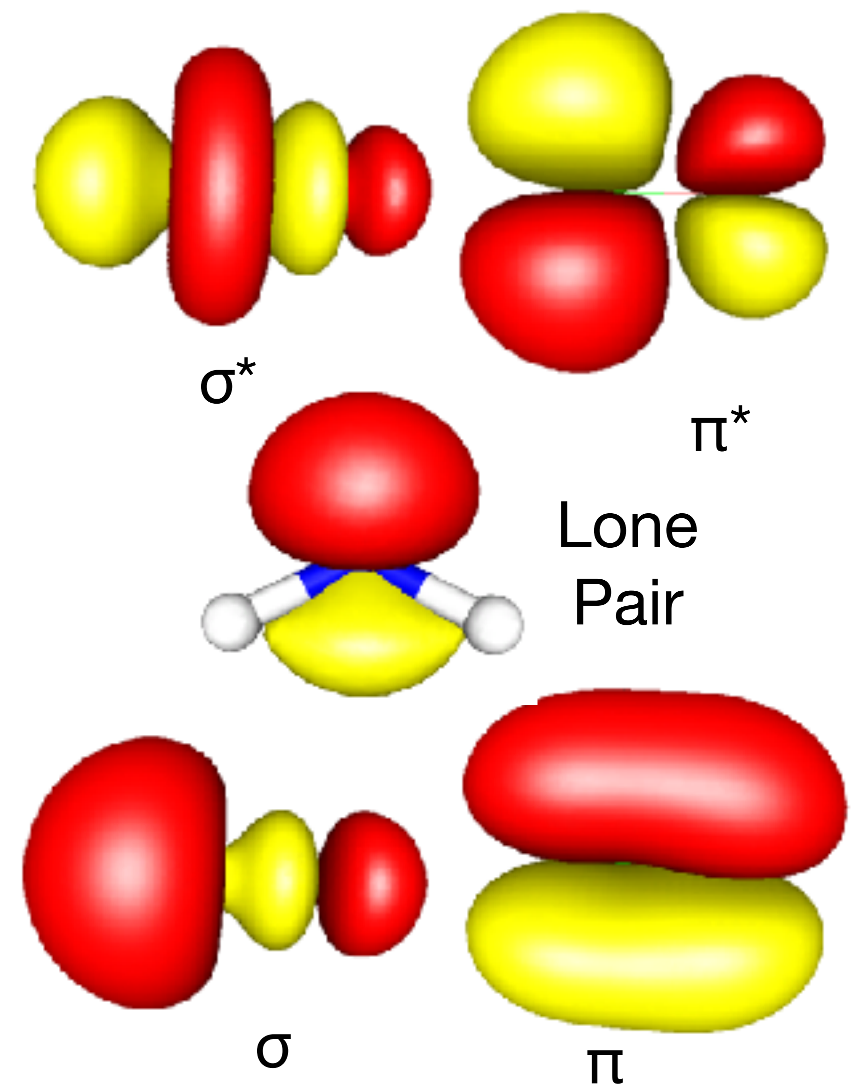
$$\frac{\lambda'\phi_a - \phi_b}{\sqrt{1+\lambda'(\lambda'-2S)}}$$



$$\frac{\phi_a + \lambda\phi_b}{\sqrt{1+\lambda(2S+\lambda)}}$$

Heteropolar Bond

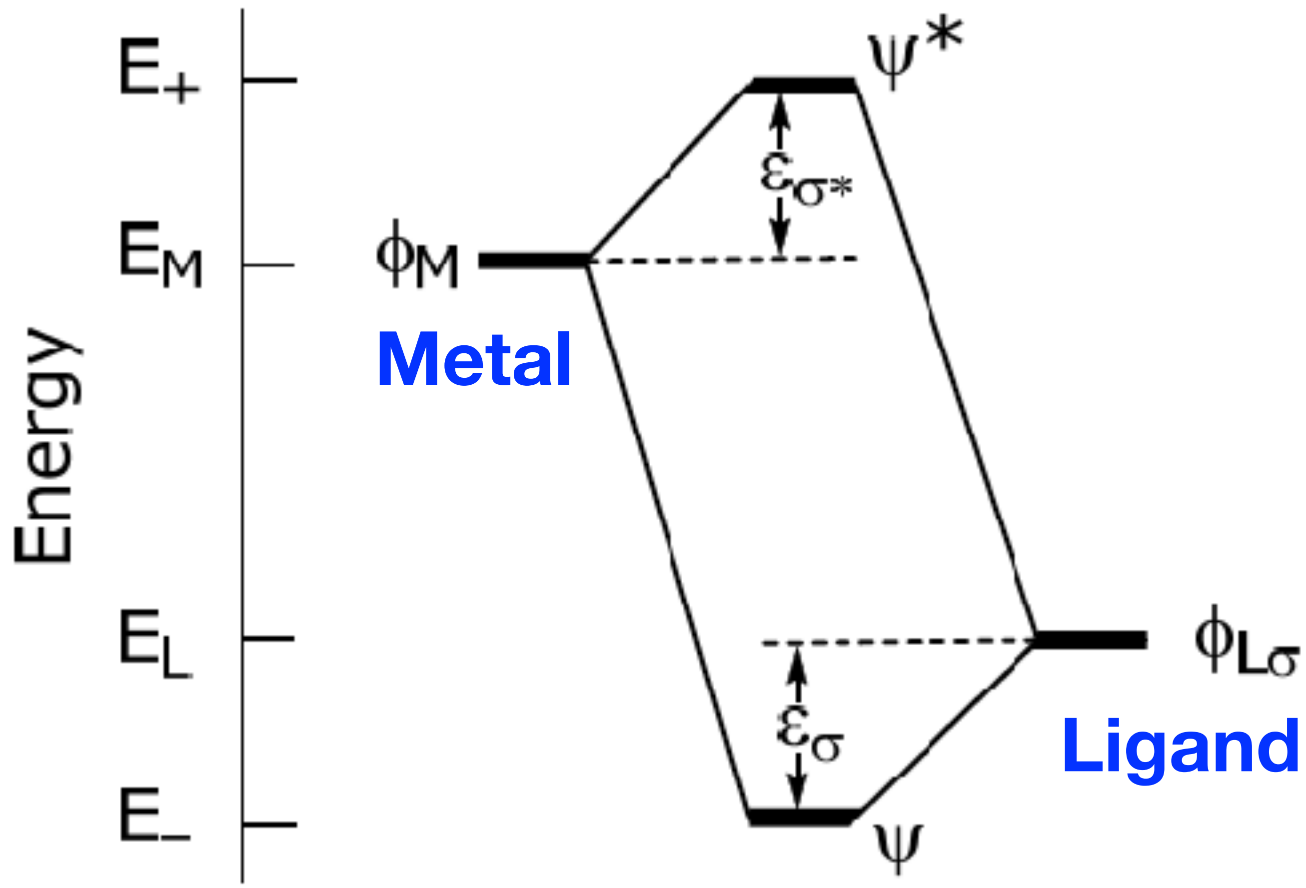
Types of MO's



Bond-Order:

$$B = \tfrac{1}{2}\left(N_B - N_A\right)$$

Rules for constructing MO diagrams…



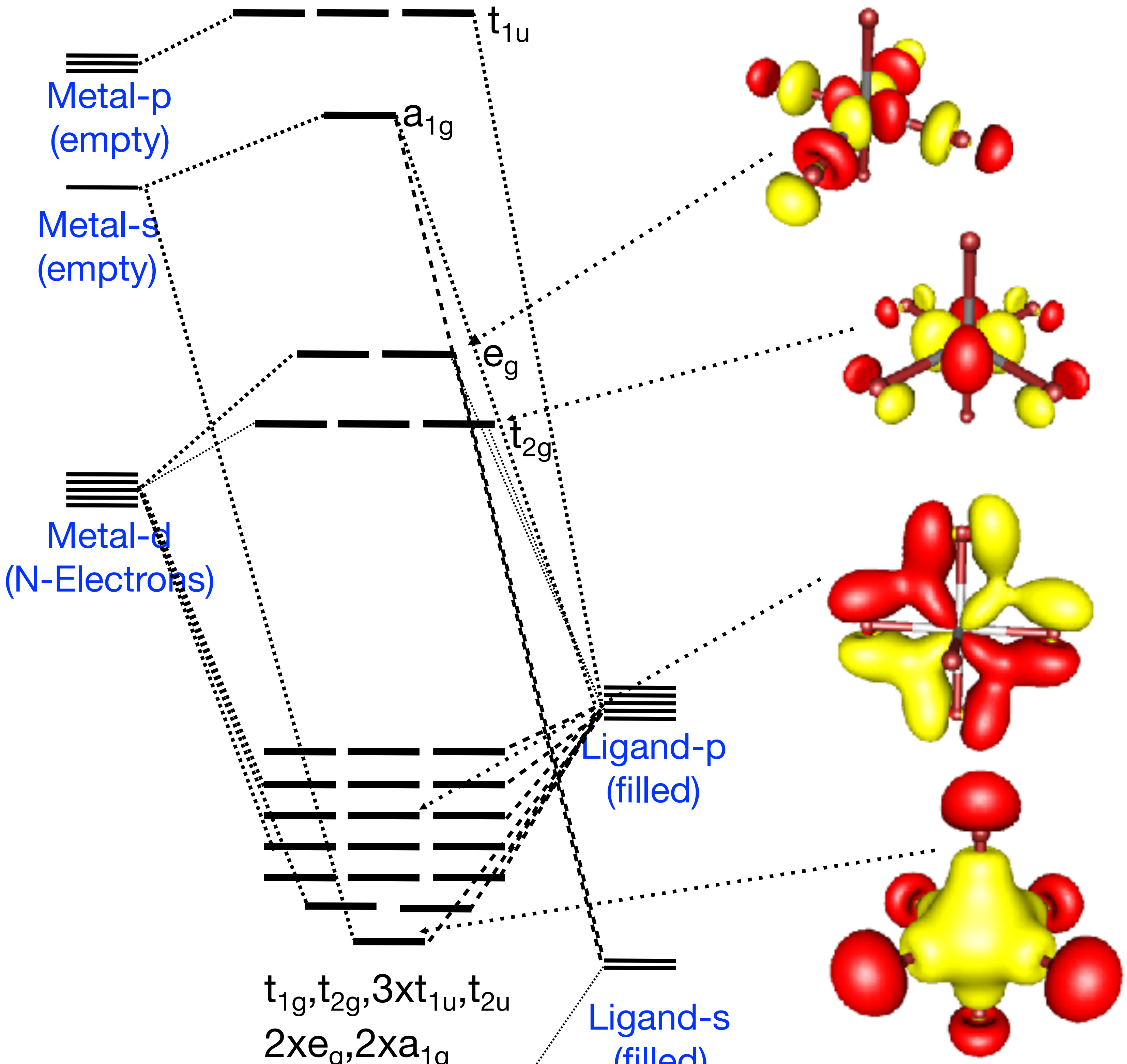
$$\varepsilon_{\sigma^*} \approx \frac{\beta^2}{\Delta E_{ML}} - \frac{\beta S_{ML}}{1 - S_{ML}^2}$$

$$\varepsilon_{\sigma} \approx -\frac{\beta^2}{\Delta E_{ML}}$$

$\beta \propto kS_{ML}$ „resonance integral“

- ✓ Metal-ligand orbital mixing is proportional to the **overlap** of the metal and ligand orbital (**S_{ML}**)
- ✓ Metal-ligand orbital mixing is inversely proportional to **energy difference** of mixing orbitals (i.e. **ΔE_{ML}**)

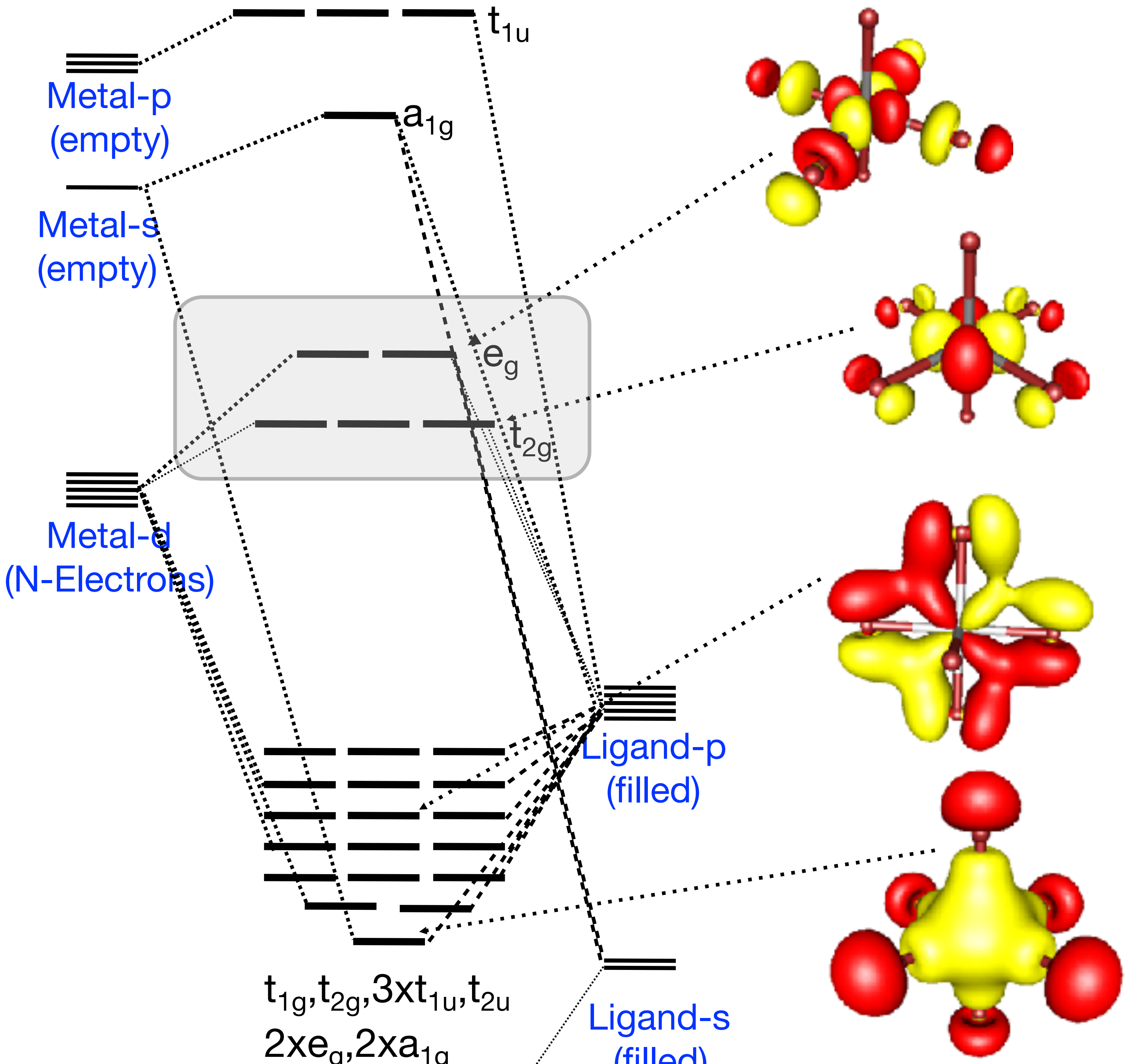
MO Theory of ML_6 Complexes



Key Points:

- Filled ligand orbitals are lower in energy than metal d-orbitals
- **The orbitals that are treated in LFT correspond to the anti-bonding metal-based orbitals in MO Theory**
- Through bonding some electron density is transferred from the ligand to the metal
- The extent to which this takes place defines the covalency of the M-L bond

MO Theory of ML_6 Complexes

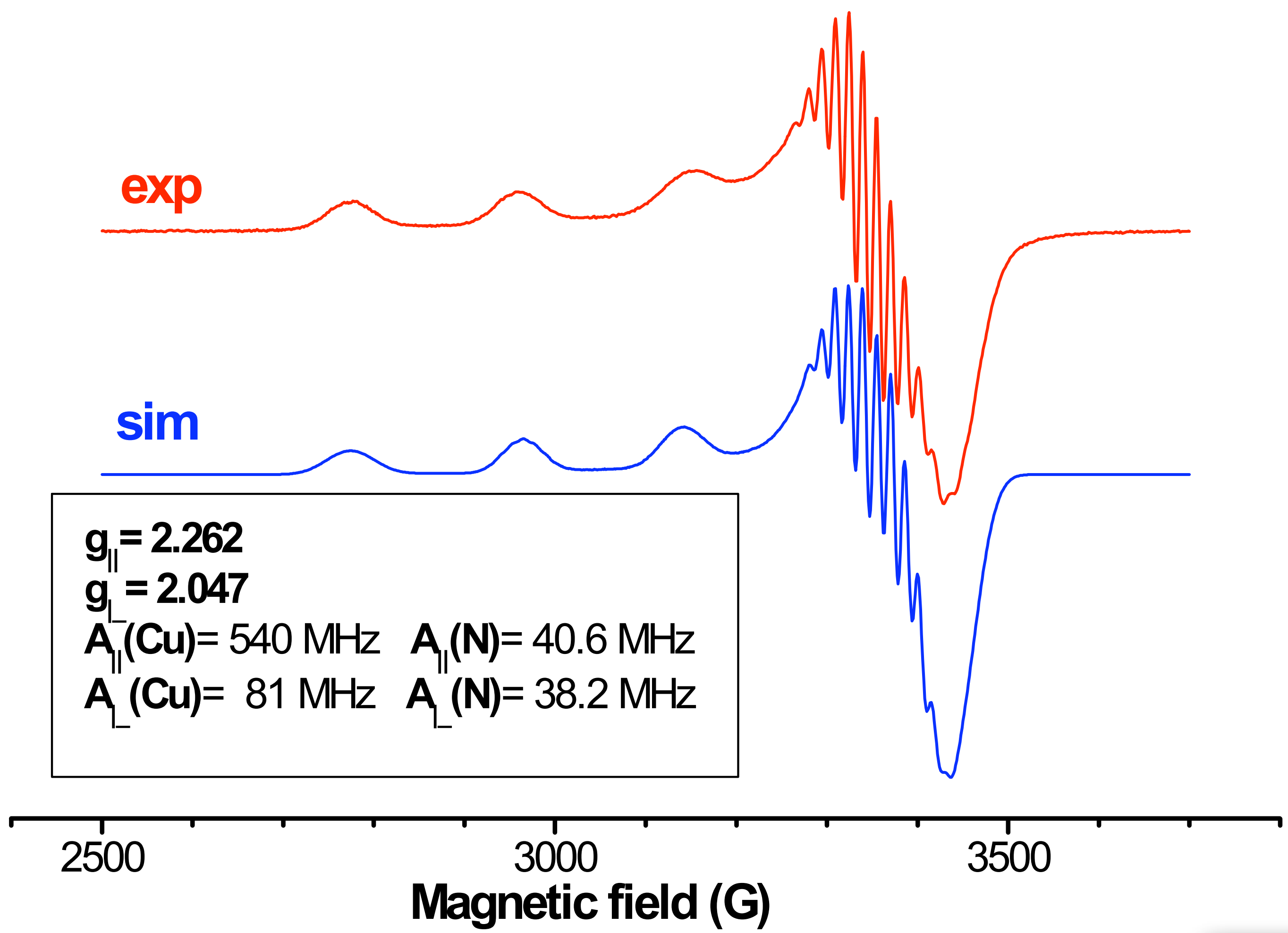


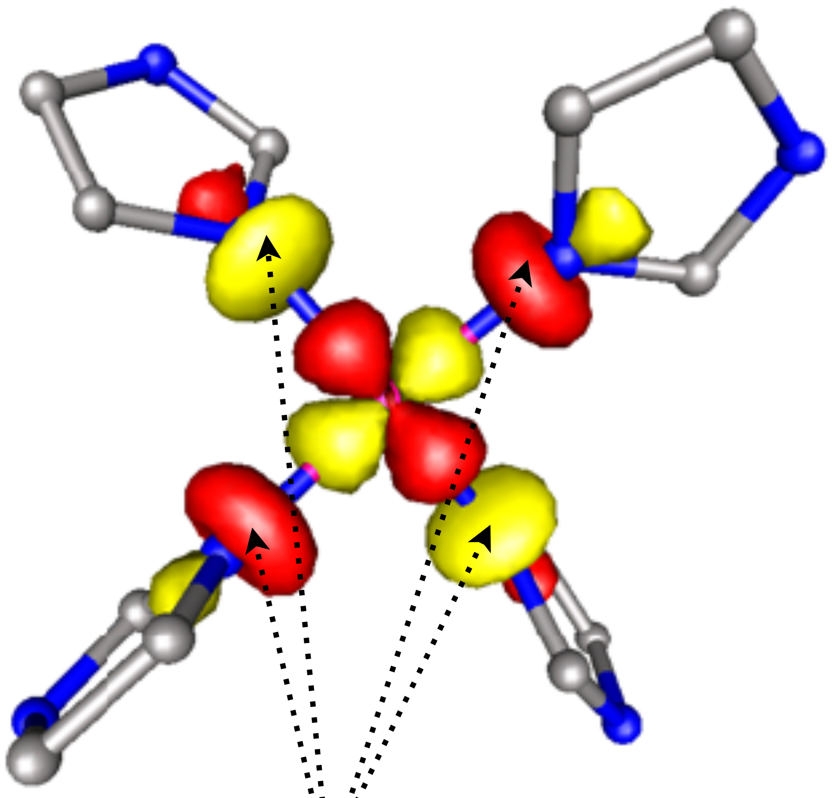
Key Points:

- Filled ligand orbitals are lower in energy than metal d-orbitals
- **The orbitals that are treated in LFT correspond to the anti-bonding metal-based orbitals in MO Theory**
- Through bonding some electron density is transferred from the ligand to the metal
- The extent to which this takes place defines the covalency of the M-L bond

MO Theory and Covalency

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



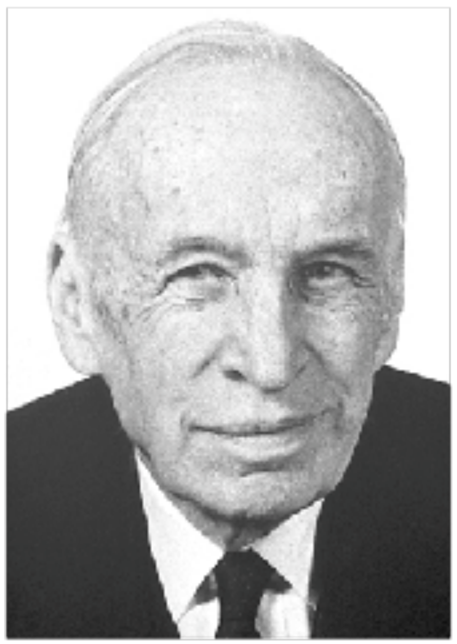


The Unpaired Electron is Partly Delocalized Onto the Ligands

Magnetic Coupling Expected

1. Theory Accounts for Experimental Facts
2. Can Make Semi-Quantitative Estimate of the Ligand Character in the SOMO

Ligand Field Theory (LFT)



John H. van Vleck
(1935)

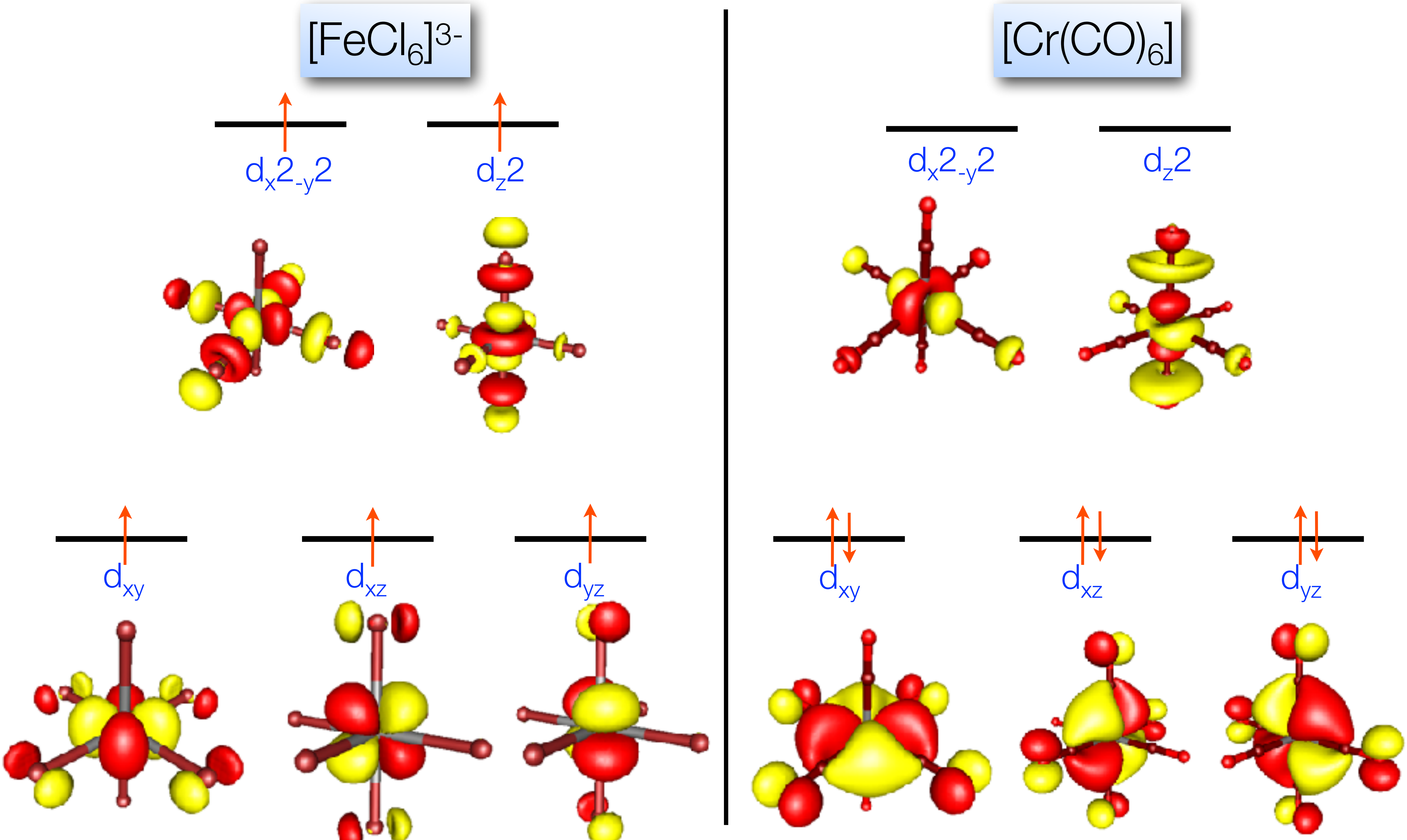
✳LFT combines principles laid out in CFT with molecular orbital theory

✳ Accounts for the *nature* of the ligand donor properties

✳Relies on **symmetry** and **covalency** to form sigma, pi and delta bonds

"In 1935 I published a paper in which I amplified and generalized…the primitive crystal field theory… I showed that Bethe's grouping of energy levels according to symmetry type was still valid even if one allowed the electrons in the unclosed shells to wander away sometimes from the central paramagnetic ion and take a look at the diamagnetic atoms clustered around it." - J.H. van Vleck's, Nobel Prize Address (1977)

π-Bonding and π-Backbonding



Interpretation of the Spectrochemical Series

$I^- < S^{2-} < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^- < CO \sim NO < NO^+$

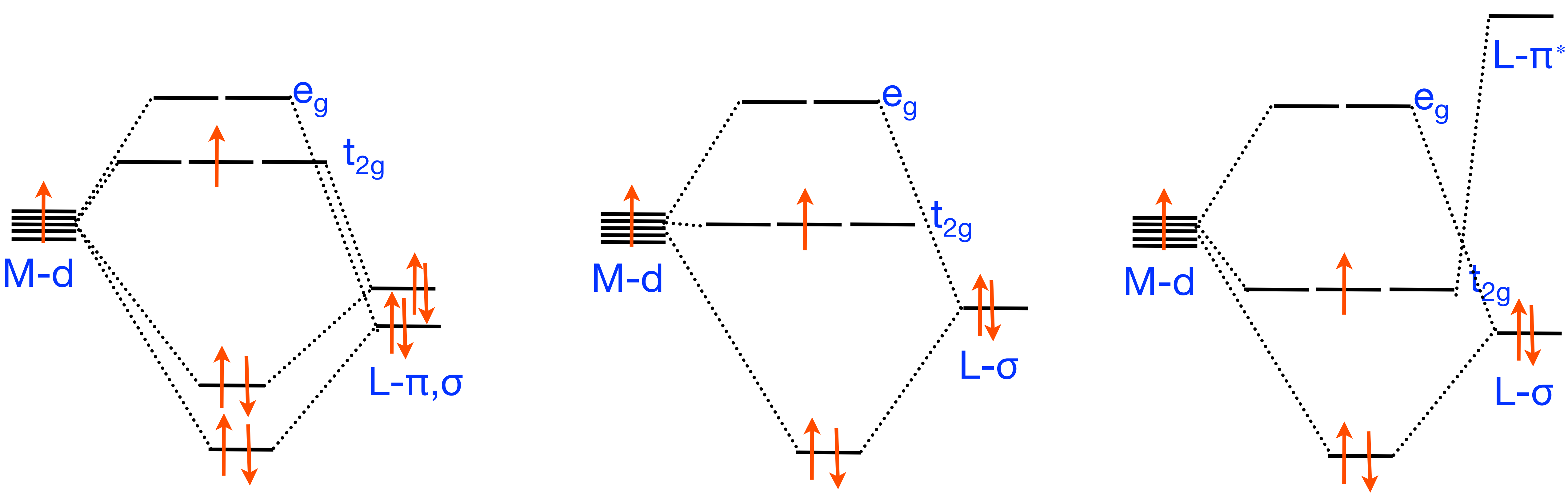
Δ SMALL

Δ LARGE

π-DONOR

π-'NEUTRAL'

π-ACCEPTOR



Oxidation States, Calculations and Chemical Thinking

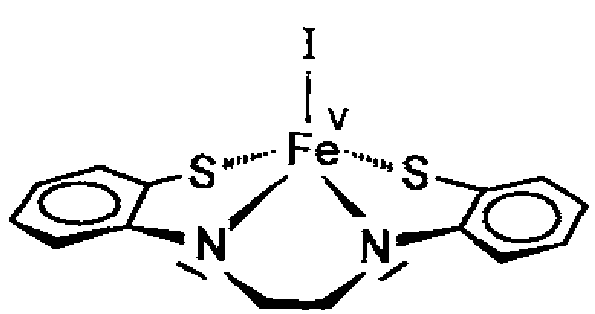
Physical versus Formal Oxidation States

The **formal oxidation state** of a metal ion in a complex is the d^N configuration that arises upon dissociating all ligands in their closed shell „standard“ states taking into account the total charge of the complex

The **physical oxidation state** of a metal ion in a complex is the d^N configuration that arises from an analysis of its electronic structure by means of spectroscopic measurements and molecular orbital calculations

Chaudhuri, P.; Verani, C.N.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.*, **2001**, 123, 2213 *„The Art of Establishing Physical Oxidation States in Transition-Metal Complexes Containing Radical Ligands “*. However, The concept goes back to CK Jörgensen

- ★ The two often coincide but may well be different! In the example before, the formal oxidation state is Ni(IV) but the physical oxidation state is Ni(II)



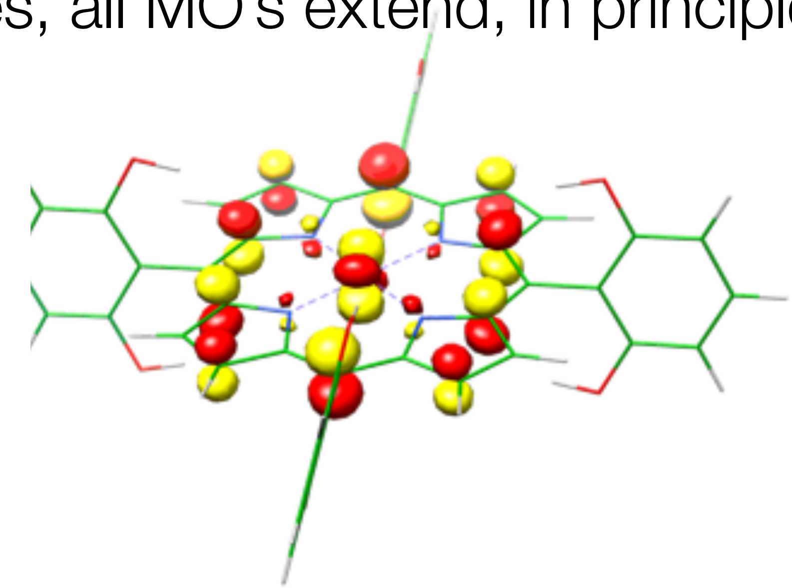
2

This complex has first been described by its formal oxidation state of Fe(V) but has a physical oxidation of Fe(III)

Chlopek, C. *et al. Chem. Eur. J.* **2007**, 13, 8390

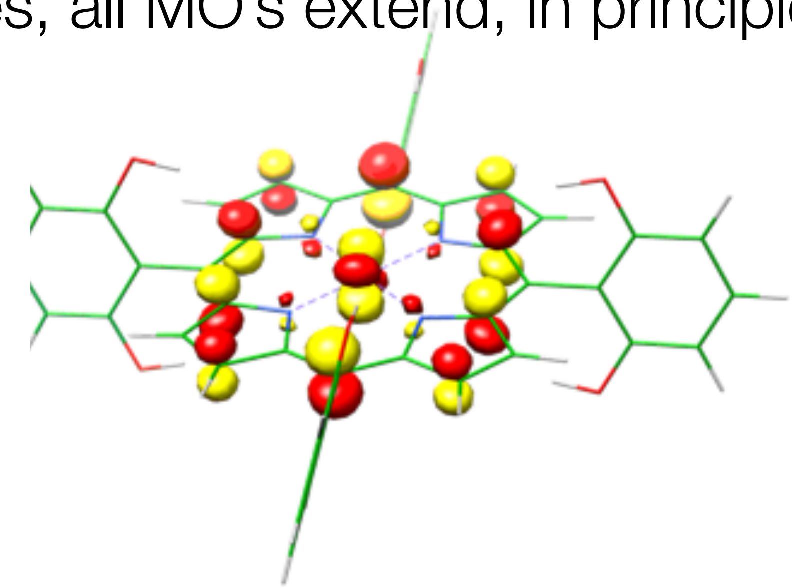
Oxidation States and MO Theory

In Molecular Orbital theories, all MO’s extend, in principle over the whole molecule



Oxidation States and MO Theory

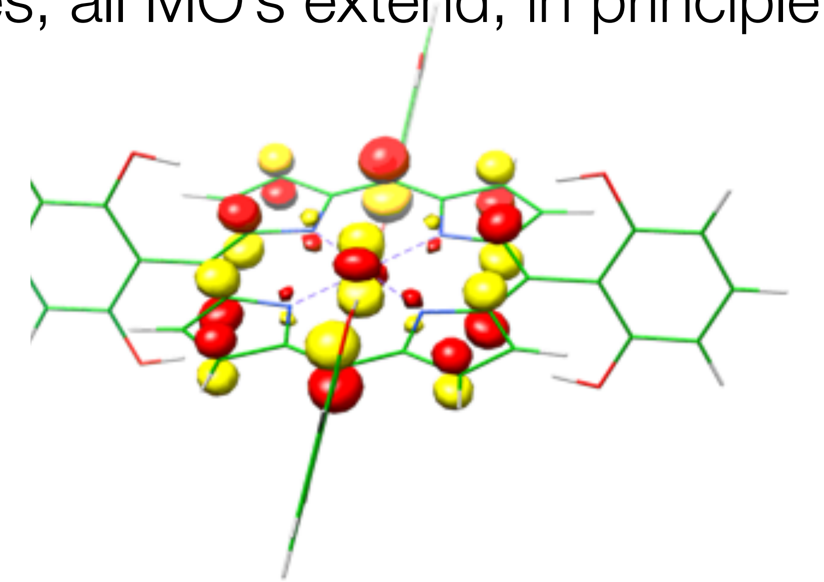
In Molecular Orbital theories, all MO's extend, in principle over the whole molecule



The concept of the oxidation state rests on the idea that one can „count“ d-electrons

Oxidation States and MO Theory

In Molecular Orbital theories, all MO’s extend, in principle over the whole molecule



The concept of the oxidation state rests on the idea that one can „count“ d-electrons

So, what does an oxidation state mean in a MO context?

(Pragmatic) Assignment of Oxidation States

- Analyze the occupied orbitals of the compound and determine the fractional d-character of the orbitals
  (In ***ORCA*** this is possible via the `NormalPrint`, `Localize` or `UNO` keywords)

(Pragmatic) Assignment of Oxidation States

- Analyze the occupied orbitals of the compound and determine the fractional d-character of the orbitals
  (In ***ORCA*** this is possible via the `NormalPrint, Localize` or `UNO` keywords)

- Orbitals that are centered more than, ***say***, 70% on the metal are counted as pure metal d-orbitals

(Pragmatic) Assignment of Oxidation States

- Analyze the occupied orbitals of the compound and determine the fractional d-character of the orbitals
  (In ***ORCA*** this is possible via the `NormalPrint, Localize` or `UNO` keywords)

- Orbitals that are centered more than, ***say***, 70% on the metal are counted as pure metal d-orbitals

- Count the number of electrons in such metal based orbitals. This gives you the **d^N configuration**

(Pragmatic) Assignment of Oxidation States

- Analyze the occupied orbitals of the compound and determine the fractional d-character of the orbitals
  (In *ORCA* this is possible via the `NormalPrint, Localize` or `UNO` keywords)

- Orbitals that are centered more than, ***say***, 70% on the metal are counted as pure metal d-orbitals

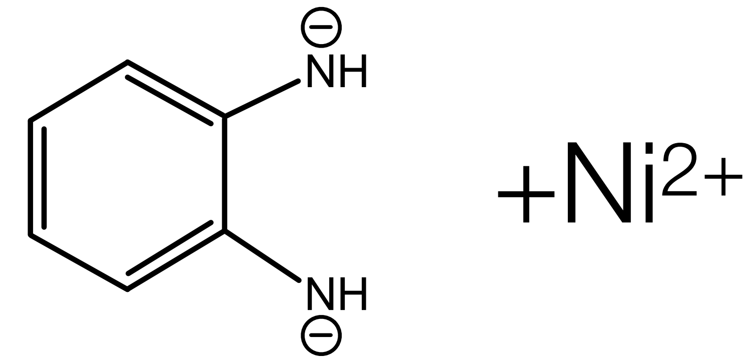
- Count the number of electrons in such metal based orbitals. This gives you the **d^N configuration**

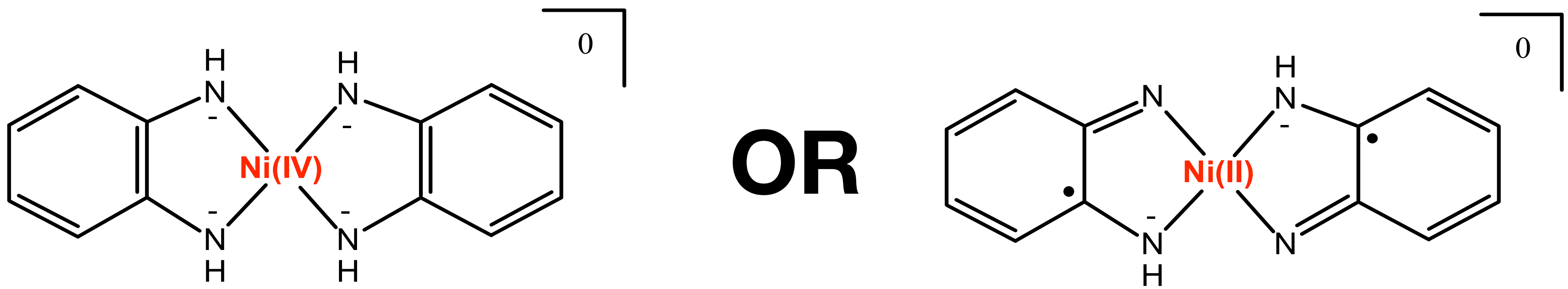
- The **local spin state** on the metal follows from the singly occupied metal-based orbitals

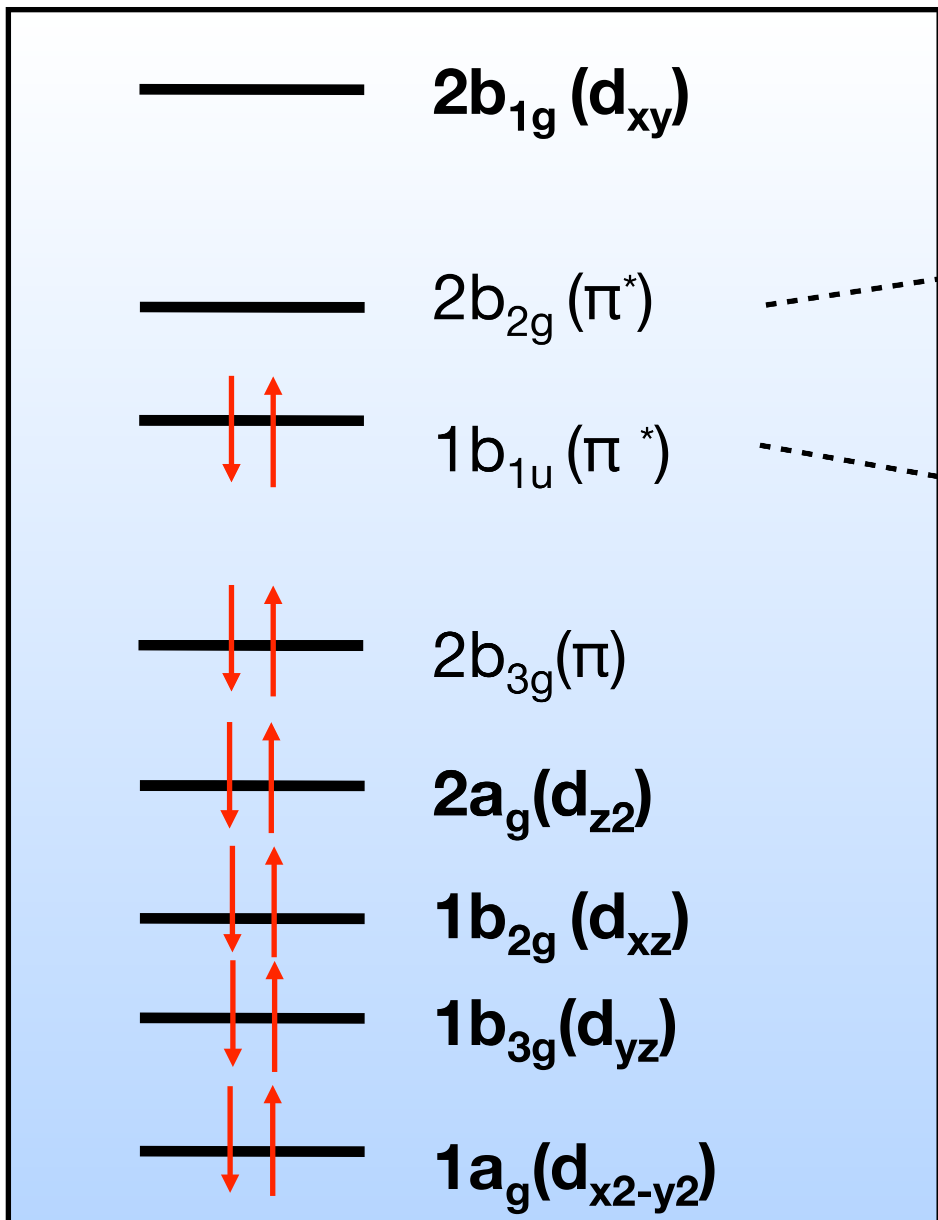
(Pragmatic) Assignment of Oxidation States

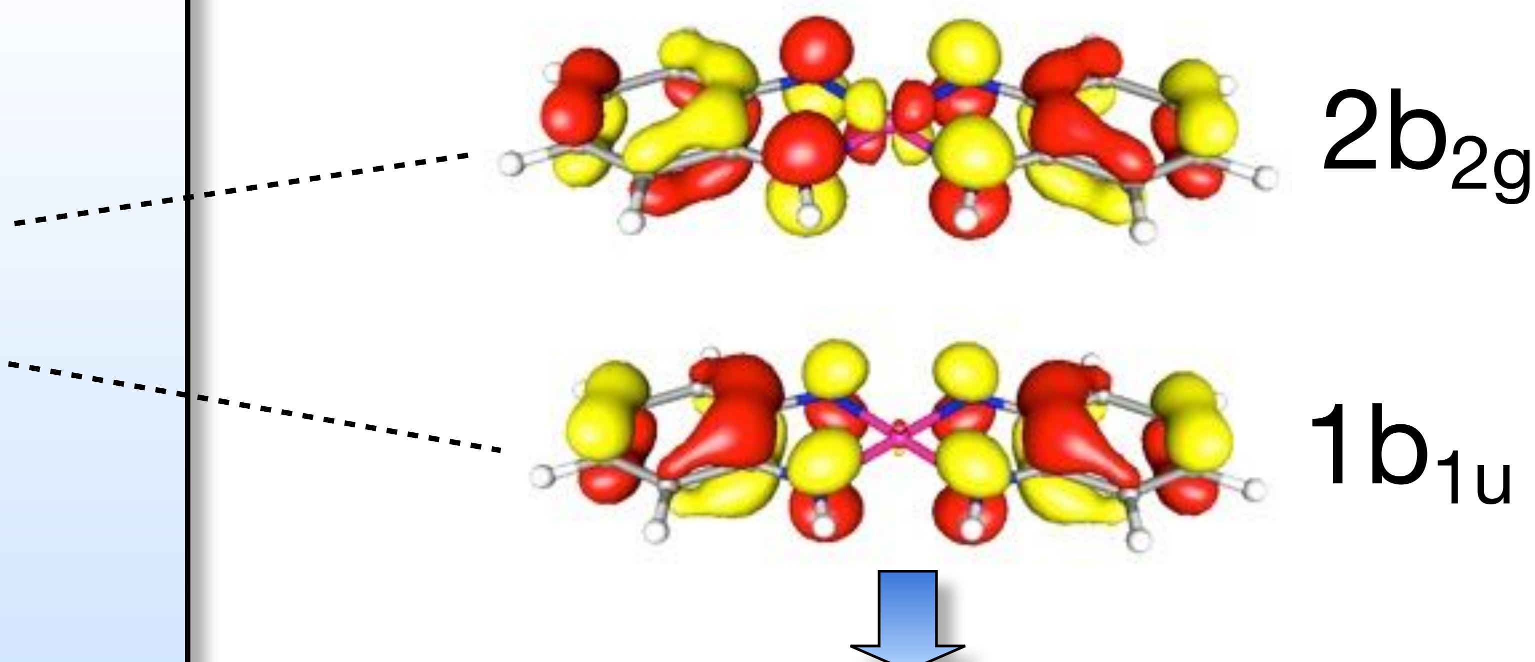
- Analyze the occupied orbitals of the compound and determine the fractional d-character of the orbitals
  (In *ORCA* this is possible via the `NormalPrint, Localize` or `UNO` keywords)
- Orbitals that are centered more than, ***say***, 70% on the metal are counted as pure metal d-orbitals
- Count the number of electrons in such metal based orbitals. This gives you the **d^N configuration**
- The **local spin state** on the metal follows from the singly occupied metal-based orbitals
- This fails, if there are some orbitals that are heavily shared with the ligands (metal character < 70%). In this case the oxidation state is ambiguous.
  (Typically, experiments are ambiguous as well in these cases)

An Example









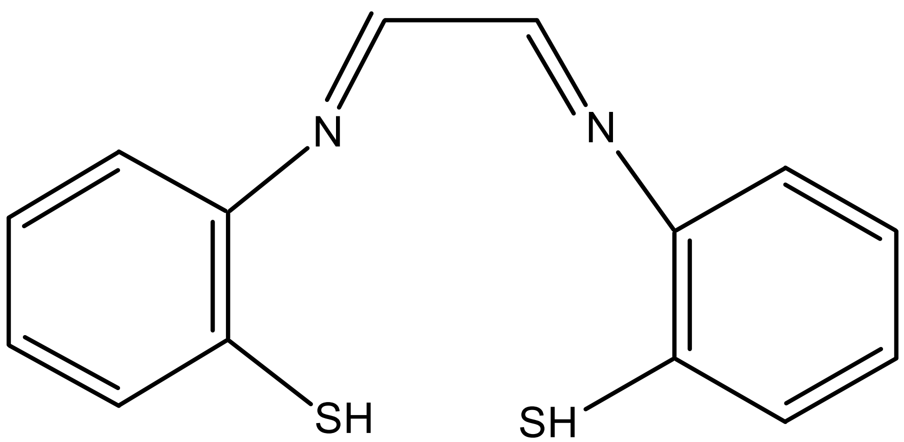
4 doubly occupied and one empty metal based orbitals

- Ni(II) oxidation state
- Ligand must be oxidized and has diradical character

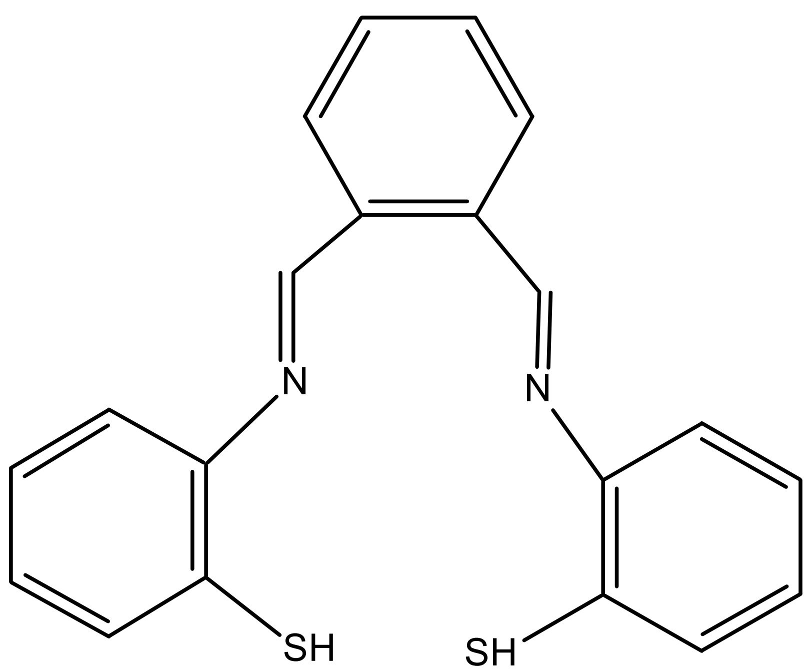
This is evidenced by close lying HOMO and LUMO that are symmetric and antisymmetric combinations

Herebian et al. *J. Am. Chem. Soc.*, **2003**, 125, 10997

An Example for an ‚Exciting‘ Oxidation State



gma



PhBMA

[Zn(gma)]
S=0 (Holm,Gray)

$[Zn(gma)]^-$
S=1/2 (Holm,Gray)

[Ni(gma)]
S=0 (Holm,Gray)

$[Ni(gma)]^-$
S=1/2 (Holm,Gray)

[Fe(gma)(py)]

$[Fe(gma)(PR_3)]$

$[Fe(gma)(CN)]^-$

S=1
(Strähle, Sellmann, Wieghardt)

[Fe(PhBMA)] S=1

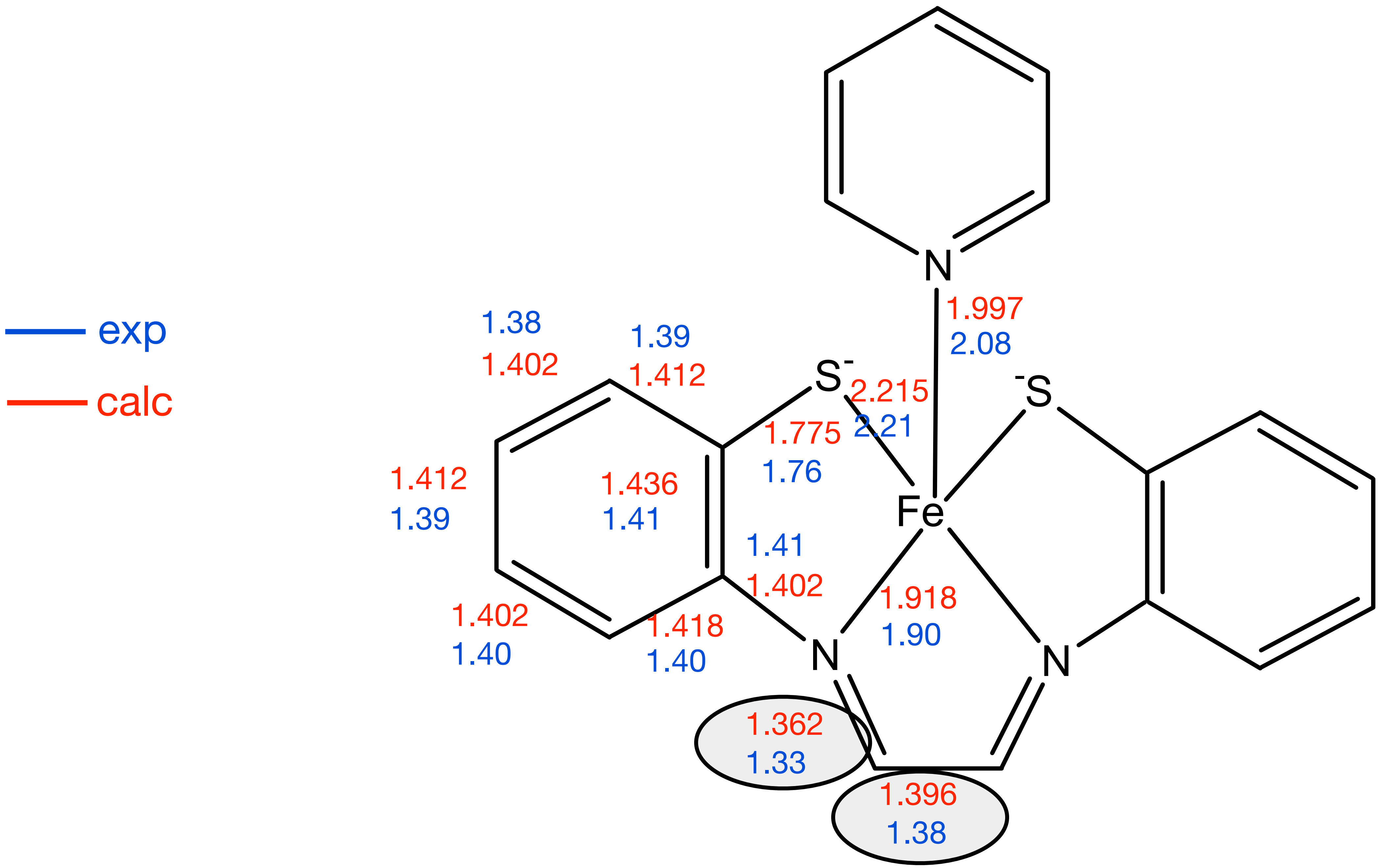
$[Fe(gma)(PR_3)_2]$ S=0

$[Fe(gma)(py)]^+$ S=1/2

(Wieghardt)

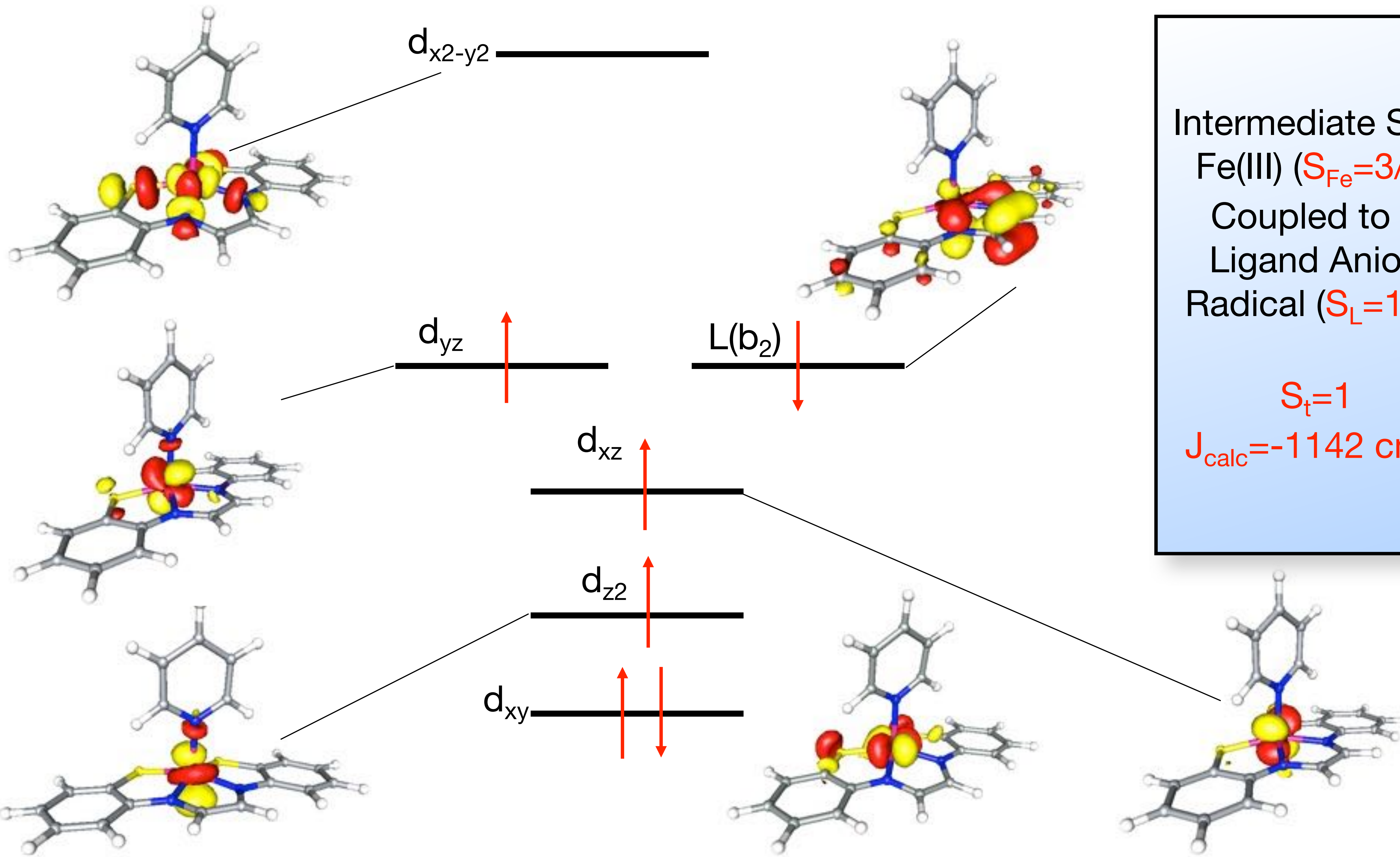
All described as ordinary metal(II) chelates

Optimized Structure of [Fe(L)(py)]



		δ_{MB}	ΔE_Q	η
[Fe(L)(py)]	Calc.	0.205	+2.371	0.084
	Exp.	0.270	+2.33	small

Electronic Structure of [Fe(gma)(py)]



Intermediate Spin Fe(III) (S_{Fe}=3/2) Coupled to a Ligand Anion Radical (S_L=1/2)

S_t=1

J_{calc}=-1142 cm^{-1}

Ghosh, P.; Bill, E.; Weyhermüller, T.; FN; Wieghardt, K. *J. Am. Chem. Soc.*, **2003**, 125, 1293

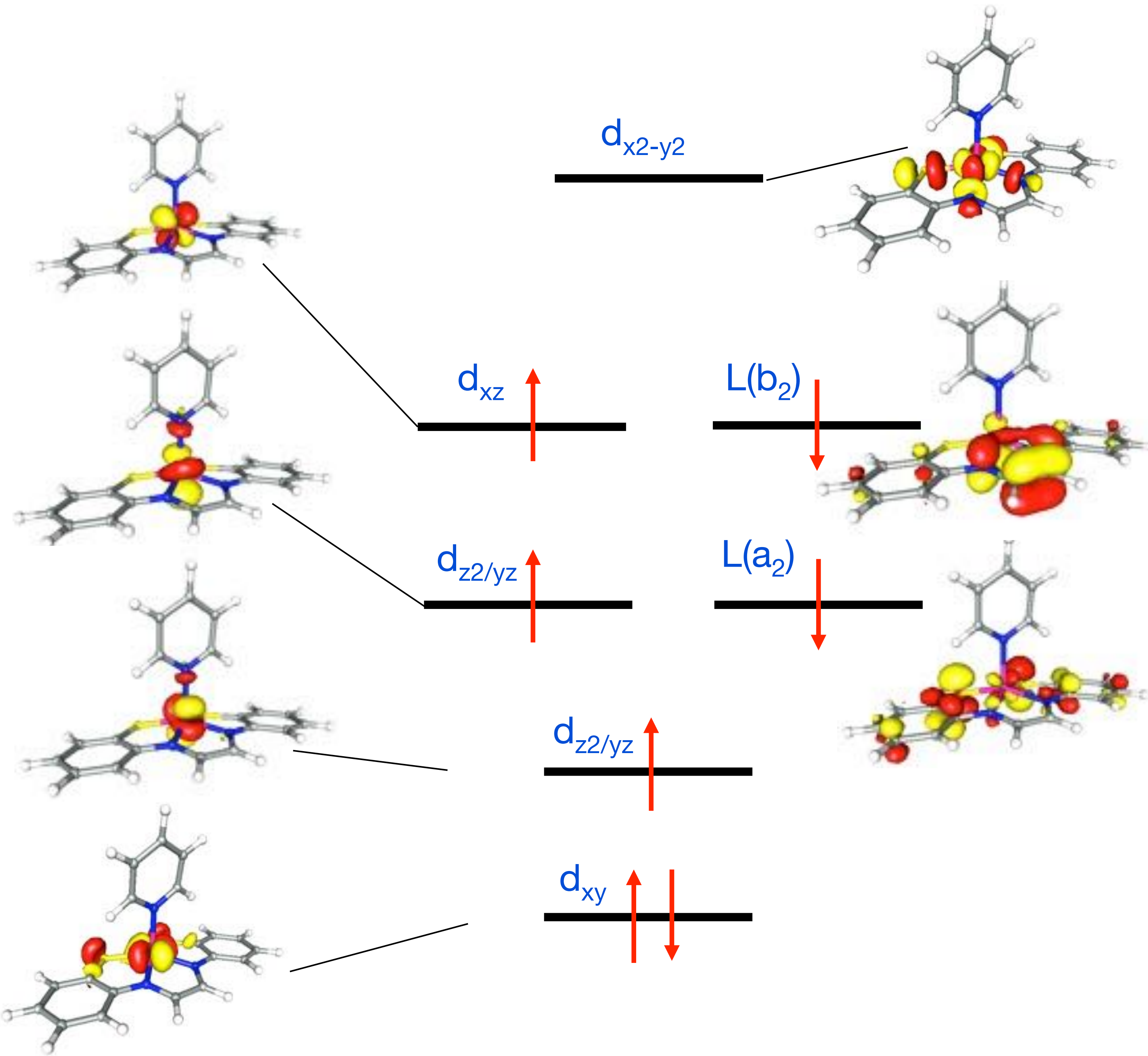
Electronic Structure of [Fe(gma)(py)]$^+$

Observation: Oxidation leaves the Mössbauer parameters invariant

Dilemma:

- ★ [Fe(gma)(py)] has a spin of 1
  - Intermediate Spin Fe(III)/Ligand Radical
- ★ Taking the Electron out of the ligand LUMO
  - Intermediate Spin Fe(III)/Closed Shell Ligand
  - S=3/2 Expected but S=1/2 Observed
- ★ Taking the Electron out of the Ligand but Changing the Spin at Fe
  - Would have been Detected in MB Experiments
- ★ Taking the Electron from the Iron gives Fe(IV)
  - Would have been Detected in MB Experiments

Electronic Structure of $[Fe(gma)(py)]^{+}$



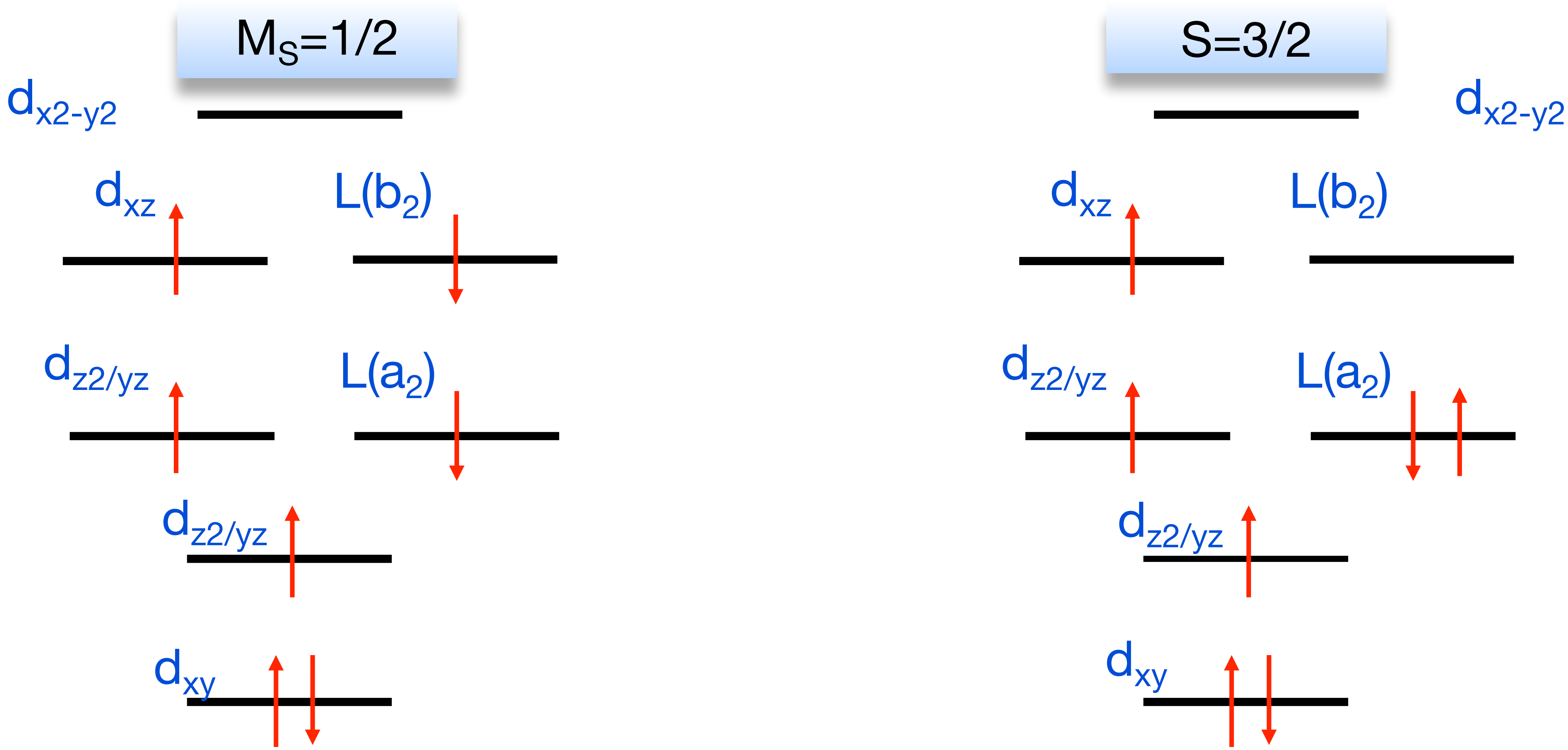
Mössbauer Parameters	δ (mm/s)	ΔE_Q (mm/s)	η
Neutral	0.205	2.371	0.084
Cation	0.246	2.430	0.023
Exp.	(0.27)	(2.33)	?

Intermediate Spin Fe(III) ($S_{Fe}=3/2$) Coupled to a Ligand Triplet State ($S_L=1$)

$S_t=1/2$ $J_{calc}=-845\ cm^{-1}$

Ghosh, P.; Bill, E.; Weyhermüller, T.; FN; Wieghardt, K. *J. Am. Chem. Soc.*, **2003**, 125, 1293

Electronic Structure of $[Fe(gma)(py)]^+$



$E(M_S=1/2)$ =-0.6 kcal/mol
E(S=1/2) ~ -5.4 kcal/mol

E(S=3/2) =0.0 kcal/mol

Large Exchange Coupling Drives Ligand Triplet State Coordination
Basis for a „Metal Field Theory“ rather than „Ligand Field Theory“

(Guihery, N.; Robert, V.; FN *J. Phys. Chem.*, 2008, 112, 12975)

Ghosh, P.; Bill, E.; Weyhermüller, T.; FN; Wieghardt, K. *J. Am. Chem. Soc.*, **2003**, 125, 1293

Making Ligand Field Theory quantitative

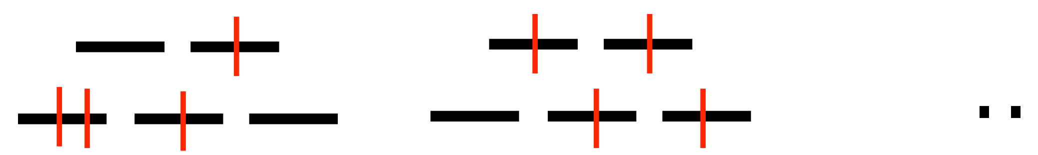
„Complete“ Ligand Field Theory

A complete LFT calculation in the strong field scheme proceeds as:

1. Build the one-electron matrix:

$$h_{\mu\nu} = f(e_\sigma^L, e_\pi^L) \qquad \mu,\nu = d - orbitals$$

2. Build all configurations



3. Build all Slater determinants: $\Phi_I(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ $\quad \Phi_1 = | d_{xy}^{\alpha} d_{xz}^{\alpha} d_{z^2}^{\beta} | \;\ldots\; \Phi_{65} = | d_{xz}^{\beta} d_{yz}^{\alpha} d_{x^2-y^2}^{\alpha} | \ldots.$

4. Build all Configuration State functions for total spin S and Irrep Γ $\quad \Theta_I = \sqrt{\tfrac{1}{3}}\Phi_{23} - \sqrt{\tfrac{2}{3}}\Phi_{51}$

5. Calculate Hamiltonian matrix elements $\quad H_{IJ}^{LFT}(\mathbf{e},B,C) = \left\langle \Theta_I \mid \hat{H}_{LFT} + H_{SB} + H_{ZE} \mid \Theta_J \right\rangle$

6. Diagonalize the ligand field Hamiltonian $\quad \mathbf{H}^{LFT}\mathbf{C}^{LFT} = E\mathbf{C}^{LFT}$

→ Yields all **ligand field multiplets** as a function of the LFT parameters. Order them in the **Tanabe-Sugano diagrams**

Parameterization : The Angular Overlap Model

In the AOM the one-electron part of the ligand field is written as:

$$h_{ab} = \sum_{L}\sum_{\lambda} F_{\lambda a}(\theta_L,\varphi_L,\psi_L)F_{\lambda b}(\theta_L,\varphi_L,\psi_L)$$

L= sum over ligands

F= angular factor (symmetry!)

$e_{\sigma,\pi}$= Interaction parameter (ligand specific, transferrable)

Two-electron part of the ligand field

$$\left\langle d_\sigma d_\sigma \middle| r_{12}^{-1} \middle| d_\pi d_\pi \right\rangle = \left\langle d_\sigma d_\sigma \middle| r_{12}^{-1} \middle| d_{\pi'} d_{\pi'} \right\rangle = F_{dd}^0 + {}^2\!/_{49} F_{dd}^2 - {}^{24}\!/_{441} F_{dd}^4$$

$$\left\langle d_i d_i \middle| r_{12}^{-1} \middle| d_i d_i \right\rangle = F_{dd}^0 + {}^4\!/_{49} F_{dd}^2 + {}^{36}\!/_{441} F_{dd}^4$$

$$\left\langle d_\delta d_\delta \middle| r_{12}^{-1} \middle| d_{\delta'} d_{\delta'} \right\rangle = F_{dd}^0 + {}^4\!/_{49} F_{dd}^2 - {}^{34}\!/_{441} F_{dd}^4$$

etc.

$$A = F_{dd}^0 - \frac{49}{441} F_{dd}^4$$

$$B = \frac{1}{49} F_{dd}^2 - \frac{5}{441} F_{dd}^4$$

$$C = \frac{35}{441} F_{dd}^4 \approx 4B$$

Racah parameters (A=arbitrary, C=4B).

Just two (one) parameter describes the electron-electron repulsion, 1-3 parameters for each ligand.

Examples of AOM parameters

Ligand	e_σ (cm^{-1})	e_π (cm^{-1})
CN^-	7530	-930
F^-	7390	1690
Cl^-	5540	1160
Br^-	4920	830
I^-	4100	670
NH_3	7030	0
en	7260	0
py	5850	-670
H_2O	7900	1850
OH^-	8670	3000

Note: $10Dq = \Delta = 3e_\sigma - 4e_\pi$

Examples of AOM parameters

Ligand	e_σ (cm^{-1})	e_π (cm^{-1})
OH^-	8670	3000

BUT

- **BIG overfitting problem**
- **No unique, precise definition of ligand field parameters**

Note: $10Dq = \Delta = 3e_\sigma - 4e_\pi$

Good numbers:
Large-Scale Multireference Calculations

Properly calculating coordination compounds?

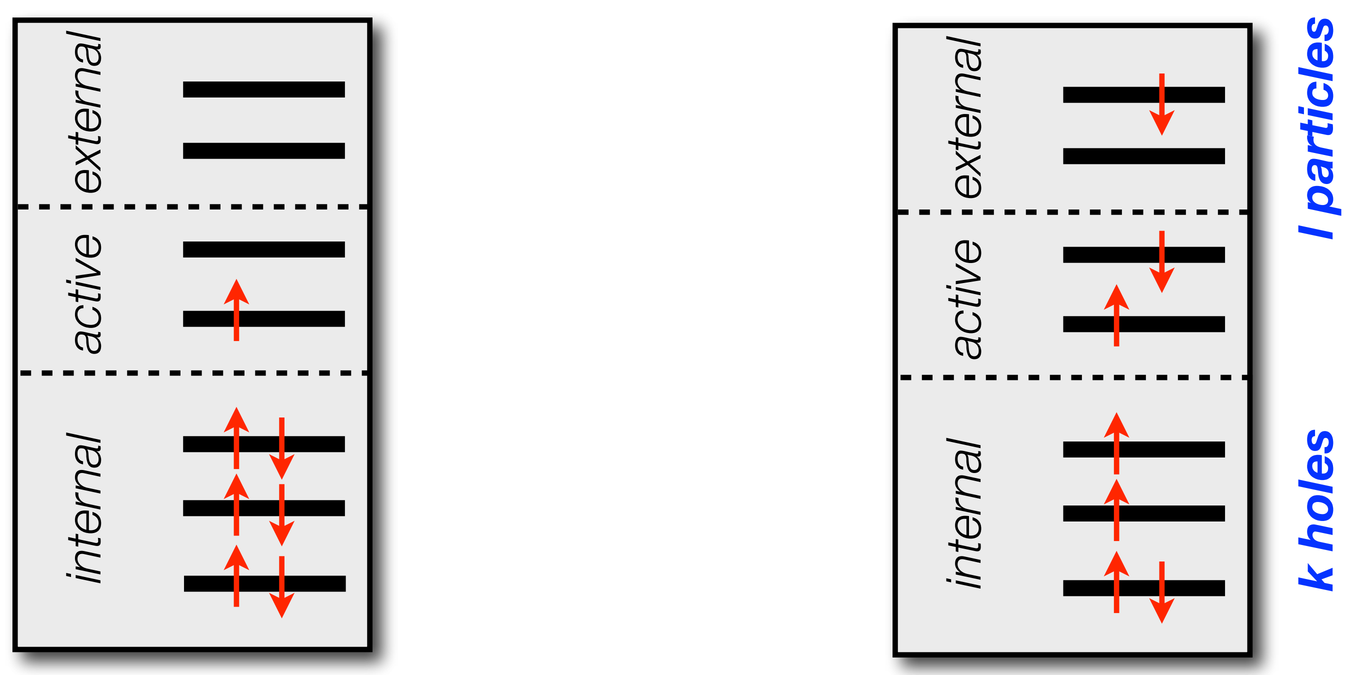
- ✓ Explicit representation of all spatial components of (nearly) degenerate states
  - Multireference wavefunction theory
- ✓ Realistic calculation of energy splittings between nearly degenerate spatial components
  - Accurate structural data!
  - Dynamic correlation
- ✓ Explicit representation of all magnetic sublevels $M = S, S\text{-}1, \ldots, -S$ of each spatial component
  - Wigner-Eckart theorem
- ✓ Interaction of all of these magnetic sublevels via the SOC (+SSC) and Zeeman operators
  - Quasi-degenerate perturbation theory
- ✓ Perhaps a significant number of excited states of various multiplicities that also interact with the degenerate pair via SOC
  - Multiroot theory

Multireference Expansions

✓ Cover differential dynamic correlation by performing excitations relative to at least the important CSFs of the CAS

$$\left|\Psi_I^{SM;MRCI}\right\rangle = \sum_{K\in CAS} C_{KI}\left|\Phi_K^{SM}\right\rangle \qquad + \qquad \sum_{K\notin CAS} C_{KI}\left|\Phi_K^{SM}\right\rangle$$

Solve:
$$\mathbf{HC} = E\mathbf{C}$$

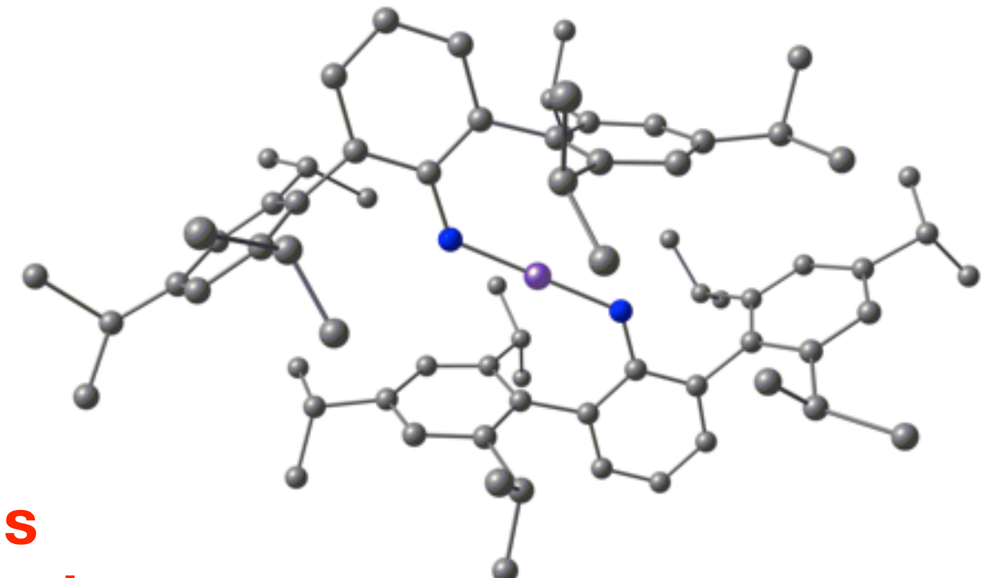


✓ Of the HUGE number of **(k-holes,l-particle)** CSFs, only a small fraction contributes to the differential dynamic correlation energy (idea of **DDCI** (Malrieu) and **SORCI** (FN))

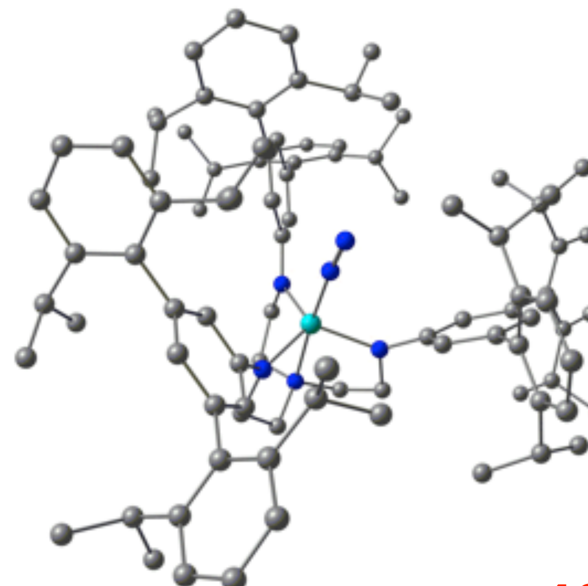
‣ Computationally affordable computation protocols are **CASSCF/CASPT2** (MOLCAS) and **CASSCF/NEVPT2** (ORCA)

Large Scale Calculations with NEVPT2

175 Atoms
2939 basis functions



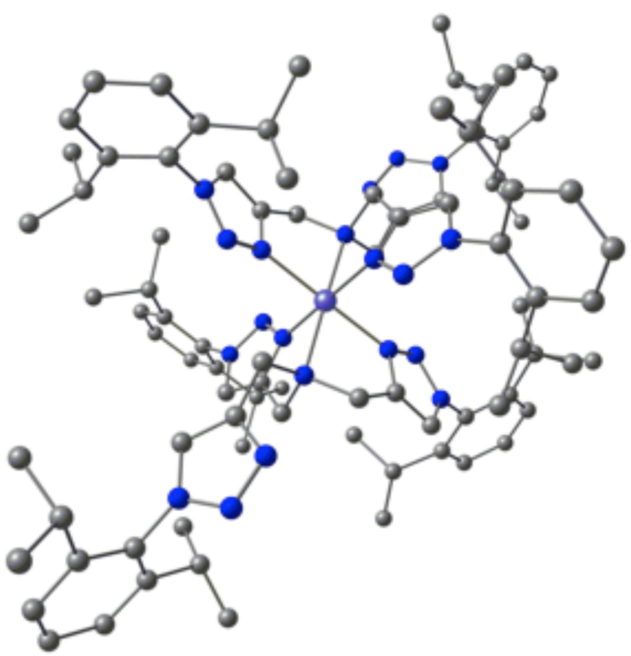
$FeC_{72}N_2H_{100}$



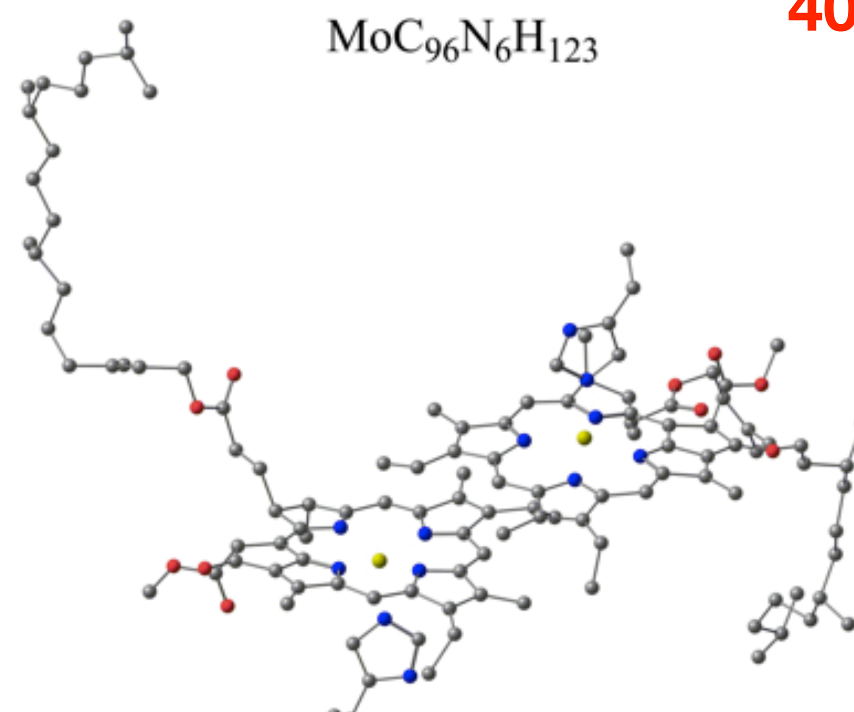
$MoC_{96}N_6H_{123}$

226 Atoms
4073 basis functions

231 Atoms
4175 basis functions



$NiC_{90}N_{20}H_{120}$



$Mg_2C_{120}N_{12}H_{160}O_{10}$

304 Atoms
5426 basis functions

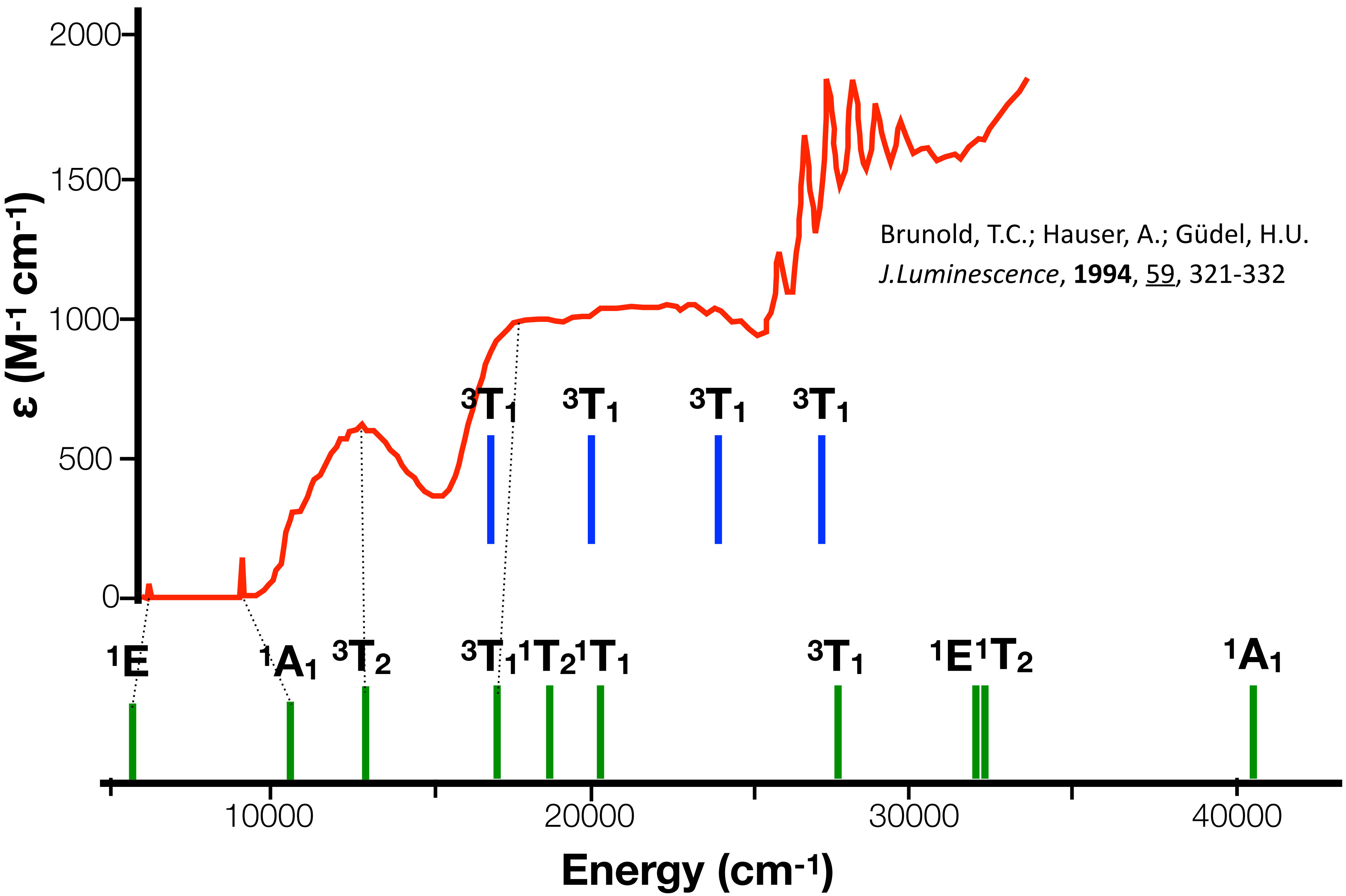
Linear scaling DLPNO-NEVPT2: Y Guo, K Silvaingam, E Valeev, FN, **2016**, *J. Chem. Phys.*, resubmitted

Ab Initio Ligand Field Theory

Ligand Field Theory as an Effective Hamiltonian

FeO_4^{2-} doped in K_2SeO_4

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN *Struc. Bond.*, **2012**, pp 149



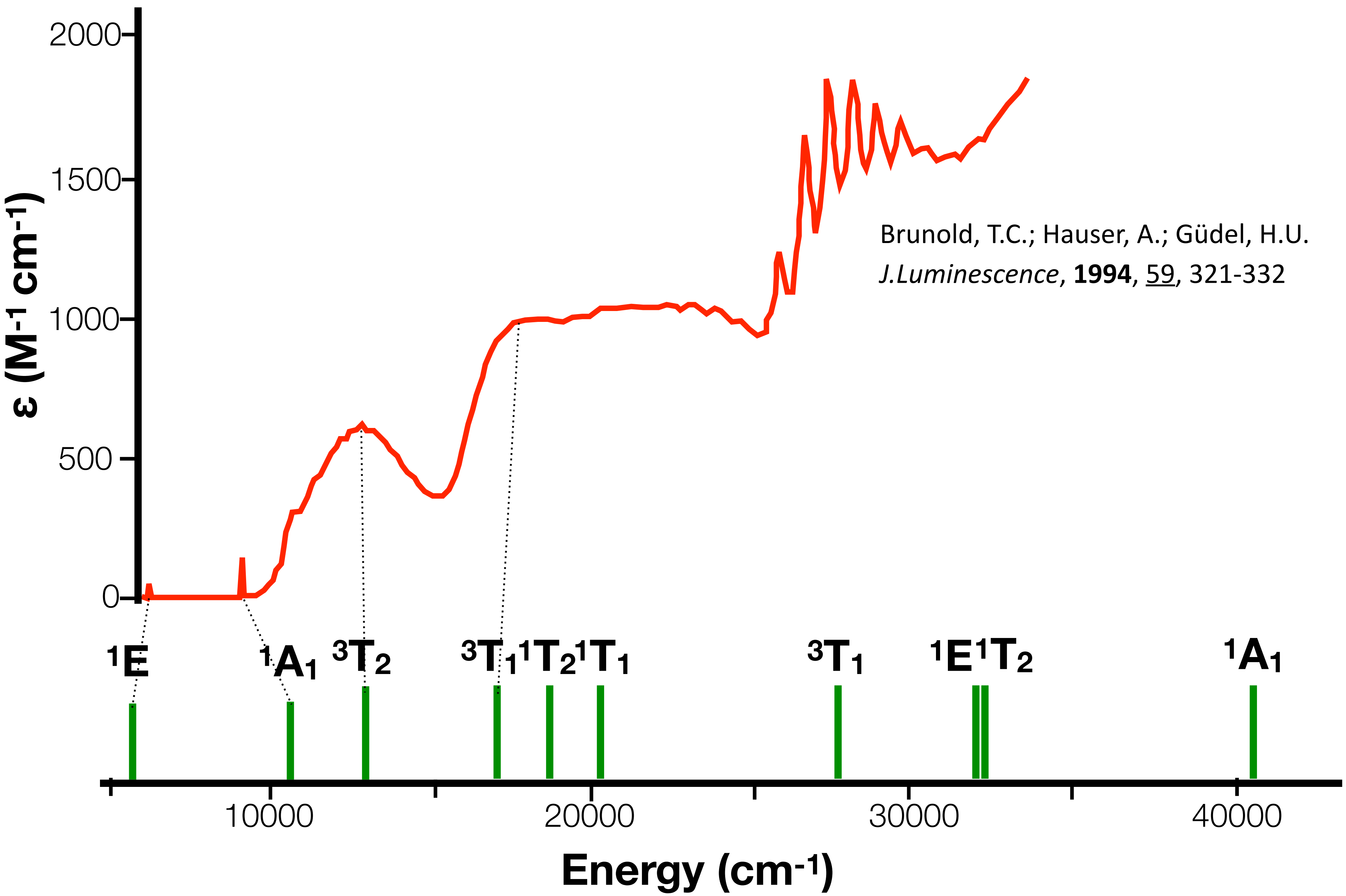
LMCT
<u>NOT</u> Covered by Ligand Field Theory

d-d
Covered by Ligand Field Theory

Ligand Field Theory as an Effective Hamiltonian

FeO_4^{2-} doped in K_2SeO_4

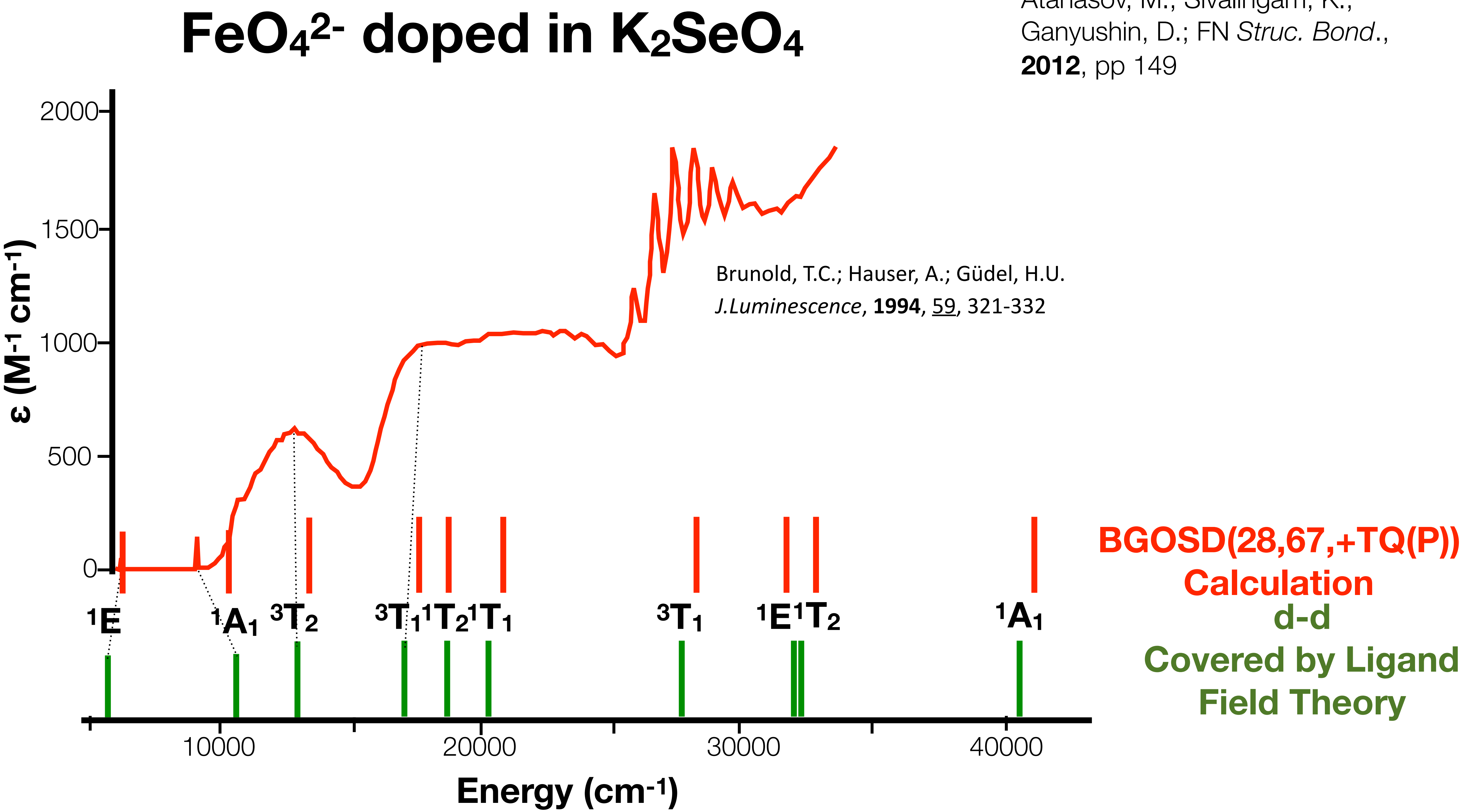
Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN *Struc. Bond.*, **2012**, pp 149



d-d
Covered by Ligand Field Theory

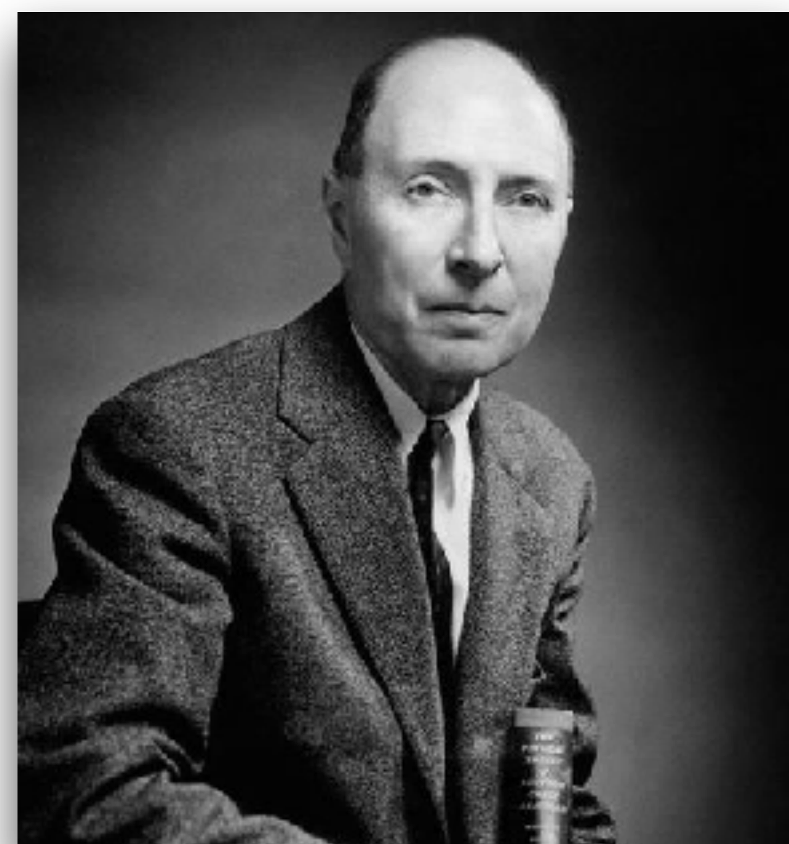
Ligand Field Theory as an Effective Hamiltonian

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN *Struc. Bond.*, **2012**, pp 149



„It is nice to know that the computer understands the problem. But I would like to understand it too.“

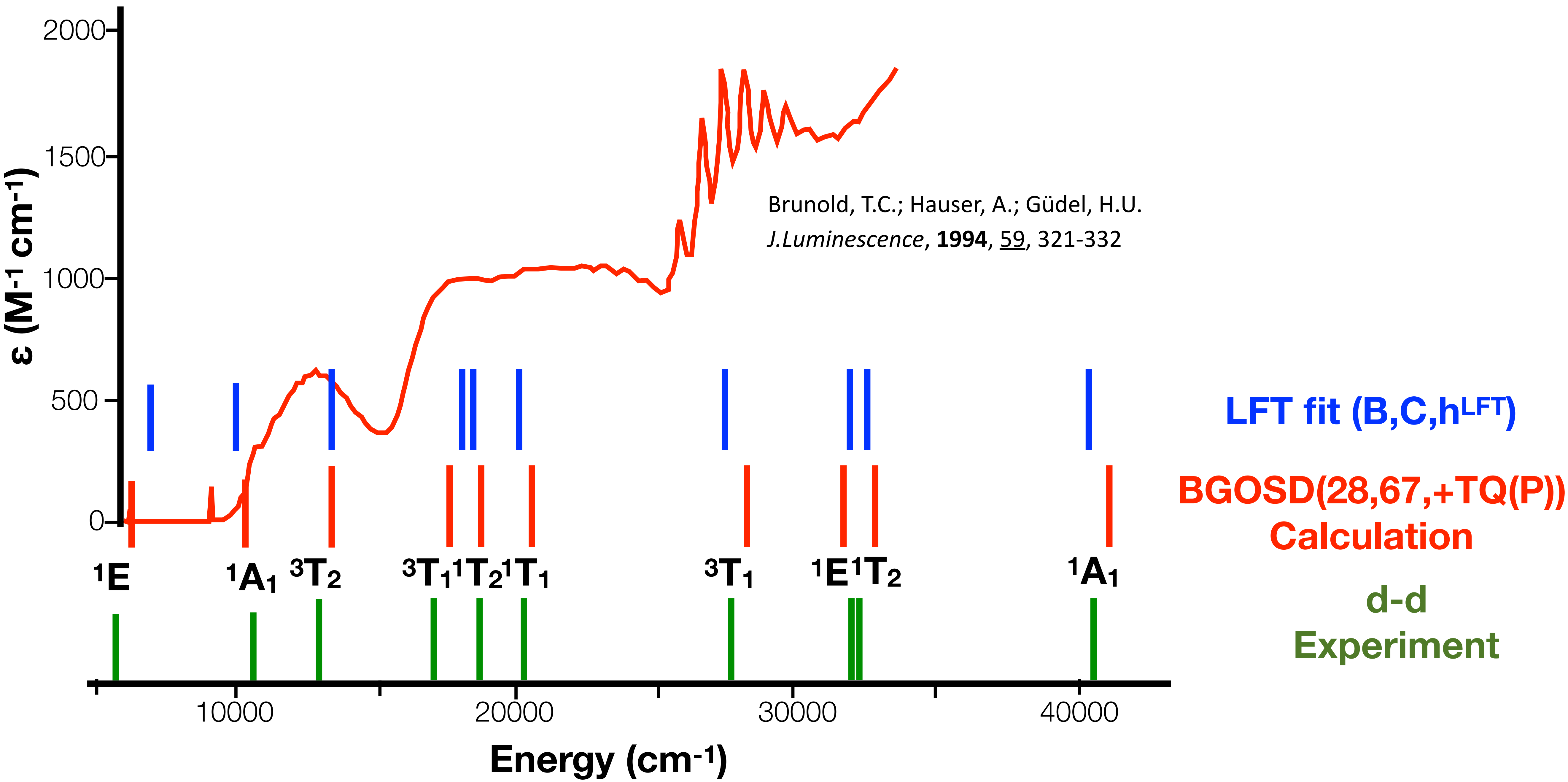
–Eugene Wigner



Ligand Field Theory as an Effective Hamiltonian

FeO_4^{2-} doped in K_2SeO_4

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN *Struc. Bond*., **2012**, pp 149



Unambiguous Match between NEVPT2 and LFT

There is a 1:1 correspondance between the ligand field CSFs and the CAS-CI CSFs.

$$\Theta_I^{LFT} = \left| d_{xy}^{\alpha} d_{xz}^{\beta} \ldots d_{z^2}^{\alpha} \right| \qquad \Theta_I^{CASSCF} = \left| \psi_{xy}^{\alpha} \psi_{xz}^{\beta} \ldots \psi_{z^2}^{\alpha} \right|$$

Ligand field pure d-orbital

***Ab initio* molecular orbital with metal d-parentage**

Thus, all we have to ensure is that ligand field d-orbitals and CASSCF molecular orbitals of the same parentage are ordered in the same way and that CSFs are constructed in the same way.

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN *Struct. Bond*, **2012**, 143, 149-220

The *ab initio* Intermediate Hamiltonian

1. We have a „**model space**“ that contains all the essential physics that we want to describe. This is the **CAS(n,5) space** of N-particle wavefunctions that cleanly maps onto the ligand field manifold

2. We have a „**outer space**“ that brings in all the remaining effects of dynamic correlation

$$H_{IJ}^{eff} = \left\langle \Phi_I \middle| H \middle| \Phi_J \right\rangle + \sum_{K \in roots} \left\langle \Phi_I \middle| \Psi_K \right\rangle \Delta E_K^{(NEVPT2)} \left\langle \Psi_K \middle| \Phi_J \right\rangle$$

- ✓ **Dynamic and non-dynamic correlation energy**
- ✓ **Same dimension as ligand field CI matrix**
- ✓ **Completely *ab initio*. No parameters!**
- ✓ **Yields a near exact eigenvalue spectrum**

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN *Struct. Bond*, **2012**, 143, 149-220

The *ab initio* Intermediate Hamiltonian

1. We have a „**model space**“ that contains all the essential physics that we want to describe. This is the **CAS(n,5) space** of N-particle wavefunctions that cleanly maps onto the ligand field manifold

2. We have a „**outer space**“ that brings in all the remaining effects of dynamic correlation

$$H_{IJ}^{eff} = \left\langle \Phi_I \,\middle|\, H \,\middle|\, \Phi_J \right\rangle + \sum_{K \in roots} \left\langle \Phi_I \,\middle|\, \Psi_K \right\rangle \Delta E_K^{(NEVPT2)} \left\langle \Psi_K \,\middle|\, \Phi_J \right\rangle$$

- ✓ **Dynamic and non-dynamic correlation energy**
- ✓ **Same dimension as ligand field CI matrix**
- ✓ **Completely *ab initio*. No parameters!**
- ✓ **Yields a near exact eigenvalue spectrum**

The condition is then that the ligand field CI matrix should resemble the *ab initio* effective Hamiltonian as closely as possible

$$\left| H_{IJ}^{LFT} - H_{IJ}^{eff} \right| = \min$$

For each matrix element!

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN *Struct. Bond*, **2012**, 143, 149-220

While this looks at first sight to be a nonlinear optimization problem, in reality things are easy ***because the ligand field matrix is linear in each and every ligand field parameter!***

$$\mathbf{H}^{LFT}(e,B,C) = \mathbf{H}^{LFT}(0) + \frac{\partial \mathbf{H}^{LFT}}{\partial B}B + \frac{\partial \mathbf{H}^{LFT}}{\partial C}C + \sum_{L}\frac{\partial \mathbf{H}^{LFT}}{\partial e_L}e_L$$

This ensures that there is a **unique least squares solution** that provides the unambiguous best fit of the ligand field and effective Hamiltonian matrices:

$$\mathbf{Ap} = -\mathbf{b} \;\Leftrightarrow\; \mathbf{p} = -\mathbf{A}^{-1}\mathbf{b}$$

$p_K =$ The k'th ligand field parameter

$$A_{KL} = \sum_{IJ}\frac{\partial H_{IJ}^{LFT}}{\partial p_K}\frac{\partial H_{IJ}^{LFT}}{\partial p_L}$$

$$b_K = \sum_{IJ}\frac{\partial H_{IJ}^{LFT}}{\partial p_K}H_{IJ}^{eff}$$

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN *Struct. Bond*, **2012**, 143, 149-220

Summary: Information Flow in AILFT

1 — *Ab Initio*

CASSCF/
NEVPT2
...

$\mathbf{H^{eff}}$

2 — AILFT

$\mathbf{h^{LFT}}$ **(5x5/7x7)**
$\mathbf{B,C/E_{1,2,3}}$
ζ

3 — Interpretation

AOM e_{σ}, e_{π}

Covalency
(Relativistic)
Nephelauxetic
Effect

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN *Struct. Bond*, **2012**, 143, 149-220

Application to CrX_6^{3-} (X=F,Cl,Br,I)

Prof. Mihail Atanasov

Calculated spectra

	CASSCF	NEVPT2	exp
$^4T_2$	13380	15365	15200
$^4T_1(1)$	21424	23449	21800
$^4T_1(2)$	34778	35307	35000
$^2E(1)$	19409	17579	16300
$^2T_1(1)$	20430	18681	16300
$^2T_2(1)$	27372	25288	23000
$^2A_1$	29674	30022	
$^2T_2(2)$	32664	32979	
$^2T_1(2)$	33736	33800	
$^2E(2)$	36009	35316	
$^2T_1(3)$	39668	39324	
$^2T_2(3)$	46237	45791	
$^2T_1(4)$	46546	48689	
$^2A_2$	51121	47612	
$^2T_2(4)$	52510	49902	
$^2E(3)$	55140	55611	

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN Struct. Bond, **2012**, 143, 149-220

Application to CrX_6^{3-} (X=F,Cl,Br,I)

Prof. Mihail Atanasov

Calculated spectra

	CASSCF	NEVPT2	exp
$^4T_2$	13380	15365	15200
$^4T_1$(1)	21424	23449	21800
$^2T_2$(3)	[illegible]	[illegible]	
$^2T_1$(4)	46546	48689	
$^2A_2$	51121	47612	
$^2T_2$(4)	52510	49902	
^2E(3)	55140	55611	

Extracted parameters

		CrF_6^{3-}			$CrCl_6^{3-}$			$CrBr_6^{3-}$		CrI_6^{3-}	
	CASSCF	NEVPT2	Exp.	CASSCF	NEVPT2	Exp.	CASSCF	NEVPT2	Exp.	CASSCF	NEVPT2
10Dq	13359	15255	15297	10941	14109	12630	9876	13542	13089	9258	13533
B	1071	863	734	988	767	632	972	729	471	943	699
C	4018	3720	3492	3907	3605	3180	3886	3631	3249	3841	3627
C/B	3.75	4.31	4.76	3.95	4.70	5	4.00	4.98	6.90	4,07	5.18

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN Struct. Bond, **2012**, 143, 149-220

Application to CrX_6^{3-} (X=F,Cl,Br,I)

Prof. Mihail Atanasov

Calculated s

CrF_6^{3-}	CASSCF	NEVPT2
$^4T_2$	-20	-111
$^4T_1(1)$	-42	-533
$^4T_1(2)$	-16	439
$^2E(1)$	-64	-283
$^2T_1(1)$	-38	-575
$^2T_2(1)$	-85	-119
$^2A_1$	25	-156
$^2T_2(2)$	88	-527
$^2T_1(2)$	20	-678
$^2E(2)$	10	-151
$^2T_1(3)$	90	-694
$^2T_2(3)$	-24	-797
$^2T_1(4)$	89	-767
$^2A_2$	-4	-480
$^2T_2(4)$	-11	762
$^2E(3)$	-166	-1017

$^4T_2$		0
$^4T_1(1)$		0
$^2T_2(3)$		
$^2T_1(4)$		
$^2A_2$		
$^2T_2(4)$		
$^2E(3)$		

Deviations from Ligand field fit and ab initio calculations

Extracted parameters

		C			$CrBr_6^{3-}$			CrI_6^{3-}	
	CASSCF	N	Exp.	CASSCF	NEVPT2	Exp.	CASSCF	NEVPT2	
10Dq	13359	1	12630	9876	13542	13089	9258	13533	
B	1071	8	632	972	729	471	943	699	
C	4018	3	3180	3886	3631	3249	3841	3627	
C/B	3.75		5	4.00	4.98	6.90	4,07	5.18	

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN Struct. Bond, **2012**, 143, 149-220

Application to CrX_6^{3-} (X=F,Cl,Br,I)

Prof. Mihail Atanasov

Calculated s[illegible]

CrF_6^{3-}	CASSCF	NEVPT2
$^4T_2$	-20	-111
$^4T_1(1)$	-42	-533
$^4T_1(2)$	-16	439
$^2E(1)$	-64	-283
$^2T_1(1)$	-38	-575
$^2T_2(1)$	-85	-119
$^2A_1$	25	-156
$^2T_2(2)$	88	-527
$^2T_1(2)$	20	-678
$^2E(2)$	10	-151
$^2T_1(3)$	90	-694
$^2T_2(3)$	-24	-797
$^2T_1(4)$	89	-767
$^2A_2$	-4	-480
$^2T_2(4)$	-11	762
$^2E(3)$	-166	-1017

$^4T_2$		0
$^4T_1(1)$		0
$^2T_2(3)$		
$^2T_1(4)$		
$^2A_2$		
$^2T_2(4)$		
$^2E(3)$		

Deviations from Ligand field fit and ab initio calculations

Extracted parameters

	[illegible]				$CrBr_6^{3-}$		CrI_6^{3-}	
	CASSCF	N[illegible]	Exp.	CASSCF	NEVPT2	Exp.	CASSCF	NEVPT2
10Dq	13359	1[illegible]	12630	9876	13542	13089	9258	13533
B	1071	8[illegible]	632	972	729	471	943	699
C	4018	3[illegible]	3180	3886	3631	3249	3841	3627
C/B	3.75		5	4.00	4.98	6.90	4,07	5.18

- ✓ Very good agreement between *ab initio* values and empirical values for 10Dq
- ✓ Still slight overestimation of electron repulsion (basis set incompleteness + 2nd order perturbation theory)
- ✓ Ligand field fit to CASSCF near perfect, to NEVPT2 within 1000 cm^{-1}

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN Struct. Bond, **2012**, 143, 149-220

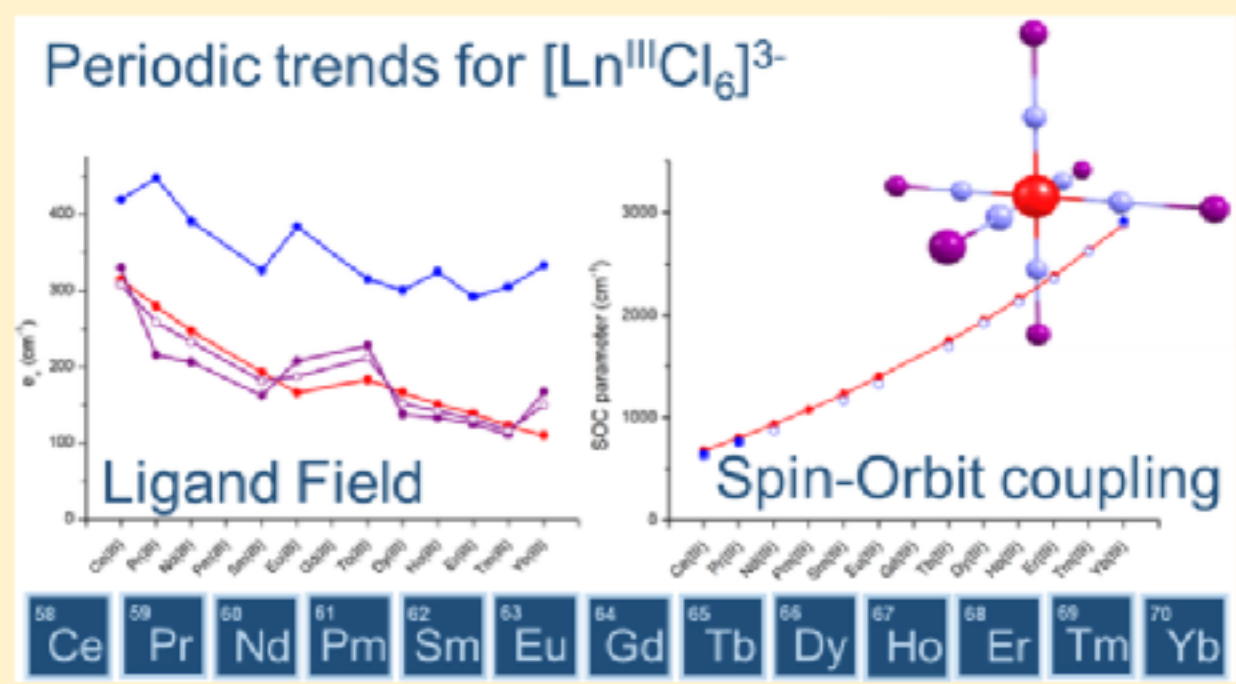
Periodic Trends in Lanthanide Compounds through the Eyes of Multireference ab Initio Theory

Daniel Aravena,[†] Mihail Atanasov,[*,‡,§] and Frank Neese[*,‡]

[†]Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile
[‡]Max Planck Institut für Chemische Energiekonversion, Stifstr 34-36, D-45470 Mülheim an der Ruhr, Germany
[§]Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Akad. Georgi Bontchev Street 11, 1113 Sofia, Bulgaria

Supporting Information

ABSTRACT: Regularities among electronic configurations for common oxidation states in lanthanide complexes and the low involvement of f orbitals in bonding result in the appearance of several periodic trends along the lanthanide series. These trends can be observed on relatively different properties, such as bonding distances or ionization potentials. Well-known concepts like the lanthanide contraction, the double−double (tetrad) effect, and the similar chemistry along the lanthanide series stem from these regularities. Periodic trends on structural and spectroscopic properties are examined through complete active space self-consistent field (CASSCF) followed by second-order *N*-electron valence perturbation theory (NEVPT2) including both scalar relativistic and spin−orbit



Inorganic Chemistry, **2016**,**2016**, *55* (9), pp 4457–4469

Case Study: Tetrahedral Co(II) Complexes

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Slow Magnetic Relaxation at Zero Field in the Tetrahedral Complex $[Co(SPh)_4]^{2-}$

Joseph M. Zadrozny and Jeffrey R. Long*

dx.doi.org/10.1021/ja2100142 | *J. Am. Chem. Soc.* 2011, 133, 20732–20734

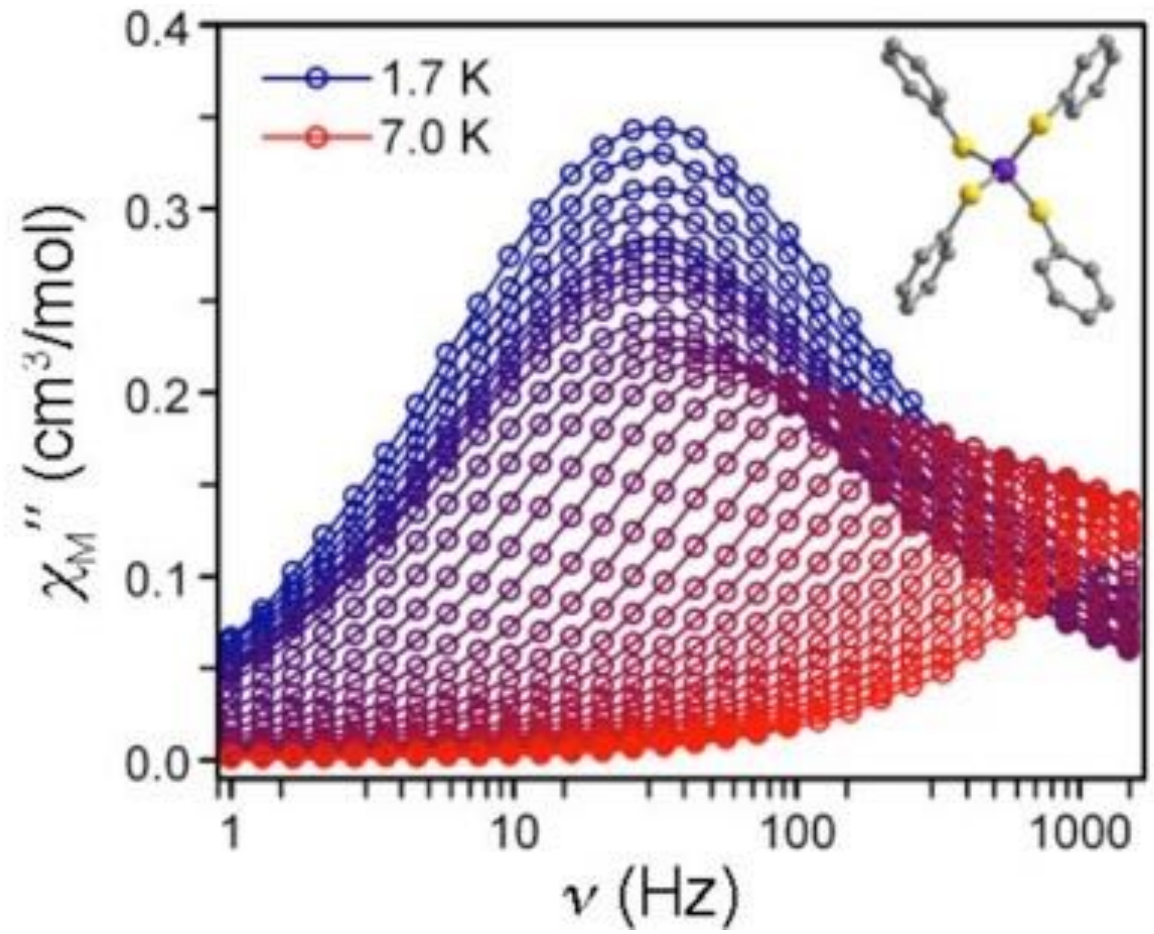
Inorganic Chemistry
ARTICLE
pubs.acs.org/IC

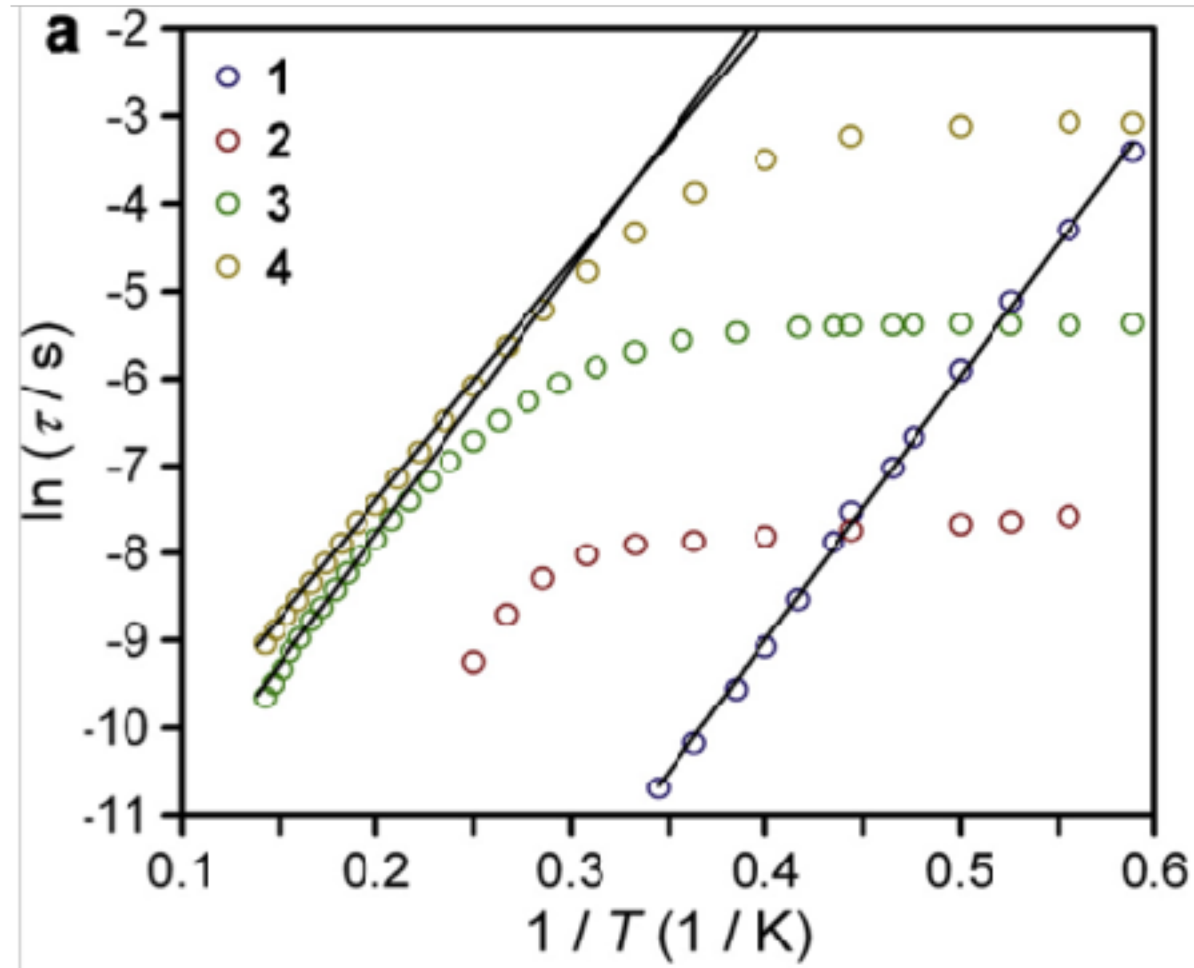
Theoretical Analysis of the Spin Hamiltonian Parameters in $Co^{(II)}S_4$ Complexes, Using Density Functional Theory and Correlated ab initio Methods

Dimitrios Maganas,[†,§] Silvia Sottini,[‡] Panayotis Kyritsis,[*,†] Edgar J. J. Groenen,[‡] and Frank Neese[*,§]

Inorg. Chem. 2011, 50, 8741–8754

$[Co^{II}(^{-}S\text{-}Ph)_4]^{2-}$ shows slow magnetic relaxation





First mononuclear TM compound with Single Molecular Magnet behavior in the absence of any external magnetic field

zfs is approximated from linear fit of the Arrhenius plot of:

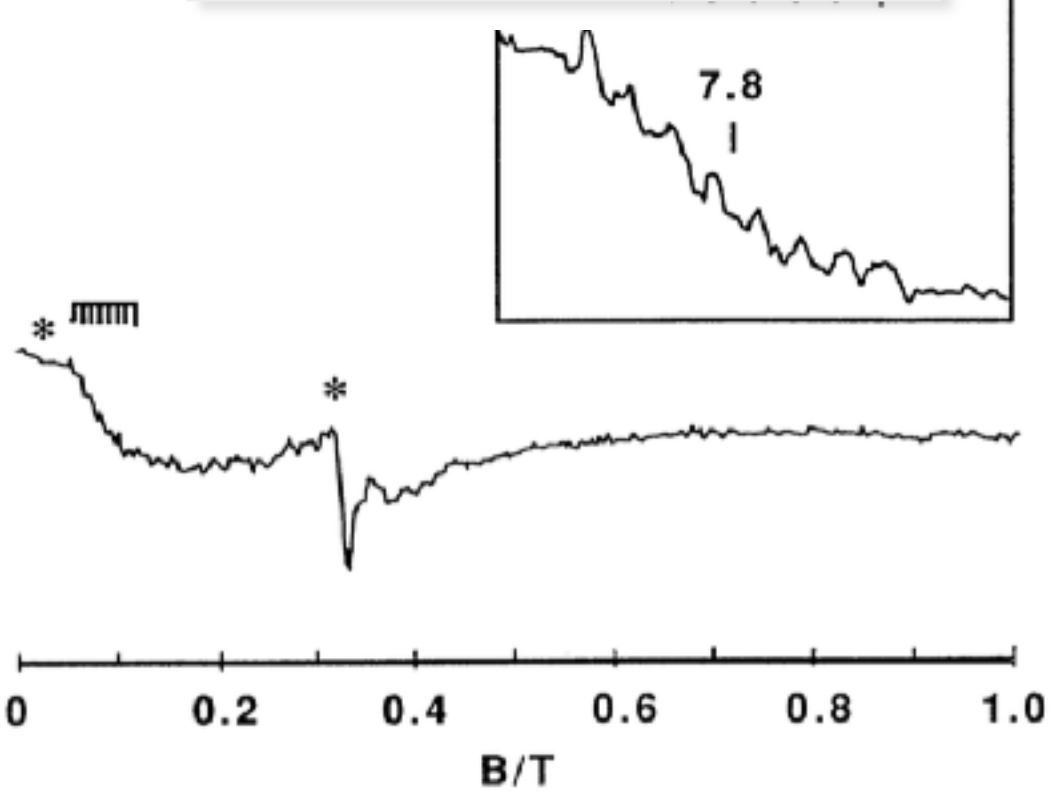
τ vs 1/T as **U_{eff}~|*D*|S^2-1/4=2*D***

- Due to relaxation processes **U_{eff}=21 cm^{-1}** (But D~70 cm^{-1} e.g. << 140 cm^{-1}
- This method is not conclusive for the magnitude of *D*

Long J. *et al.*, *J. Am. Chem.Soc.* **2011**, 133, 20732−20734

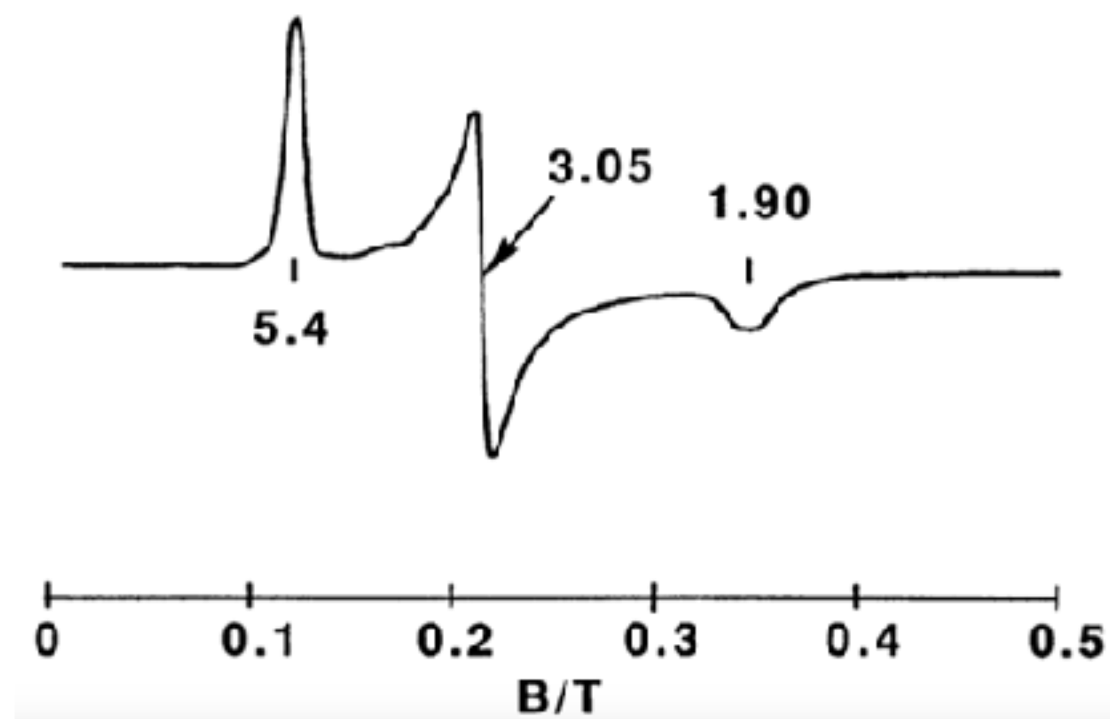
Serendipity: Giant Counterion Effects in $[Co^{II}(RS)_4]^{2-}$

$[Co^{II}(SPh)_4](Ph_4P)_2$



Strange Co(II) with large ZFS

$[Co^{II}(SPh)_4](Et_4N)_2$



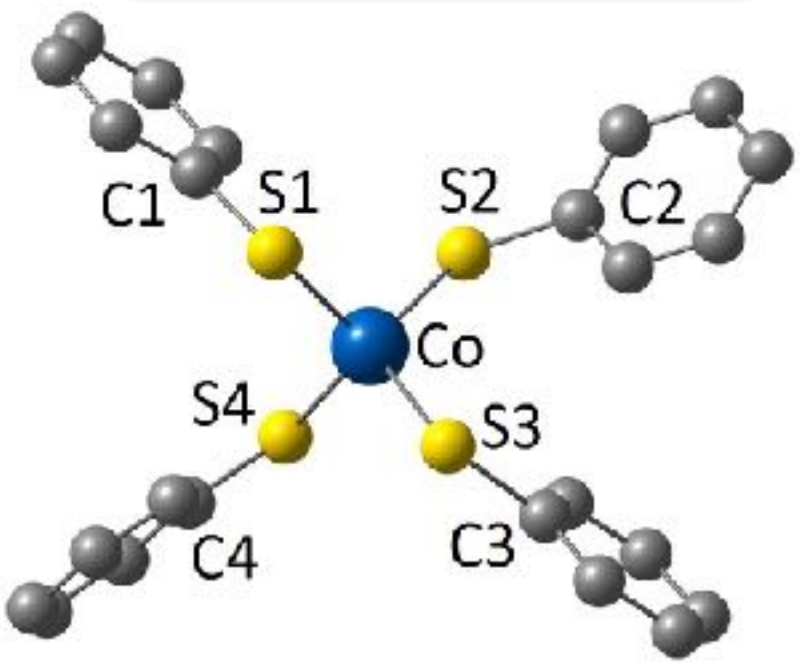
Regular Co(II) with moderate ZFS

We need to understand these giant changes if we want to design a SMM

K. Fukui et al., *Inorg. Chem.* **1992**, *Inorg. Chem. Acta* **1995**, *Bull. Chem. Soc. Jpn.*, **1991**

Geometric Origin of Counterion Effects

$[Co^{II}(SPh)_4](Ph_4P)_2$

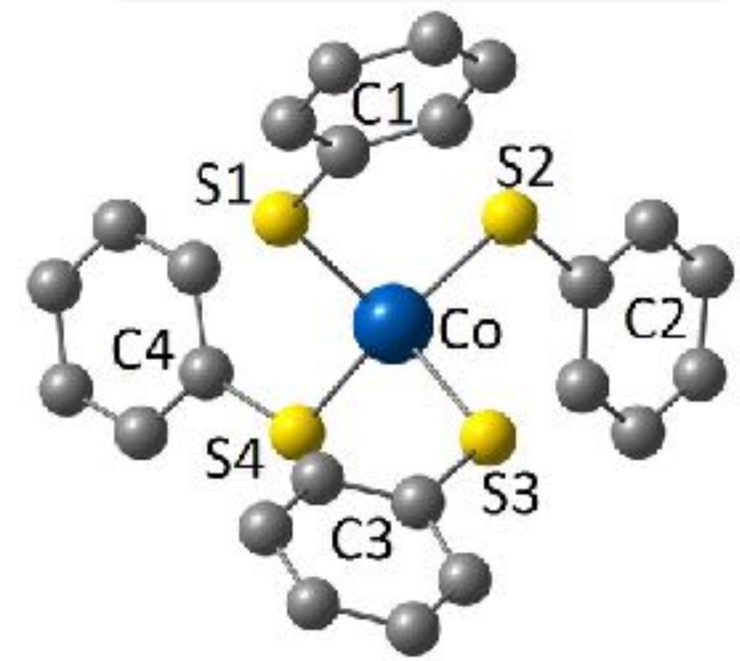


Elongated tetrahedron

Tasks:

- Careful experimental study
- Detailed understanding of the electronic structure origin of the observed magnetic parameters

$[Co^{II}(SPh)_4](Et_4N)_2$



Compressed tetrahedron

<table>
<tr><th></th><th colspan="2">$[Co^{II}(SPh)_4](Ph_4P)_2$</th><th>Opt1</th><th colspan="2">$[Co^{II}(SPh)_4](Et_4N)_2$</th><th>Opt2</th></tr>
<tr><td>S1-Co1-S2</td><td>114</td><td rowspan="4">116</td><td rowspan="4">117</td><td>106</td><td rowspan="4">105</td><td rowspan="4">105</td></tr>
<tr><td>S2-Co1-S3</td><td>120</td><td>105</td></tr>
<tr><td>S3-Co1-S4</td><td>112</td><td>101</td></tr>
<tr><td>S4-Co1-S1</td><td>116</td><td>107</td></tr>
<tr><td>S1-Co1-S3</td><td>98</td><td rowspan="2">98</td><td rowspan="2">96</td><td>119</td><td rowspan="2">120</td><td rowspan="2">119</td></tr>
<tr><td>S2-Co1-S4</td><td>97</td><td>121</td></tr>
</table>

Energy difference between optimized structures ~1.3 kcal/mol

Quantitative Comparison

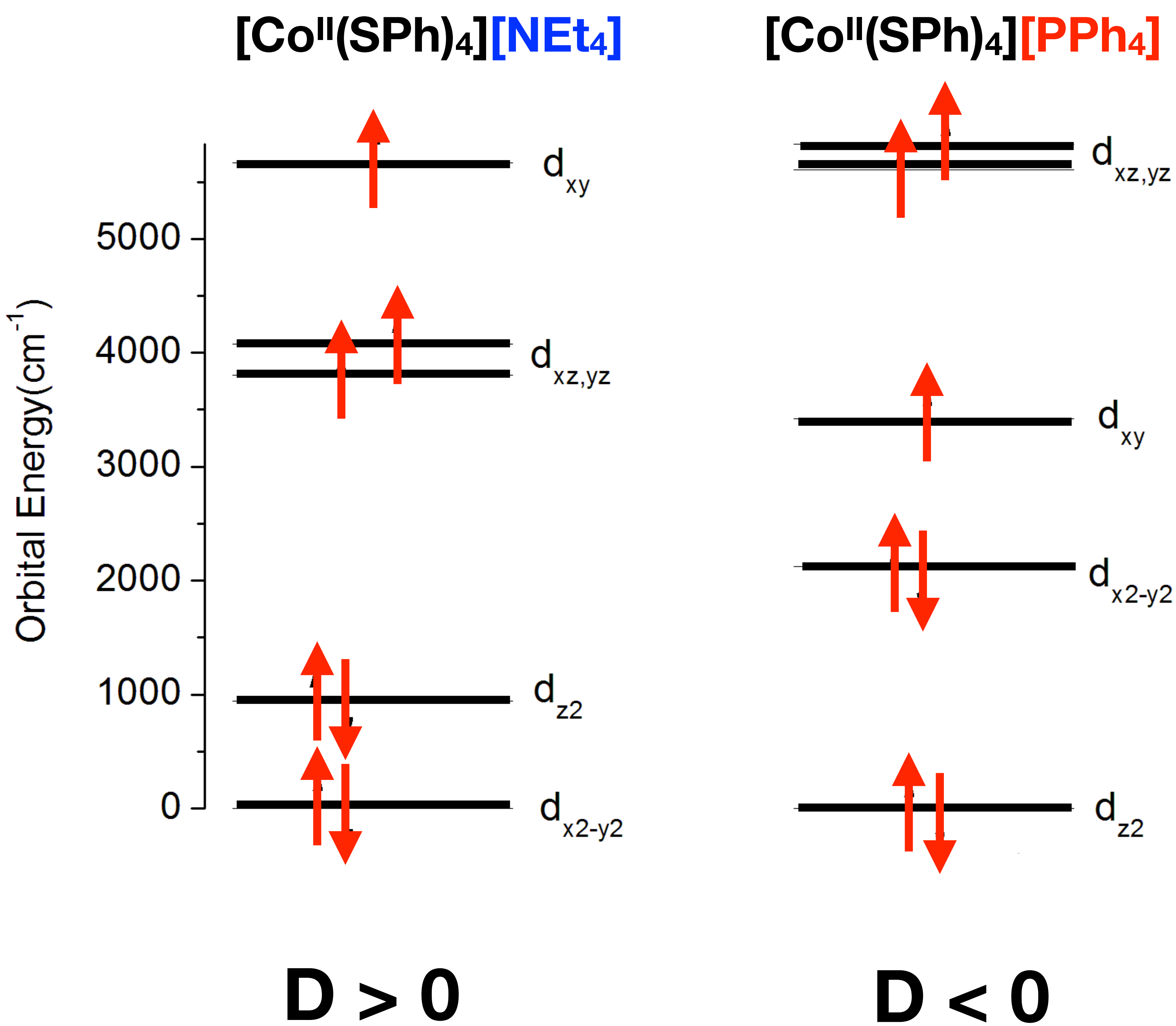
		D (cm^{-1})	E/D	g_z	g_x	g_y
$[Co^{II}(SPh)_4](Ph_4P)_2$	M and χT fitting	-54(5)	<0.01	2.587(3)	2.1(1)	
	single crystal χT and	-70(10)	<0.09	2.6(1)	2.2(1)	
	MCD	<-20	~0	2,5	2,8	
	NEVPT2/X-Ray	**-46,7**	**0,03**	**2,71**	**2,13**	**2,18**
	NEVPT2/Opt	**-48,0**	**0,00**	**2,69**	**2,12**	**2,12**
$[Co^{II}(SPh)_4](Et_4N)_2$	M and χT fitting	12(1)	0.31(2)	2.10(1)		
	MCD	+7	0.3	2.35		
	NEVPT2/X-Ray	**11,5**	**0,16**	**2,16**	**2,29**	**2,33**
	NEVPT2/Opt	**3,0**	**0,00**	**2,19**	**2,23**	**2,23**

Good to excellent numerical agreement with experiment

Can now explore structural variations

D3-BP86/def2-TZVP structures; CASSCF(7,5)/NEVPT2 DKH2 def2-TZVP: 10 quartets & 40 doublets

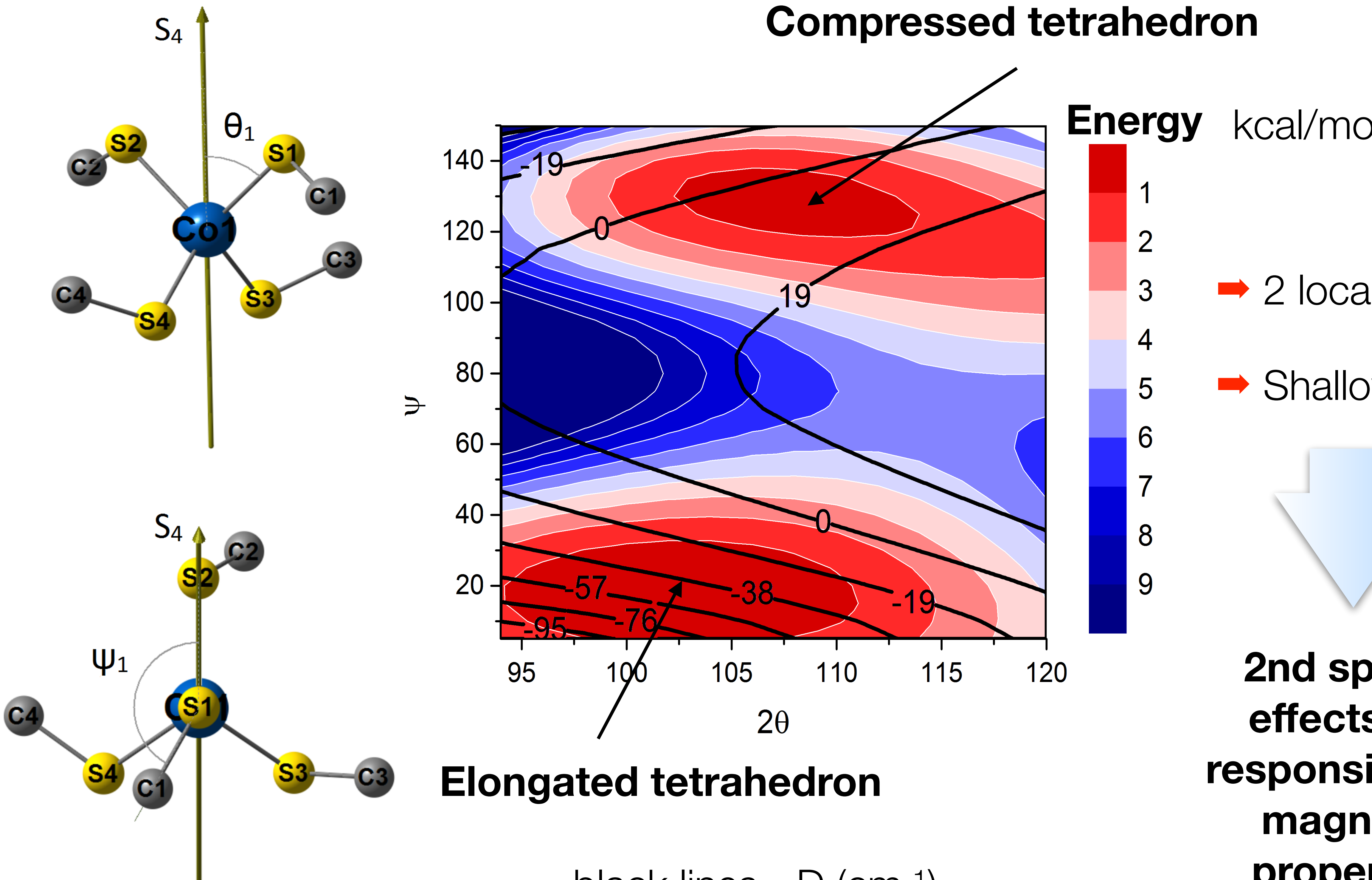
Ab Initio Ligand Field Reconstruction



$$D \simeq \frac{4}{9}\zeta_{eff}^{2}\frac{E(^4T_{2z}) - E(^4T_{2x,y})}{(10Dq)^2}$$

- ✓ Splittings of opposite sign induced by ‚low-symmetry' ligand field.
- ✓ Much larger splittings for $[PPh_4]$.
- ✓ Predicted sign of *D* consistent with observation

Magneto-Structural Correlations



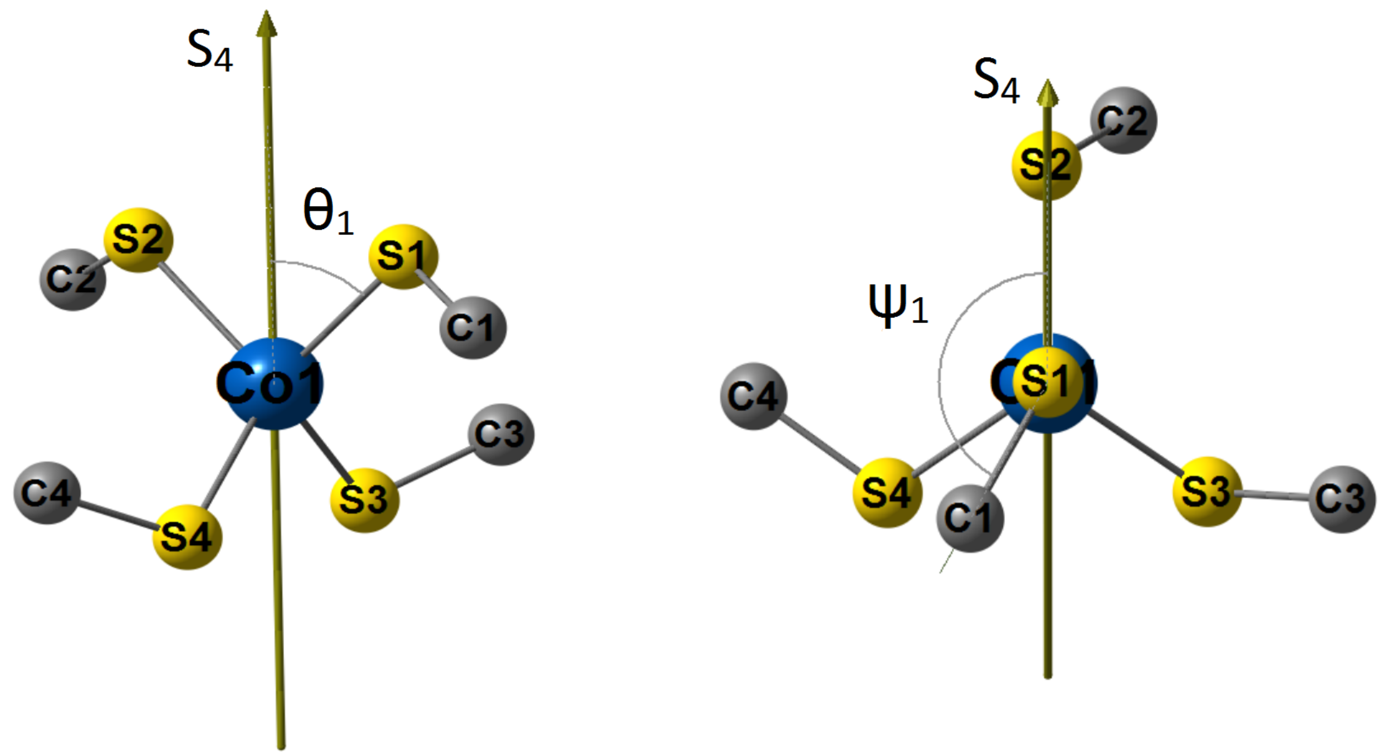
black lines - D (cm^{-1})

➡ 2 local minima

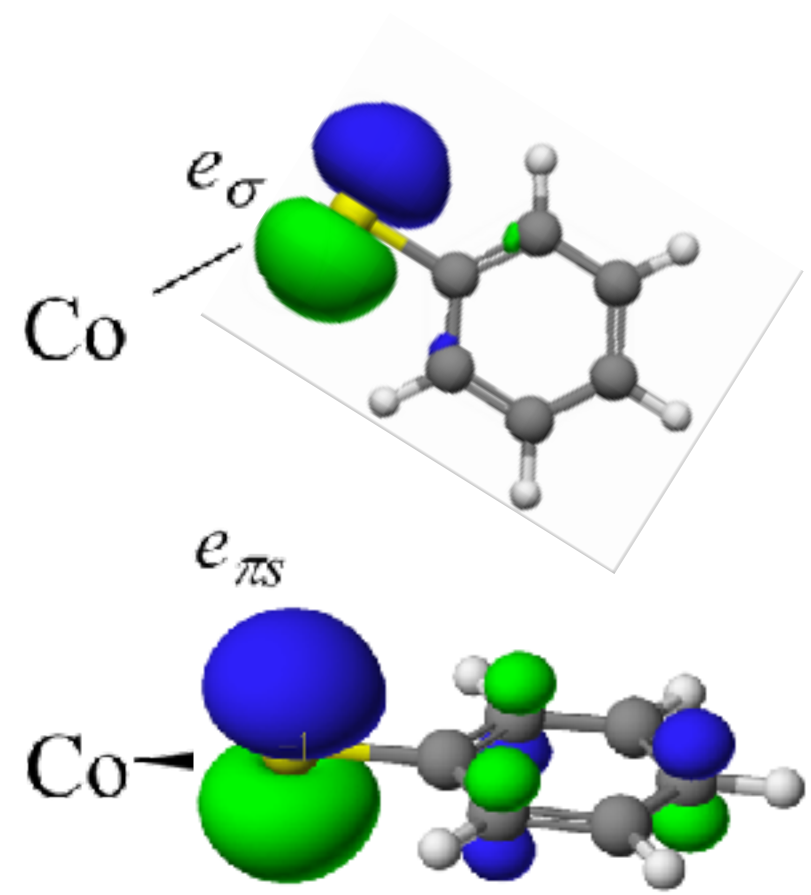
➡ Shallow barrier

2nd sphere effects are responsible for magnetic properties

Qualitative Interpretation: Misdirected Valence



π-anisotropy of metal-ligand bonding:



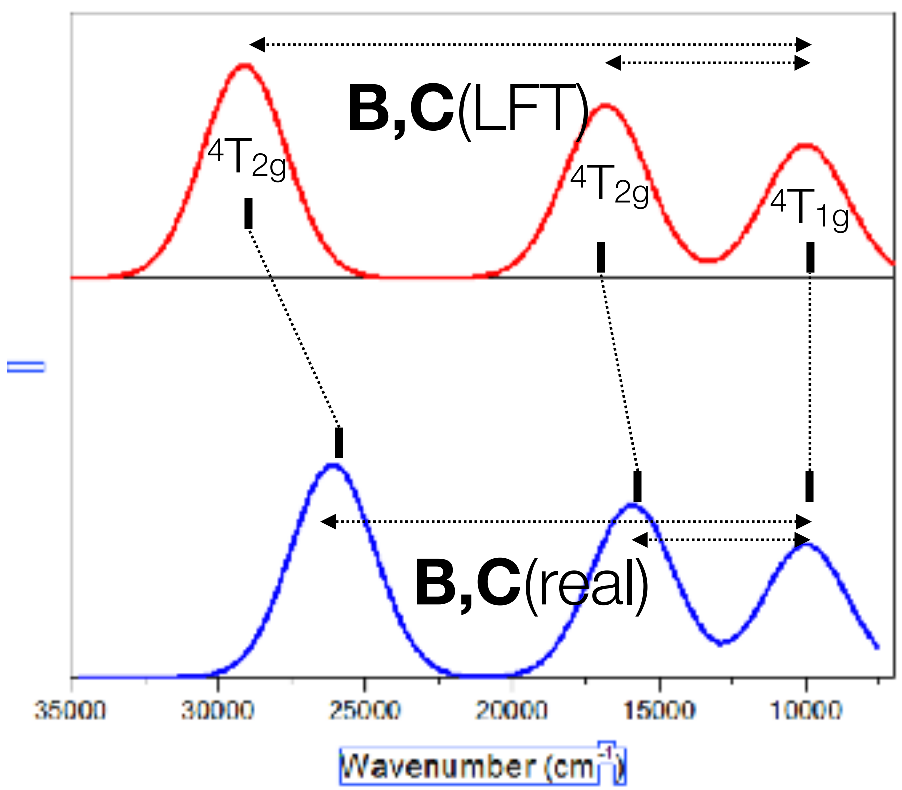
- *Counter Ion/Ligand interactions determine the ligand orientation.*
- Ligand orientation determines lone pair orientations
- Metal/lone-pair interaction determines orbital splittings
- Orbital splittings determine magnetic properties through spin-orbit coupling

} **HUGE second sphere effect on magnetic properties**

Covalency, Oxidation States and MO Theory

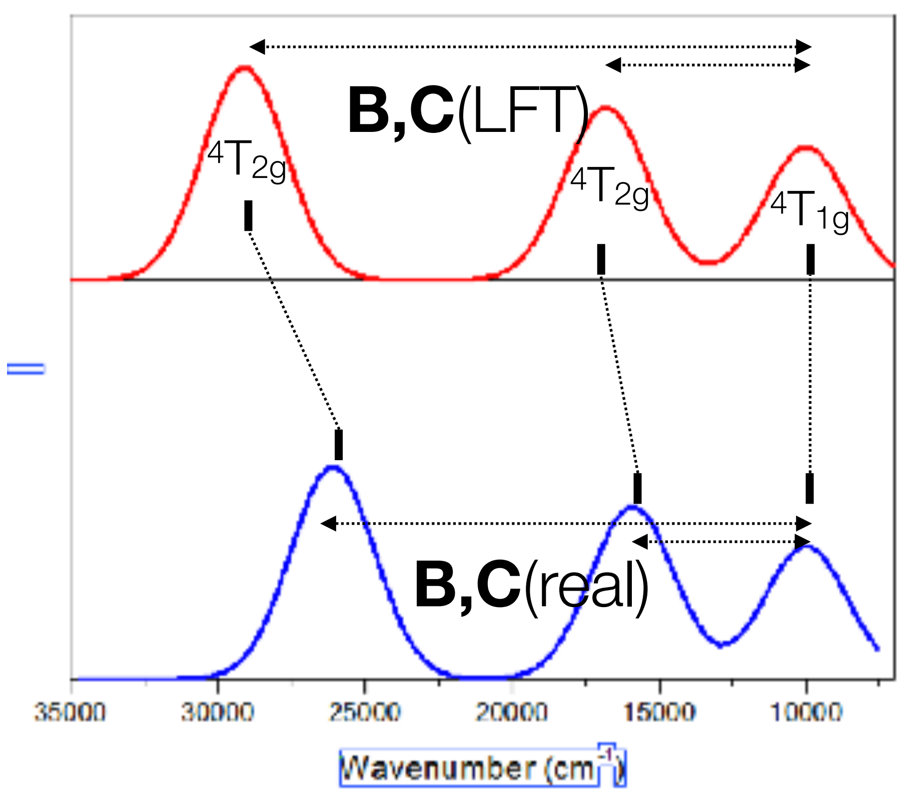
The Nephelauxetic Effects

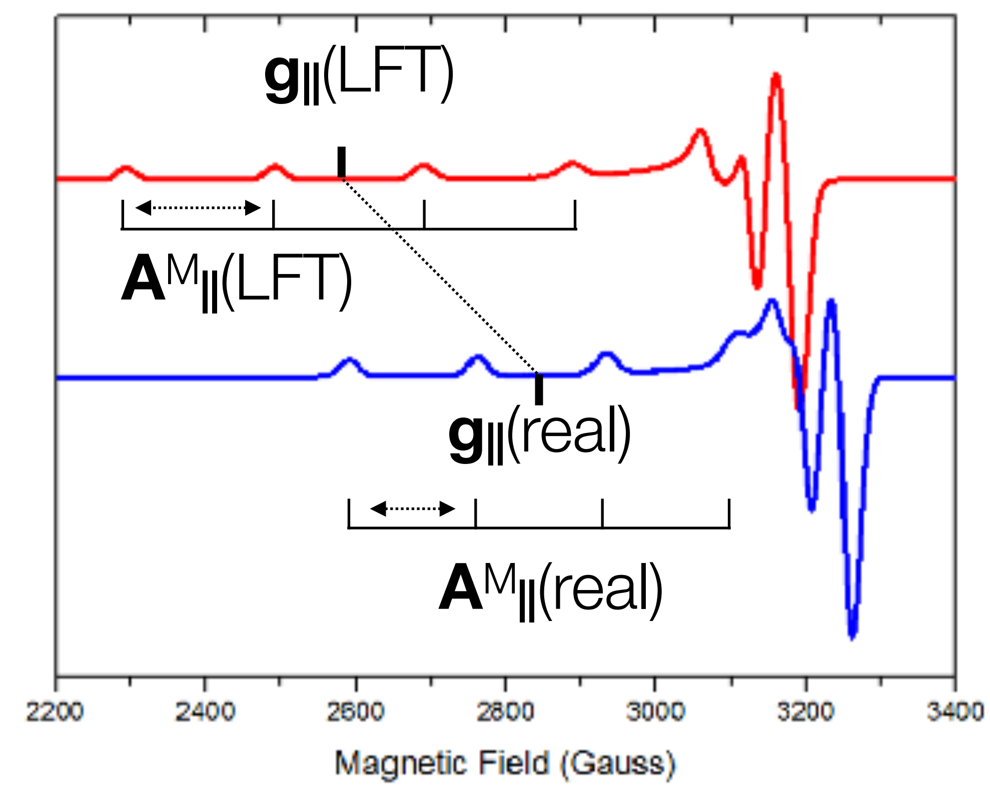
➡ Observation 1: **Racah parameters** fitted for ions in complexes are smaller than those obtained for free-ions from atomic spectroscopy (**nephelauxetic effect**)



The Nephelauxetic Effects

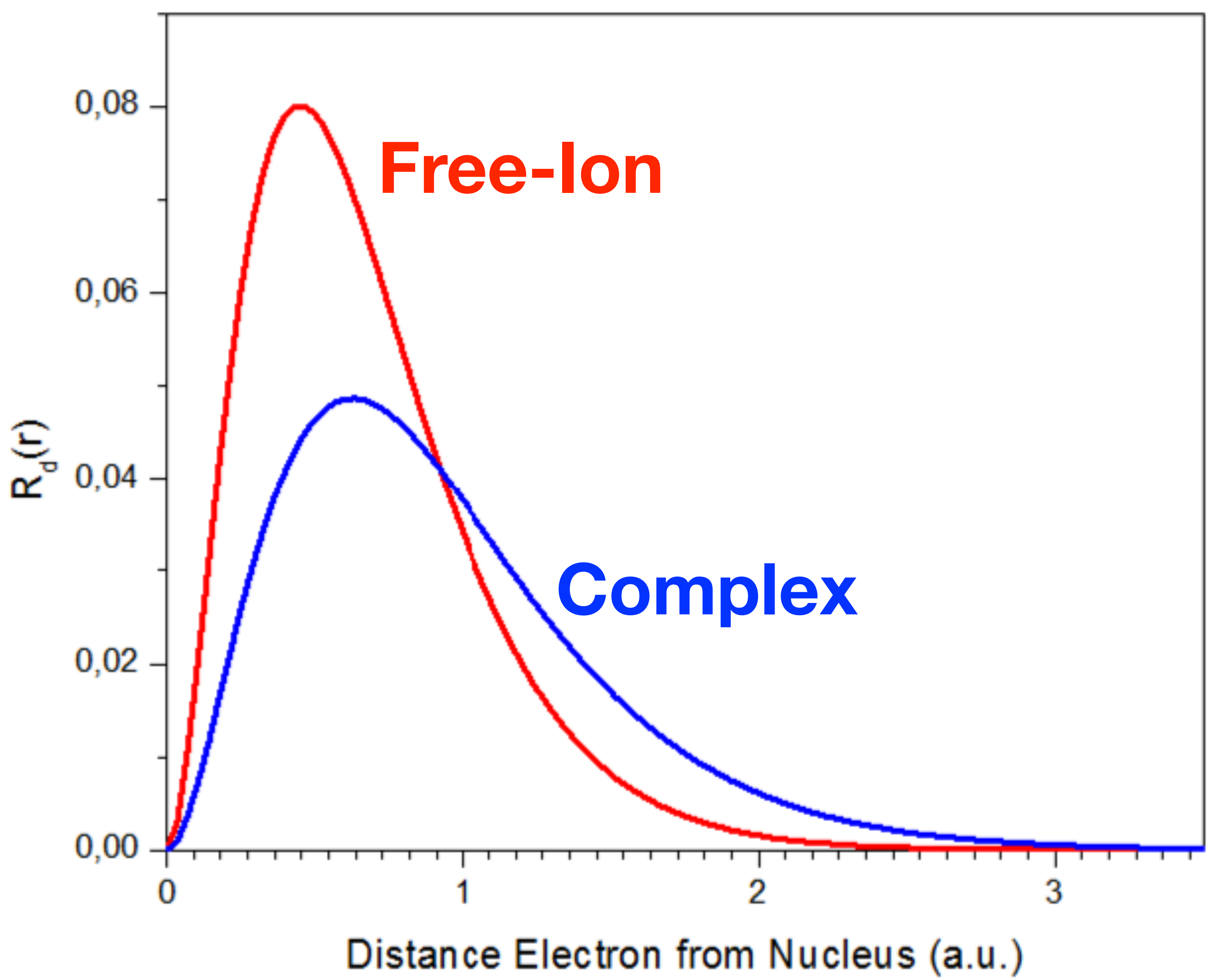
- ➡ Observation 1: **Racah parameters** fitted for ions in complexes are smaller than those obtained for free-ions from atomic spectroscopy (**nephelauxetic effect**)
- ➡ Observation 2: **Spin-Orbit coupling parameters** fitted for ions in complexes are smaller than those obtained for free-ions from atomic spectroscopy (**relativistic nephelauxetic effect**)





Interpretation of the Nephelauxetic Effects

Traditional Interpretation: The radial wavefunction of the metal d-orbitals expand in the complex and hence B and ζ are reduced (*nephelauxetic=‚cloud expanding‘*)



Radial wavefunction

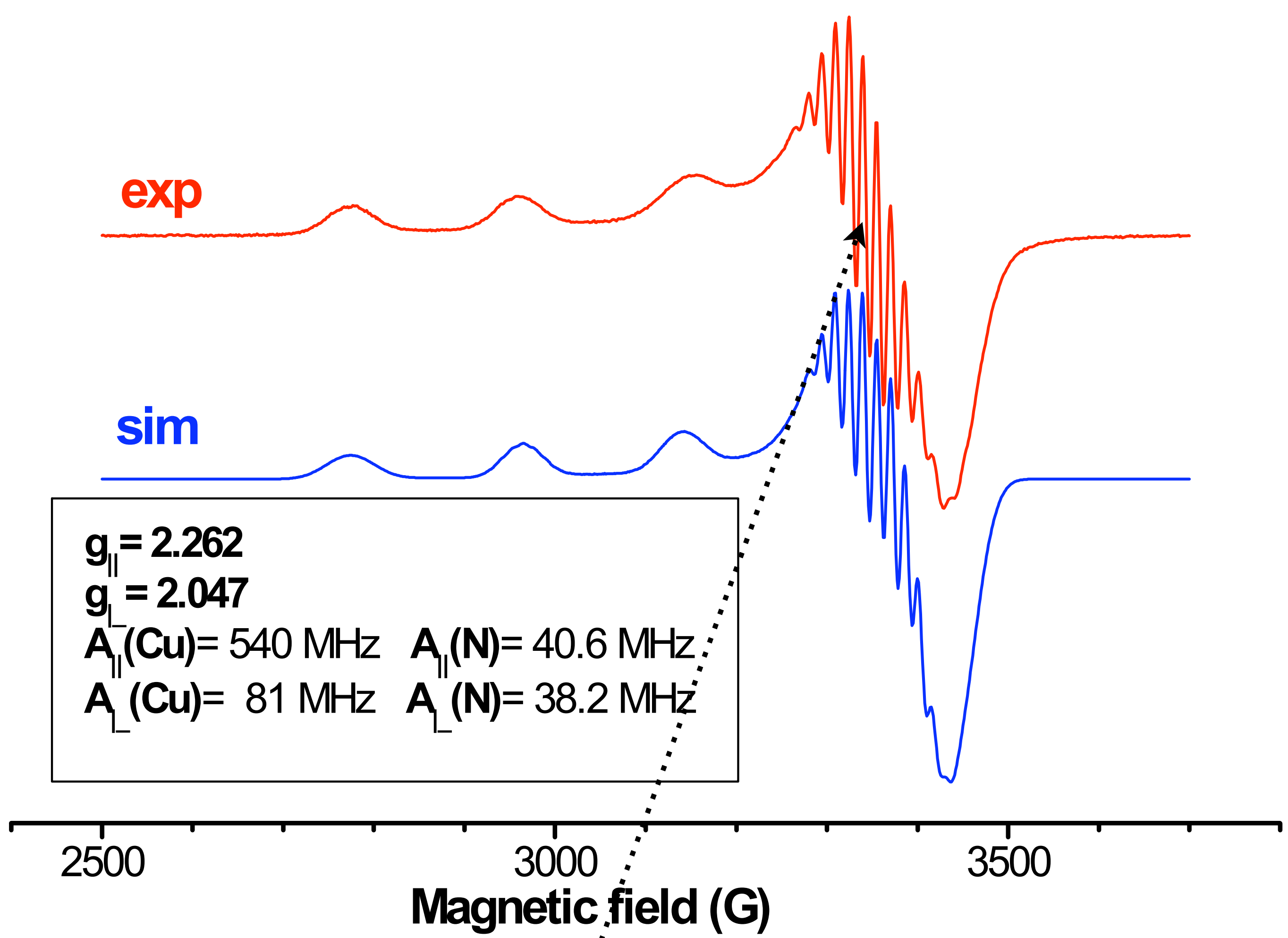
$$R_d(r) = \sqrt{\frac{(2\kappa)^7}{720}}\, r^2 \exp(-\kappa r)$$

$$\zeta_M = \tfrac{1}{30} Z_M^{eff} c^{-2} \kappa^3$$

$$B = \tfrac{143}{80640}\kappa$$

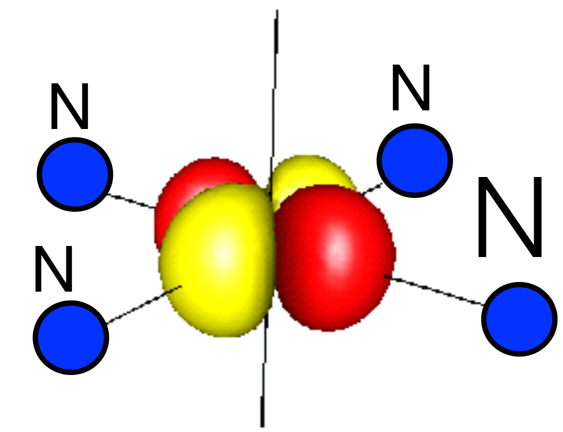
Experimental Proof of the Inadequacy of LFT

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



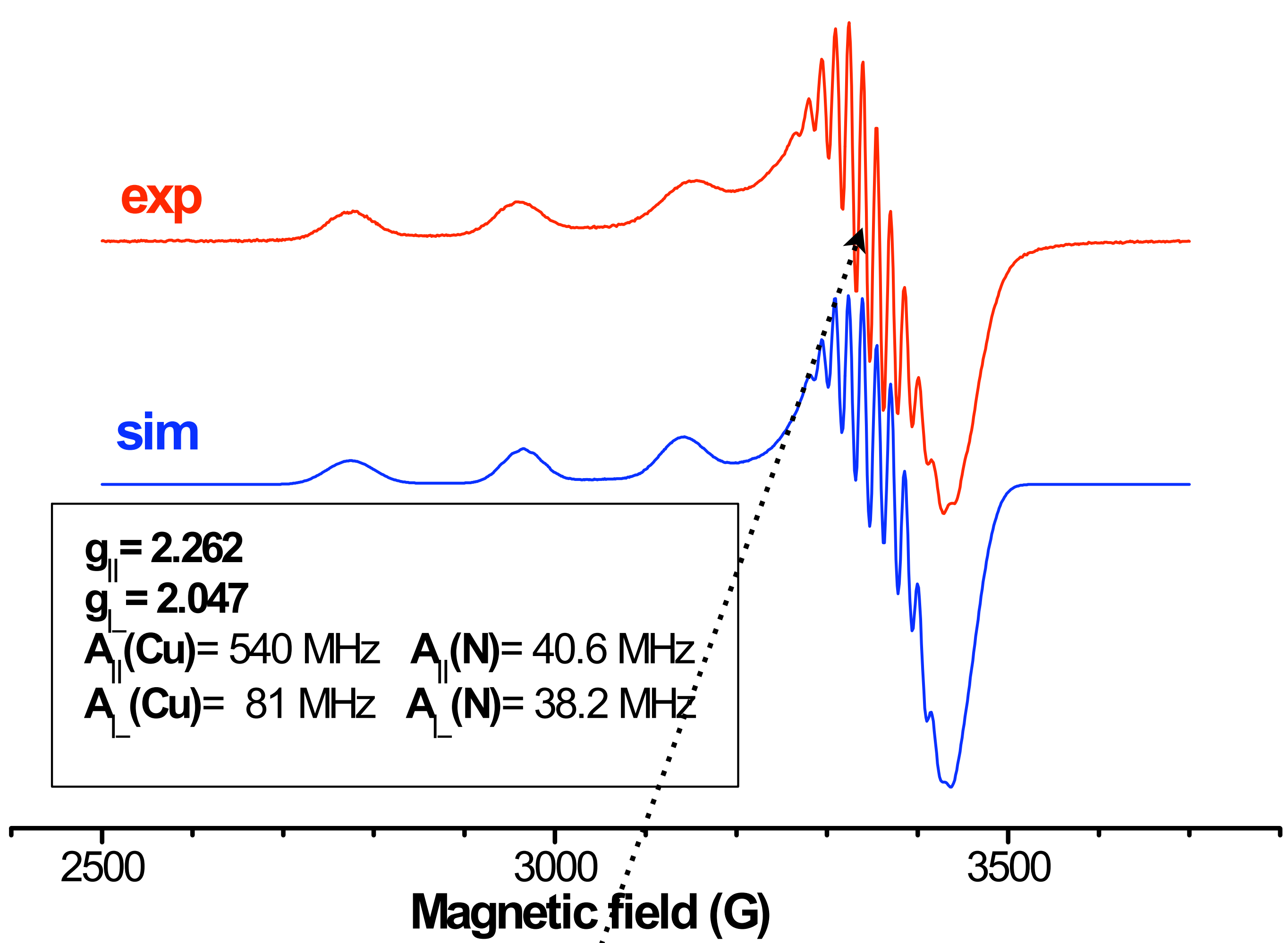
Clearly Observed Coupling Between The Unpaired Electron and the Nuclear Spin of Four ^{14}N Nitrogens (I=1)

Ligand Field Picture



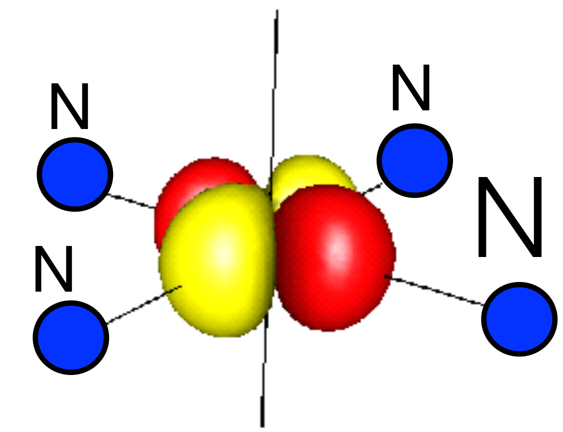
Experimental Proof of the Inadequacy of LFT

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

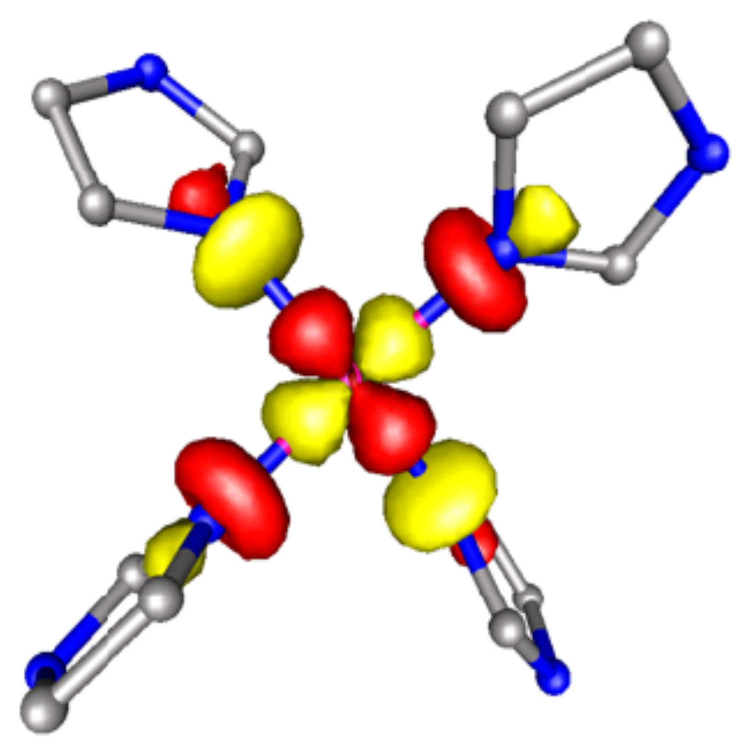


Clearly Observed Coupling Between The Unpaired Electron and the Nuclear Spin of Four ^{14}N Nitrogens (I=1)

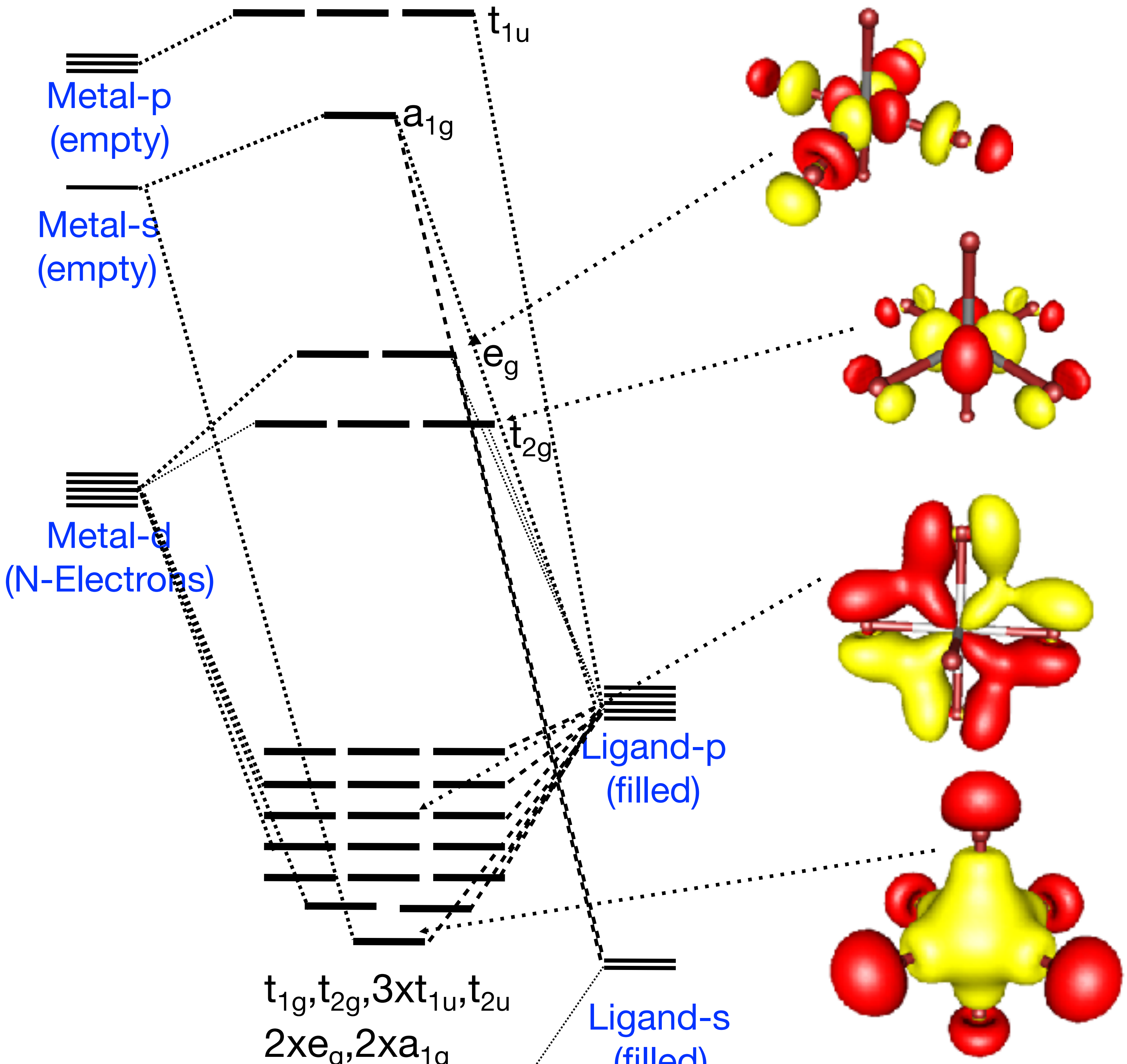
Ligand Field Picture



Molecular Orbital Picture



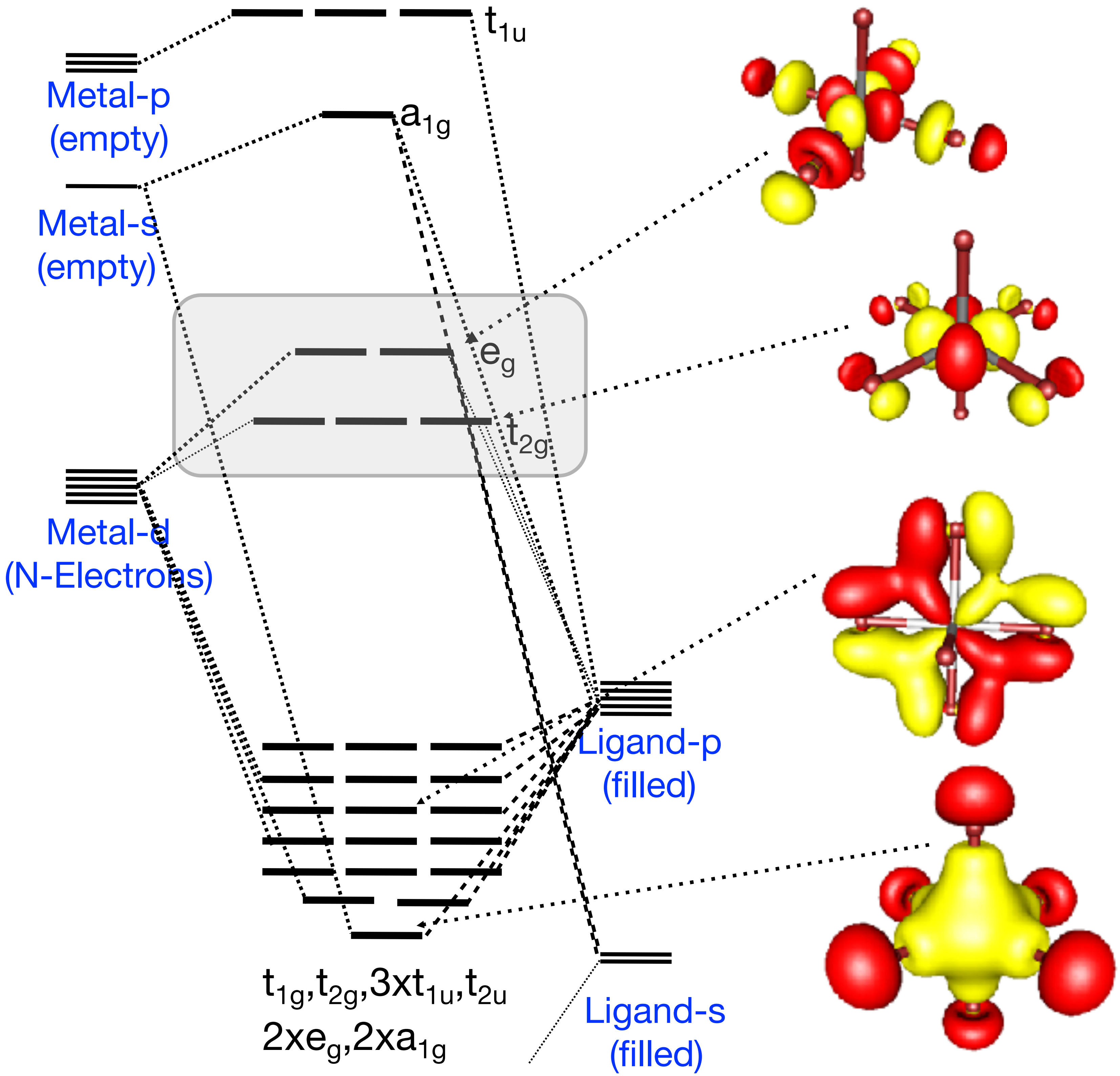
MO Theory of ML_6 Complexes



Key Points:

- **The orbitals that are treated in LFT correspond to the anti-bonding metal-based orbitals in MO Theory**
- Through bonding some electron density is transferred from the ligand to the metal
- The extent to which this takes place defines the covalency of the M-L bond

MO Theory of ML_6 Complexes



Key Points:

- **The orbitals that are treated in LFT correspond to the anti-bonding metal-based orbitals in MO Theory**
- Through bonding some electron density is transferred from the ligand to the metal
- The extent to which this takes place defines the covalency of the M-L bond

Alright then: Now we understand

„Covalency is just the dilution of the d-orbitals with ligand orbitals and the founding fathers where wrong about the cloud expansion“

$$\psi_d \cong \alpha\left|M_d\right\rangle - \sqrt{1-\alpha^2}\left|L\right\rangle$$

Aha effect: The (in)famous ‚Stevens reduction factor‘ is just the d-character in the respective MO squared (α^2)

Alright then: Now we understand

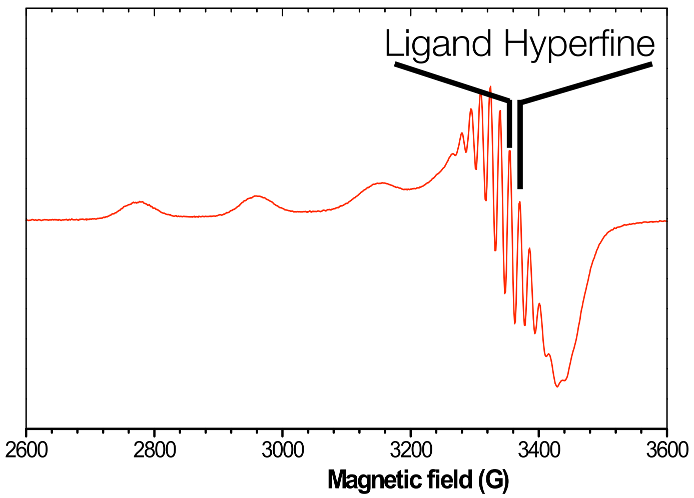
„Covalency is just the dilution of the d-orbitals with ligand orbitals and the founding fathers where wrong about the cloud expansion“

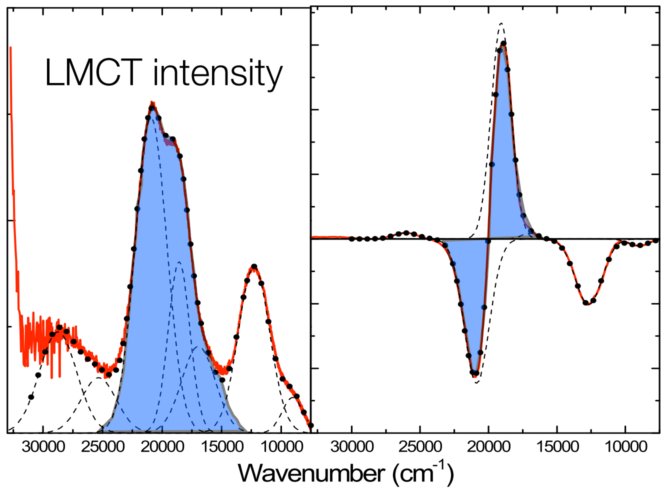
$$\psi_d \cong \alpha \left| M_d \right\rangle - \sqrt{1-\alpha^2} \left| L \right\rangle$$

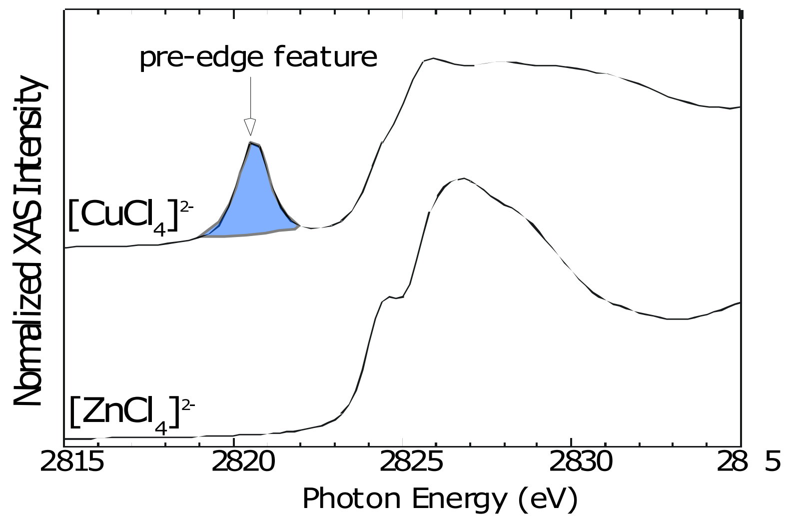
Aha effect: The (in)famous ‚Stevens reduction factor‘ is just the d-character in the respective MO squared (α^2)

„Measurements“ of Covalency?

- Can covalency be measured?
  - Rigorously speaking: NO! Orbitals are not observables!
  - On a practical level: (more or less) YES. Covalency can be correlated with a number of spectroscopic properties
    - **EPR metal- and ligand hyperfine couplings**
    - **Ligand K-edge intensities**
    - **Ligand-to-metal charge transfer intensities**
  - As all of this is „semi-qualitiative“ you can not expect numbers that come out of such an analysis to agree perfectly well. If they do this means that you have probably been good at fudging!





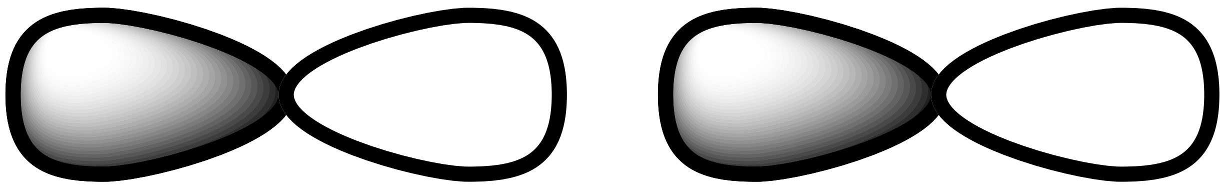


ALL proportional to 1-α²

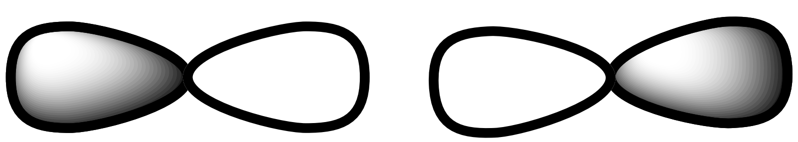
… but that is still too simple …

Rüdenberg's Analysis of the Chemical Bond

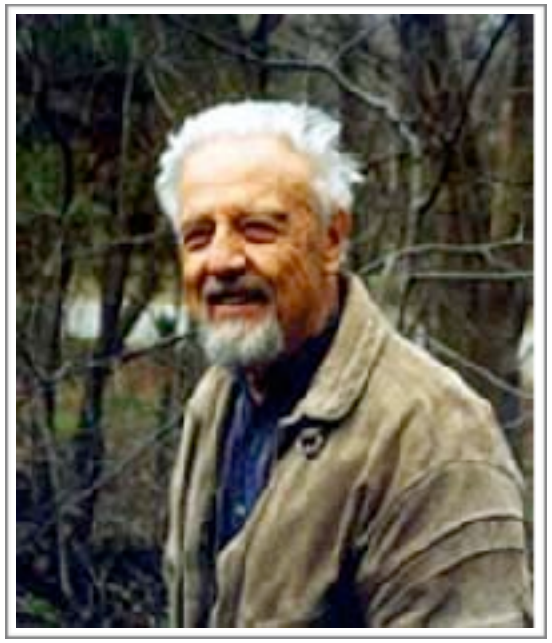
In order to maintain the balance between potential and kinetic energy required by the viral theorem (-2T=V) orbitals have to expand or contract upon bond formation



Antibonding orbital: ***expansion***



Bonding orbital: ***contraction***

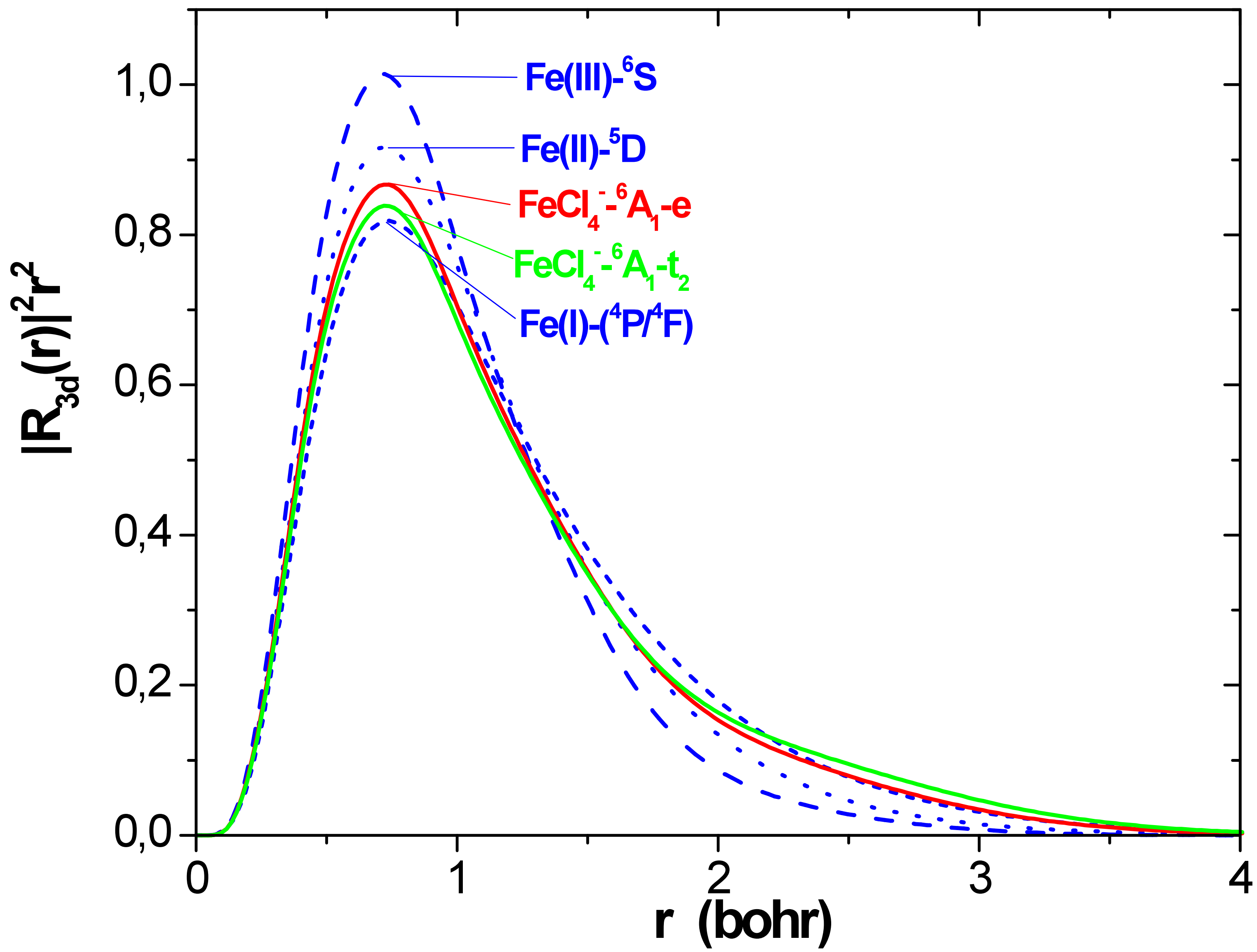


Klaus Rüdenberg
(1920-)

➡ Metal d-based molecular orbitals are anti bonding - hence there is radial expansion!

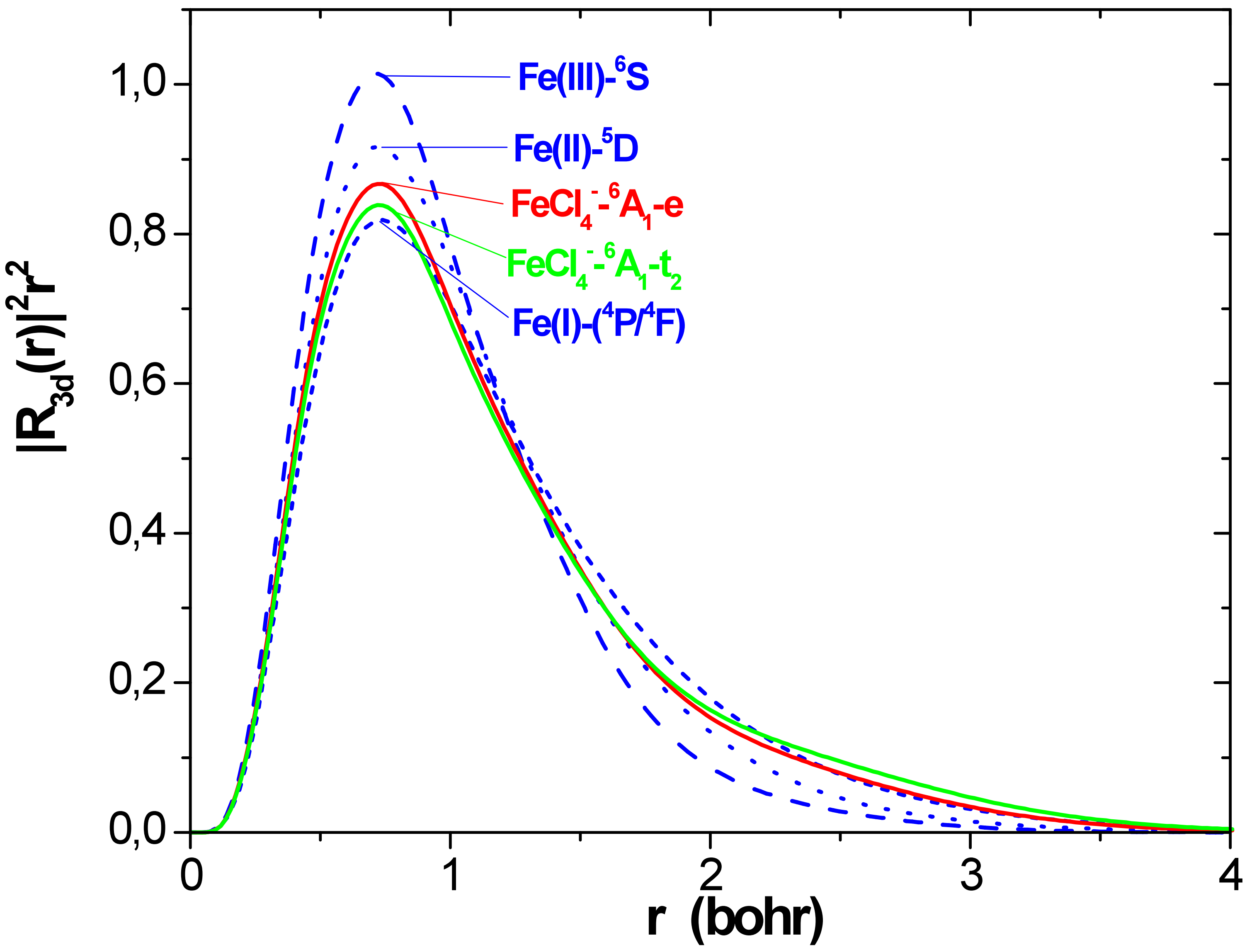
a) Rüdenberg, K. *Rev. Mod. Phys.* **1962**, *34*, 326 b) Feinberg, M. J.; Rüdenberg, K.; Mehler, E. L. *Adv. Quantum Chem.* **1970**, *5*, 27 c) Feinberg, M. J.; Rüdenberg, K. *J. Chem. Phys.* **1971**, *59*, 1495.

Central Field Covalency



F. Neese, E. I. Solomon, *Inorg. Chem.* **1998**, *37*, 6568-6582.

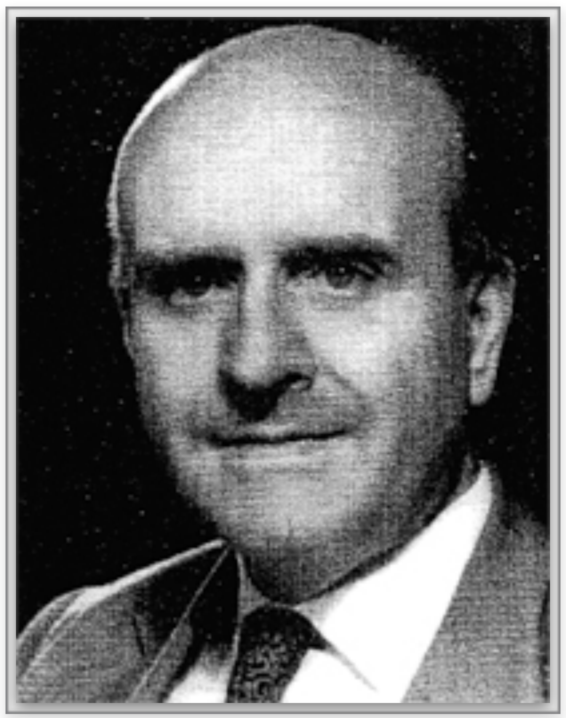
Central Field Covalency



- The founding fathers of ligand field were partially right by assuming cloud expansion
- However: the magnitude of the effect was grossly overestimated
- The explanation given (electrostatic effects, effective nuclear charge) was wrong

F. Neese, E. I. Solomon, *Inorg. Chem.* **1998**, *37*, 6568-6582.

Bottom line up to this point:



Christian Klixbüll Jörgensen

(1931-2001)

There are 2 types of covalency:

1) Symmetry restricted covalency

Metal d-orbital dilution

(entirely correct)

2) ‚Central field' covalency

Metal radial expansion

(effect correct but mechanism incorrect)

… but is that the whole picture then?

… but is that the whole picture then?

… We need to be able to calculate ligand field parameters (10Dq, B,C) from accurate first principles electronic structure theory!

Unambiguous Match between NEVPT2 and LFT

Overwhelming importance:

There is a 1:1 correspondance between the ligand field CSFs and the CAS-CI CSFs.

$$\Theta_I^{LFT} = | d_{xy}^{\alpha} d_{xz}^{\beta} \ldots d_{z^2}^{\alpha} | \qquad \Theta_I^{CASSCF} = | \psi_{xy}^{\alpha} \psi_{xz}^{\beta} \ldots \psi_{z^2}^{\alpha} |$$

Ligand field pure d-orbital

***Ab initio* molecular orbital with metal d-parentage**

Thus, all we have to ensure is that ligand field d-orbitals and CASSCF molecular orbitals of the same parentage are ordered in the same way and that CSFs are constructed in the same way.

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN Struct. Bond, **2012**, 143, 149-220

Unambiguous Match between NEVPT2 and LFT

Overwhelming importance:

There is a 1:1 correspondance between the ligand field CSFs and the CAS-CI CSFs.

$$\Theta_I^{LFT} = \left| d_{xy}^{\alpha} d_{xz}^{\beta} \ldots d_{z^2}^{\alpha} \right| \qquad \Theta_I^{CASSCF} = \left| \psi_{xy}^{\alpha} \psi_{xz}^{\beta} \ldots \psi_{z^2}^{\alpha} \right|$$

Ligand field pure d-orbital

***Ab initio* molecular orbital with metal d-parentage**

Thus, all we have to ensure is that ligand field d-orbitals and CASSCF molecular orbitals of the same parentage are ordered in the same way and that CSFs are constructed in the same way.

The condition is then that the ligand field CI matrix should resemble the *ab initio* effective Hamiltonian as closely as possible

$$\left| H_{IJ}^{LFT} - H_{IJ}^{eff} \right| = \min$$

For each matrix element!

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN Struct. Bond, **2012**, 143, 149-220

While this looks at first sight to be a nonlinear optimization problem, in reality things are easy ***because the ligand field matrix is linear in each and every ligand field parameter!***

$$\mathbf{H}^{LFT}(e,B,C) = \mathbf{H}^{LFT}(0) + \frac{\partial \mathbf{H}^{LFT}}{\partial B}B + \frac{\partial \mathbf{H}^{LFT}}{\partial C}C + \sum_L \frac{\partial \mathbf{H}^{LFT}}{\partial e_L}e_L$$

This ensures that there is a **unique least squares solution** that provides the unambiguous best fit of the ligand field and effective Hamiltonian matrices:

$$\mathbf{A}\mathbf{p} = -\mathbf{b} \;\Leftrightarrow\; \mathbf{p} = -\mathbf{A}^{-1}\mathbf{b}$$

$p_K =$ The k'th ligand field parameter

$$A_{KL} = \sum_{IJ} \frac{\partial H_{IJ}^{LFT}}{\partial p_K}\frac{\partial H_{IJ}^{LFT}}{\partial p_L}$$

$$b_K = \sum_{IJ} \frac{\partial H_{IJ}^{LFT}}{\partial p_K} H_{IJ}^{eff}$$

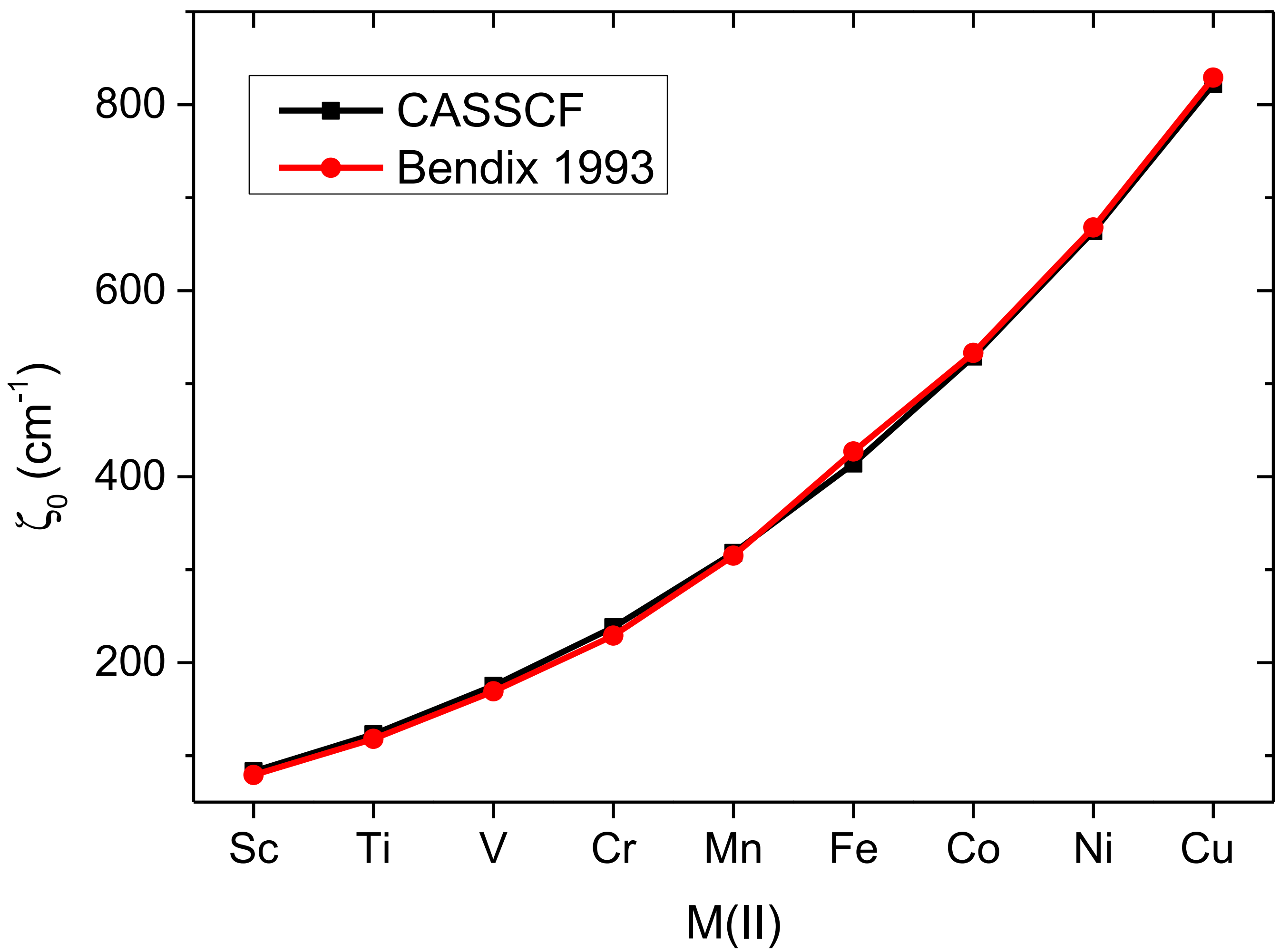
This implies the strategy:

1. Choose your AOM scheme
2. Perform a QD-NEVPT2 calculation to obtain H^{eff}
3. Solve linear equation system to obtain the ligand field parameters

Atanasov, M.; Sivalingam, K.; Ganyushin, D.; FN Struct. Bond, **2012**, 143, 149-220

Revisiting Covalency from an *Ab Initio* Ligand Field Perspective

Results for The Spin-Orbit Coupling Constant



➡ Spin-Orbit Coupling parameters are *extremely* well reproduced, already at CASSCF

A model for the Relativistic Mephelauxetic Effect

For Molecules: Decomposition of the SOC constant into contributions from symmetry restricted and central field covalency

$$\zeta_{complex} = \zeta_{ion}\left(1 - \underbrace{\gamma_M^{SR}}_{\text{covalent dilution proportional to } \alpha^2} - \underbrace{\gamma_{CF}}_{\text{Central Field}} - \underbrace{\gamma_L}_{\text{Ligand SOC part}}\right)$$

proportional to κ^3

$$h_{SOC} \propto \frac{1}{c^2}\sum_A \frac{Z_A^{eff}}{\left|\mathbf{r}-\mathbf{R}_A\right|^3}\mathbf{l}^{(A)}\mathbf{s}$$

Hence

$$\left\langle \psi_d \mid h_{SOC} \mid \psi_{d'} \right\rangle \approx \sum_A \alpha_A^2 \zeta^{(A)} \left\langle \psi_d \mid \mathbf{l}^{(A)}\mathbf{s} \mid \psi_{d'} \right\rangle$$

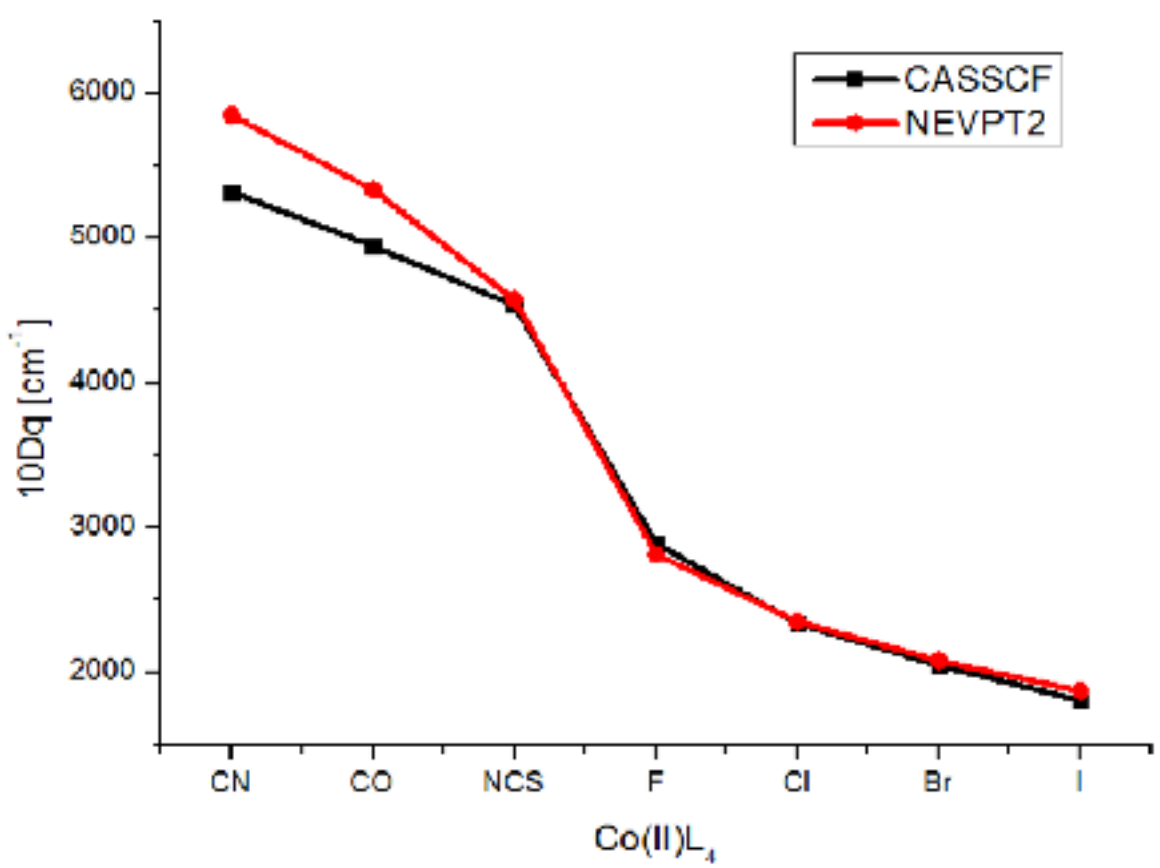
A very local operator! To a good approximation sum of quasi-atomic contributions weighted by covalent dilution factors

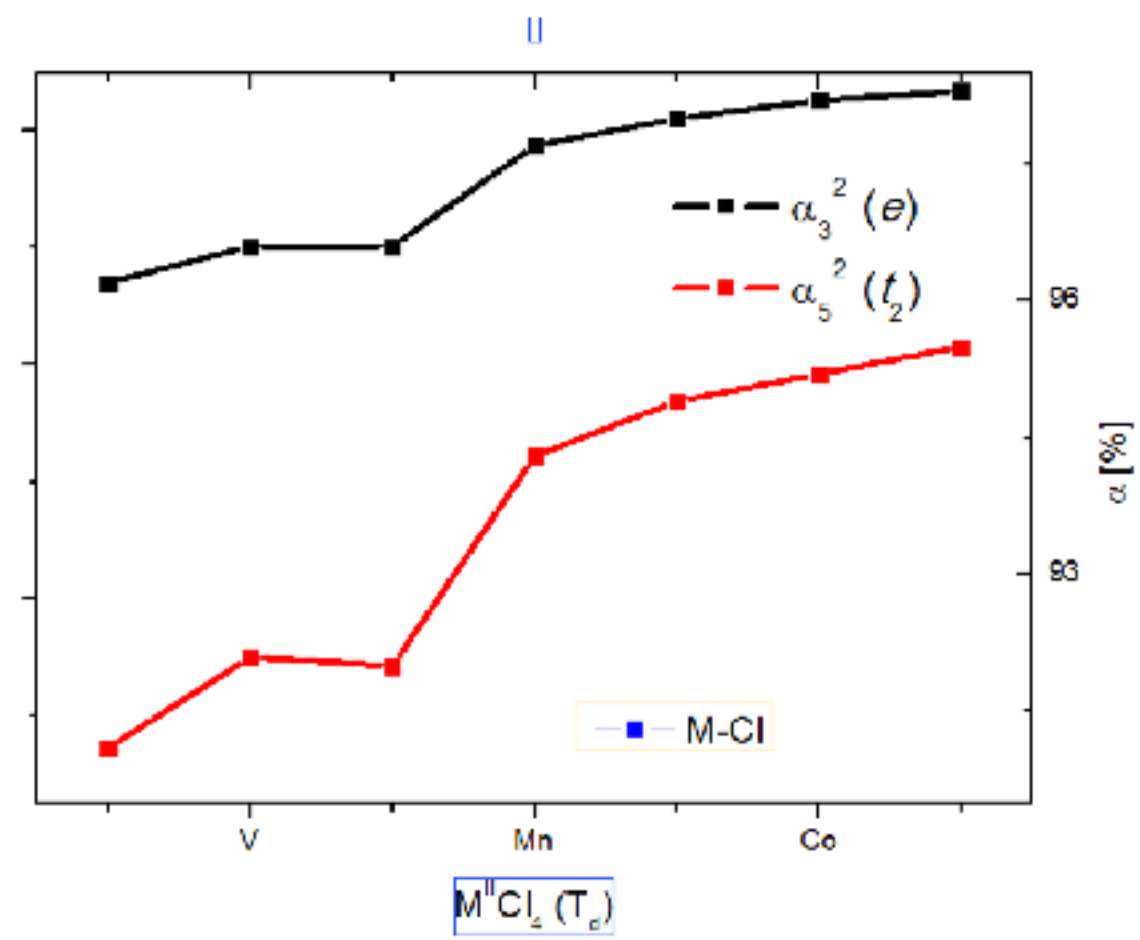
Very similar to an anisotropic version of the ‚classical' Steven's reduction factors

Results for Molecules

In silico Studies: **$[M^{II}Cl_4]^{2-}$ (M=Ti-Zn)** Metal-variation

$[Co^{II}L_4]^{2-}$ ($L=F^-,Cl^-,Br^-,I^-,CN^-,NCS^-$) Ligand-variation





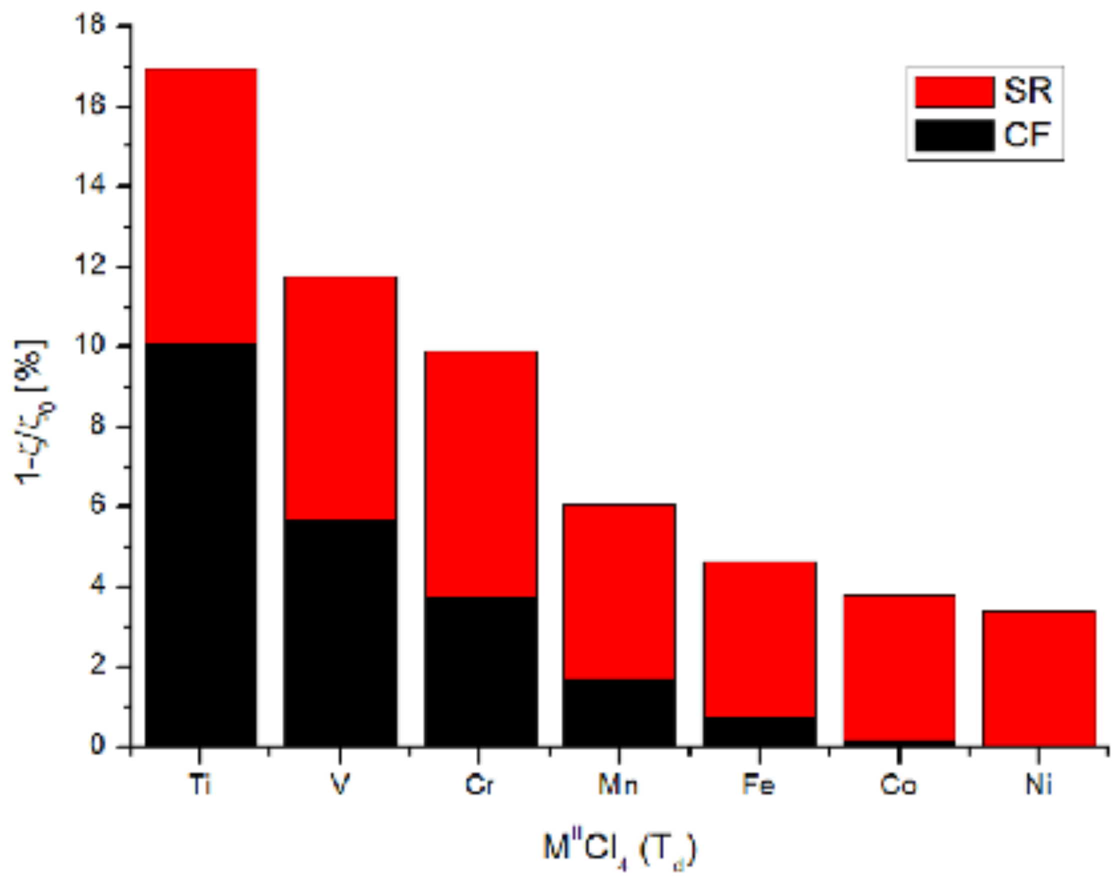
➡ Expected trends in Ligand Fields

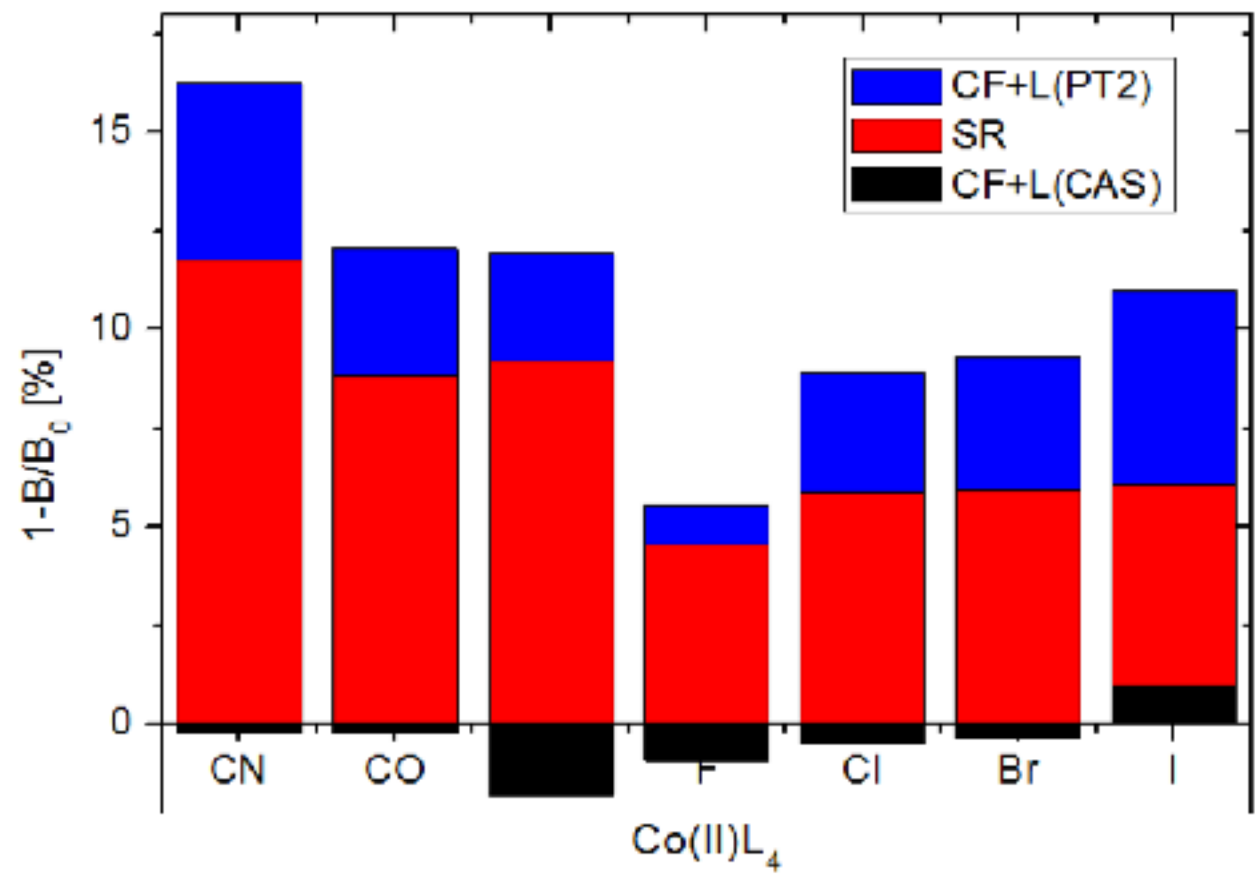
➡ Expected trends in symmetry restricted covalency

Everything chemically reasonable: Now analyze

The Relativistic Nephelauxetic Effect: Results

$$\gamma_{SR} = 1 - \alpha^2 \qquad \gamma_{CF} = 1 - \frac{\zeta_M}{\alpha^2 \zeta_{ion}} \qquad \gamma_L = 1 - \frac{\zeta_{complex} - \zeta_M}{\zeta_{ion}}$$



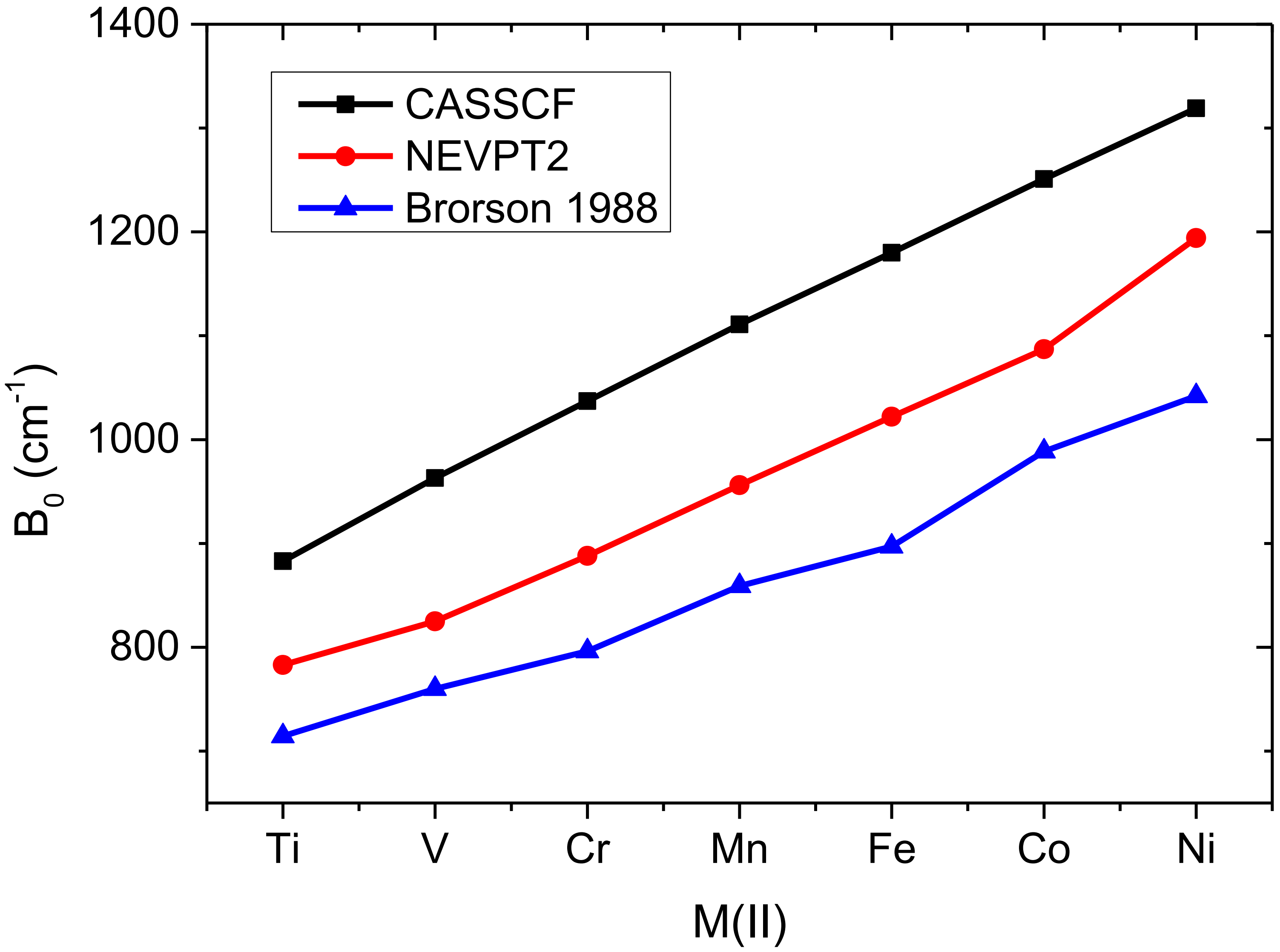


- ➡ For late transition metals symmetry restricted covalency dominates, for early, central field covalency
- ➡ Ligand contribution only sizable for heavy ligand; typically negative

Bottom Line:

The classical picture of interplay between central field and symmetry restricted covalency works well for the interpretation of the relativistic nephelauxetic effect

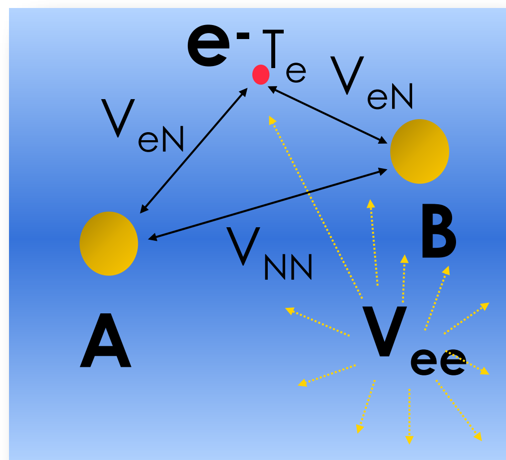
AILFT Results for B-Parameters of Free Ions



- ➡ Racah parameters are overestimated by CASSCF and only slightly overestimated by NEVPT2
- ➡ **DYNAMIC ELECTRON CORRELATION**

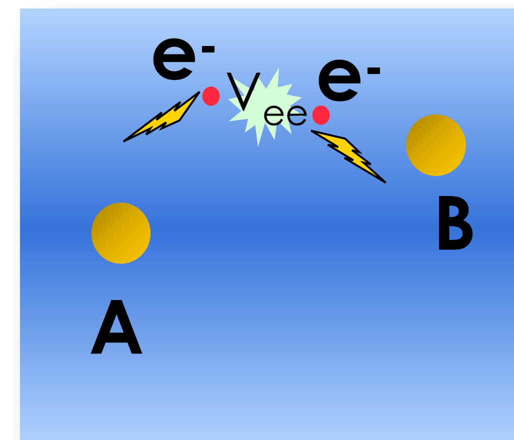
What is Dynamic Electron Correlation?

Exact Energy =



"Mean Field"
Hartree-Fock

+

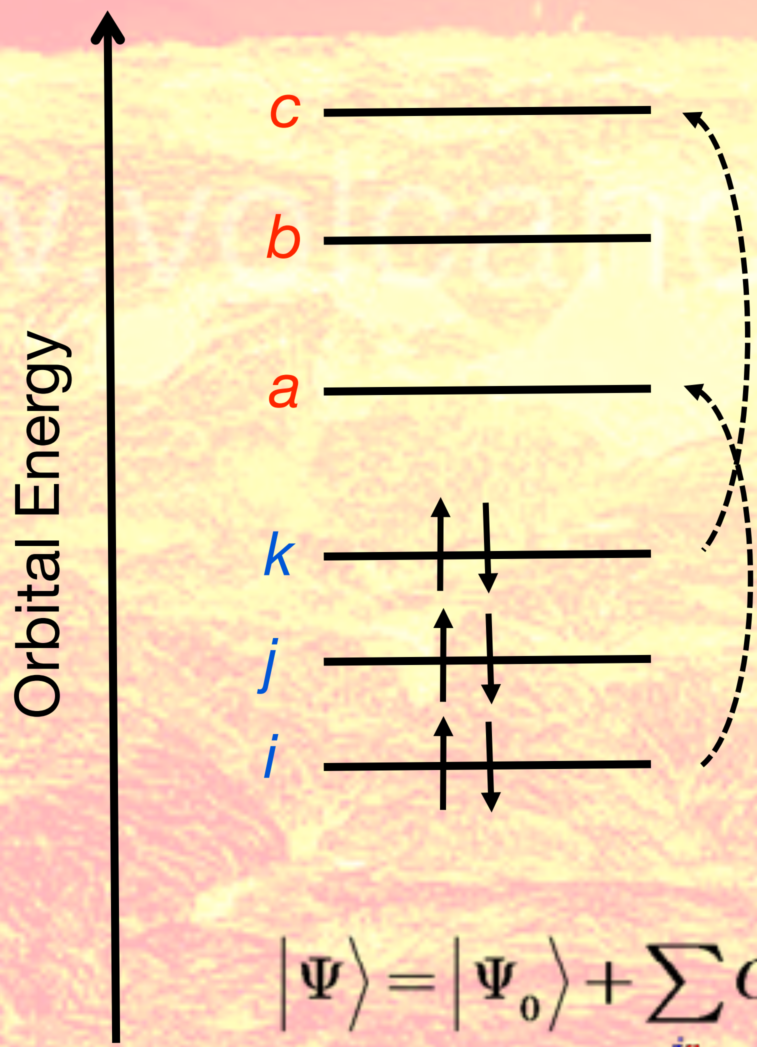


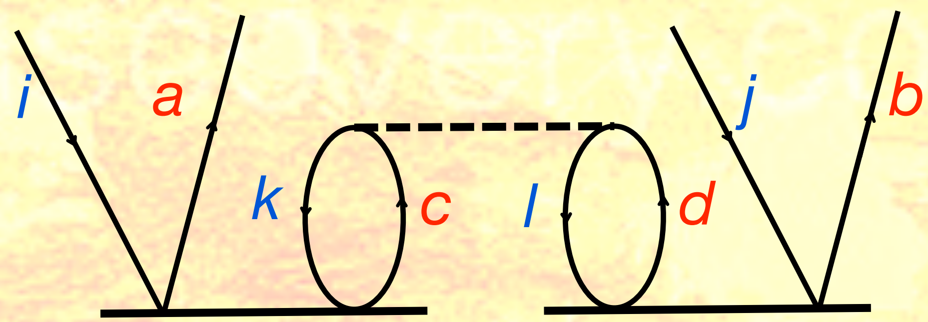
Instantaneous electron-electron interaction

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

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

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

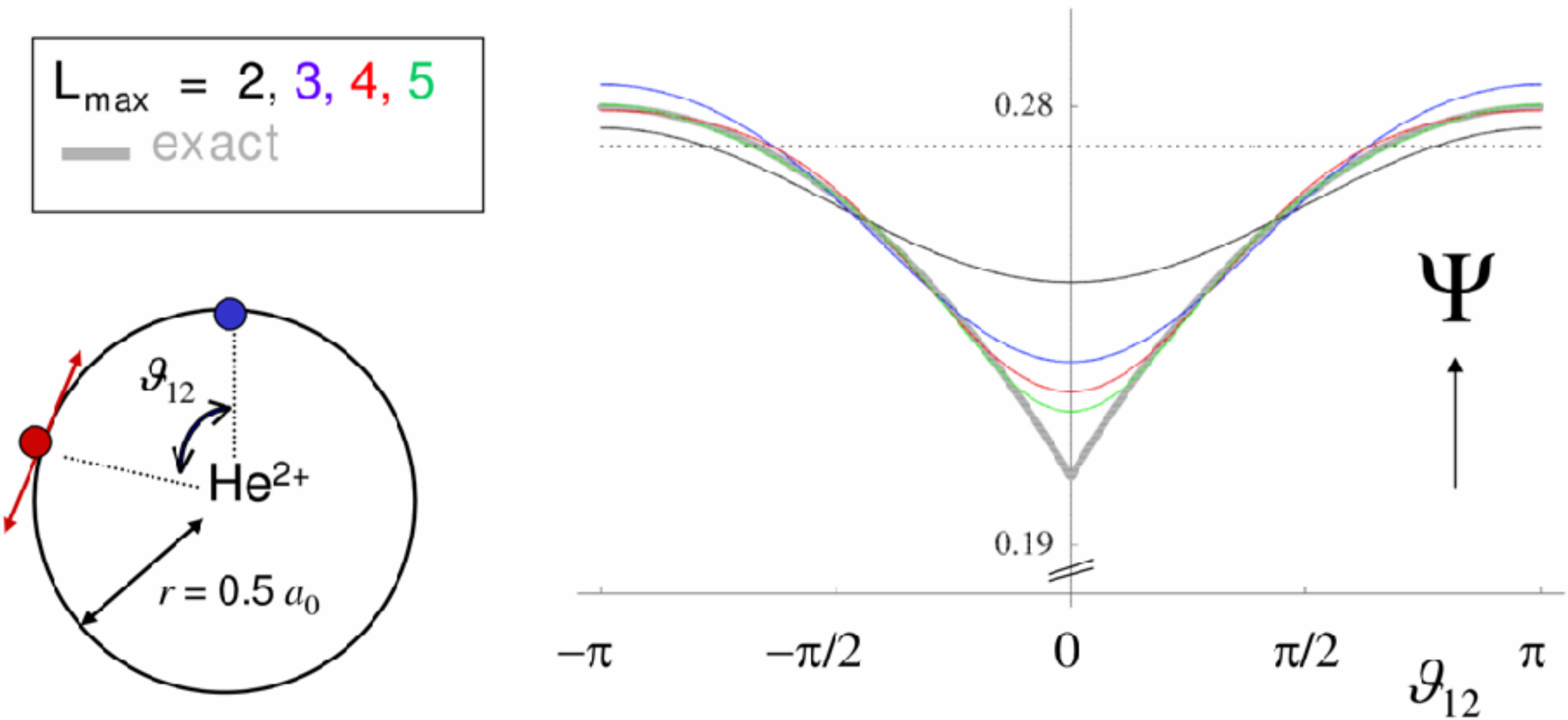




$$\tfrac{1}{2}P_{ij}P_{ab}\sum_{klcd}\langle kl \| cd\rangle t^{ik}_{ac}t^{lj}_{db}$$

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

Another View: The Electron-Electron Cusp

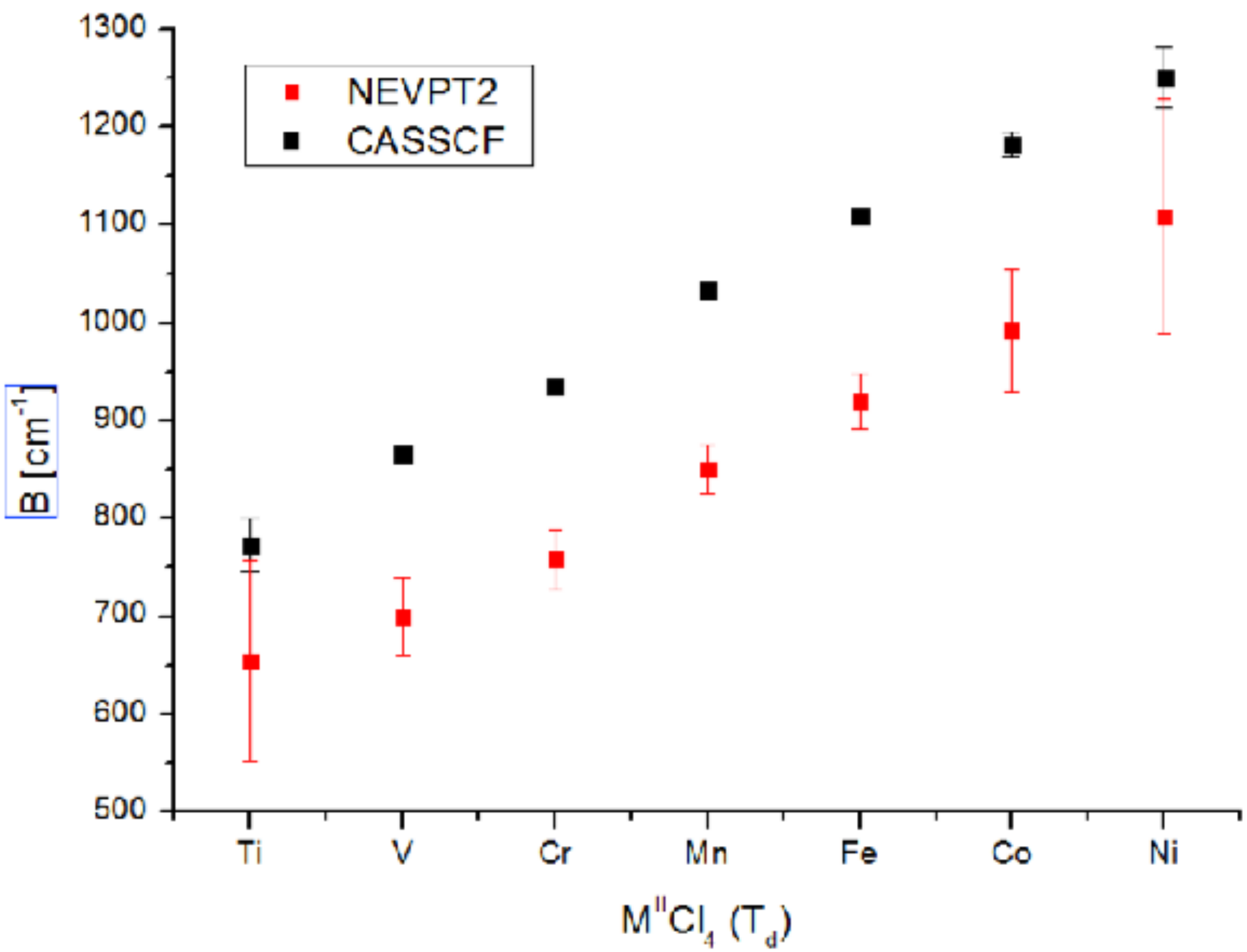


$$\Psi(r_{12}) = \Psi(r_{12}{=}0)(1 + 0.5r_{12} + \ldots)$$

Racah B Parameters for Complexes

In Silico Studies: **$[M^{II}Cl_4]^{2-}$ (M=Ti-Zn)** Metal-variation

$[Co^{II}L_4]^{2-}$ ($L=F^-,Cl^-,Br^-,I^-,CN^-,NCS^-$) Ligand-variation



- ➡ Expected trends in Racah B -parameters
- ➡ Similary **LARGE** effects of dynamic correlation (10-30% of B!)

Attempted Decomposition of B

Try the equivalent decomposition

$$B_{complex} = B_{ion}(1 - \delta_M^{SR} - \delta_{CF} - \delta_L)$$

covalent dilution prop. to α^4	***Central Field prop. to κ***	*Ligand repulsion part*
Compared to α^2 for ζ	***Compared to κ^3 for ζ***	

- ➡ **There is no intrinsic locality in B**
- ➡ **B can NOT be decomposed as ζ**

Attempted Decomposition of B

Try the equivalent decomposition

$$B_{complex} = B_{ion}\left(1 - \delta_M^{SR} - \delta_{CF} \boxed{- \delta_L}\right)$$

covalent dilution prop. to α^4

Central Field prop. to κ

Ligand repulsion part

Compared to α^2 for ζ

Compared to κ^3 for ζ

NOT small NOT local

- ➡ **There is no intrinsic locality in B**
- ➡ **B can NOT be decomposed as ζ**

Effect of Dynamic Correlation on B

Gedankenexperiment:

We can nicely decompose ζ.

- ✓ Hence, we can use the value of ζ_M to deduce an effective orbital exponent κ
- ✓ We can then use this exponent to calculate B
- ✓ This would gives us the central field field effect on B

However:

- ➡ Because of dynamic correlation this value of B is MUCH too large!
- ➡ Which exponent would we need to reproduce the molecular B?

Example: $[Co^{II}(SR)_4]^{2-}$

From ζ: $\kappa = 4.46$

Compared to κ=3.95 for a free ion (Clementi)

From B: $\kappa = 2.78$

MUCH too diffuse
effective treatment of dynamic correlation!

Bottom Line:

The analysis of the covalent dilution and radial distortion is missing two key contributions to B:

(1) DYNAMIC ELECTRON CORRELATION

(2) The fact that B is NOT LOCAL

Summing up: What really is Covalency?

➡ **Covalency** is strictly a **ONE-ELECTRON PHENOMENON**:

Symmetry restricted covalency: Covalent ‚dilution‘ of metal orbitals

Central Field covalency: Radial distortion due to BONDING

Both effects work differently for B and ζ.

	Symmetry	Central Field	Local
B	α^4	κ_{eff}	NO
ζ	α^2	κ_{eff}^3	YES

➡ **A single reduction factor does NOT cover both effects**

➡ B can **not** be understood without recourse to ‚dynamic electron correlation‘, which is strictly a **TWO-ELECTRON PHENOMENON**. It is not part of covalency
(*disclaimer*: covalency as I understand it)

Measuring Covalency?

What is Covalency?

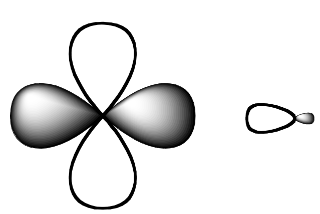
★ **Covalency refers to the ability of metal and ligand to share electrons** („soft“ concept with no rigorous definition)

★ Operationally, covalency can be defined in MO theory from the mixing coefficients of metal- and ligand orbitals

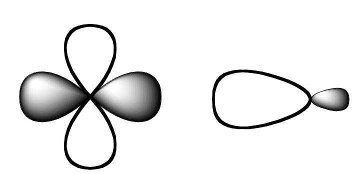
$$\psi_i \cong \alpha_i \left| M_i \right\rangle - \sqrt{1-\alpha_i^2} \left| L_i \right\rangle \qquad \text{(overlap neglected)}$$

★ The value $1-\alpha^2$ can be referred to as „the covalency“ of the specific metal ligand bond. It is the probability of finding the electron that occupies ψ_i at the ligand

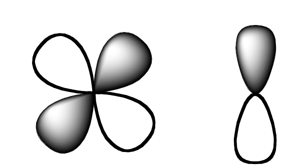
- *The maximal covalency is 0.5, e.g. complete electron sharing*
- *The covalency might be different in σ- and π-bonds (e.g. it is anisotropic)*
- *In σ-donor and π-donor bonds these are antibonding. The bonding counterparts are occupied and lower in energy*
- *In π-acceptor bonds these orbitals are bonding. The antibonding counterparts are higher in energy and unoccupied*



Typical Ionic bond; hard ligands
Werner type complexes
α^2=0.8-0.9



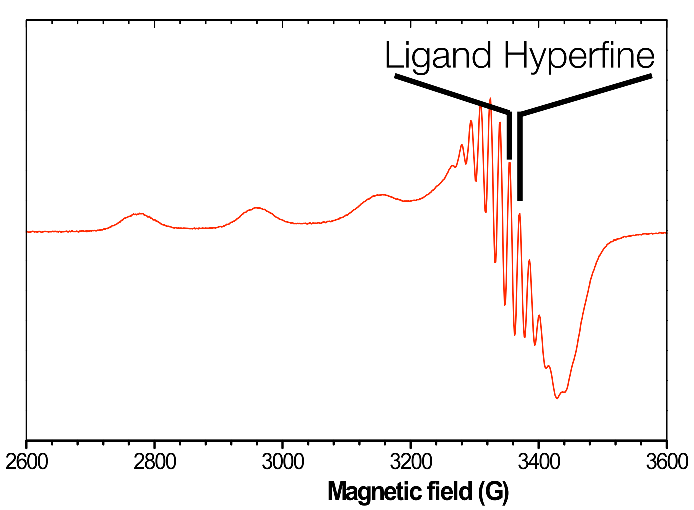
Typical covalent bond
Organometallics; soft ligands
α^2=0.5-0.8

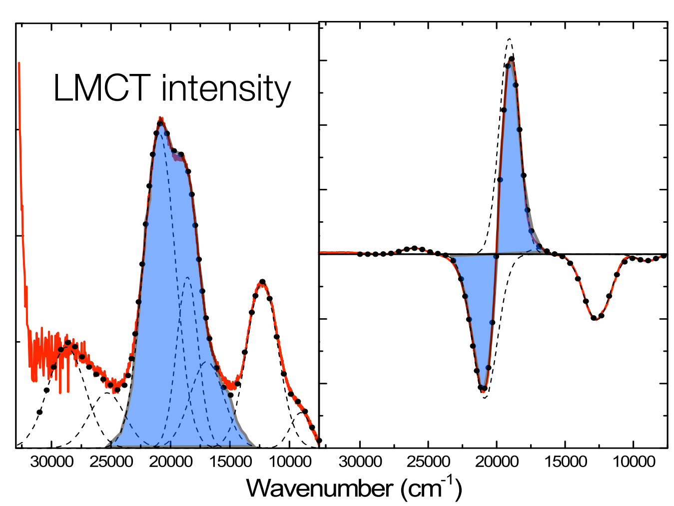


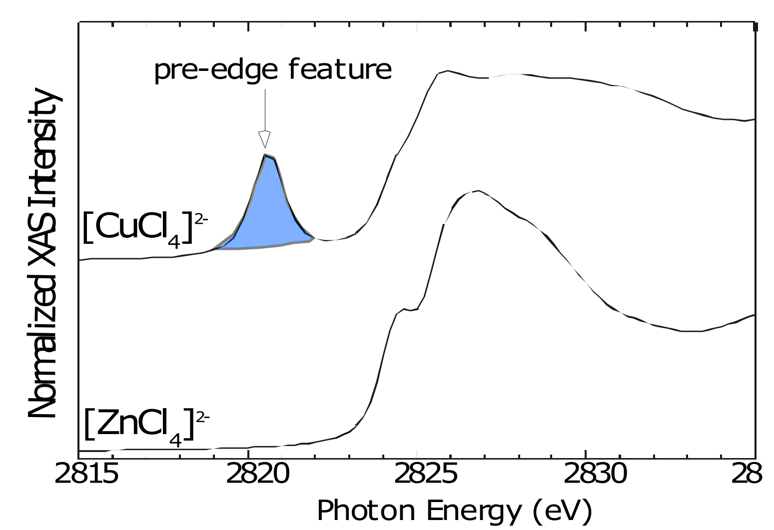
Typical π-backbond
Heterocyclic aromatic ligands ; CO, NO^+...
α^2=0.7-0.95

„Measurements“ of Covalency?

- ★ Can covalency be measured?
  - ➡ Rigorously speaking: **NO**! Orbitals are not observables!
  - ➡ On a practical level: (more or less) **YES**. Covalency can be correlated with a number of spectroscopic properties
    - **EPR metal- and ligand hyperfine couplings**
    - **Ligand K-edge intensities**
    - **Ligand-to-metal charge transfer intensities**
  - ➡ As all of this is „semi-qualitiative“ you can not expect numbers that come out of such an analysis to agree perfectly well. If they do this means that you have probably been good at fudging!







ALL proportional to 1-α^2

Covalency and Molecular Properties

Metal-Ligand Covalency Affects Many Chemical Properties!

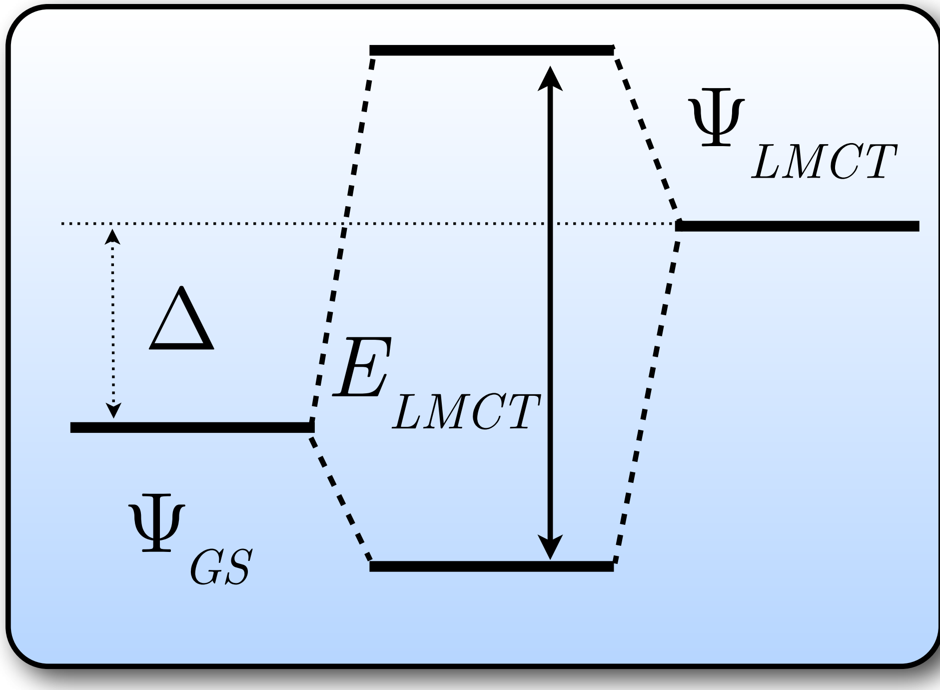
1. The **stability** of a complex increases with metal-ligand covalency
2. Covalency reflects charge-donation. The larger the charge donation the more negative the **redox potential**
3. Covalency may affect ‚**electron transfer pathways**‘
4. Covalency taken to the extreme might mean that ligands are activated for **radical chemistry**
5. ...

Covalency and Ligand-to-Metal Charge Transfer Spectra

$$\Psi_{GS} = \left|\psi_L \bar{\psi}_L \psi_M\right| \qquad \Psi_{LMCT} = \left|\psi_L \bar{\psi}_M \psi_M\right|$$

Energy Difference $\Delta = I_L - A_M$

Interaction $\beta = F_{LM} \propto S_{LM}$



Transition Energies:

- ★ Low if ligand is easy to ionize
- ★ Low if metal is strongly oxidizing (high oxidation state)
- ★ Increases for large ML overlap
- ★ Overlap increases for highly polarizable (soft) ligands

Transition Intensities:

- ★ High for large covalent binding (beta=large, Delta=small)
- ★ Maximal for equal mixing (Delta=0)
- ★ Transitions are always most intense for bonding to antibonding excitations (polarized along the M-L bond)

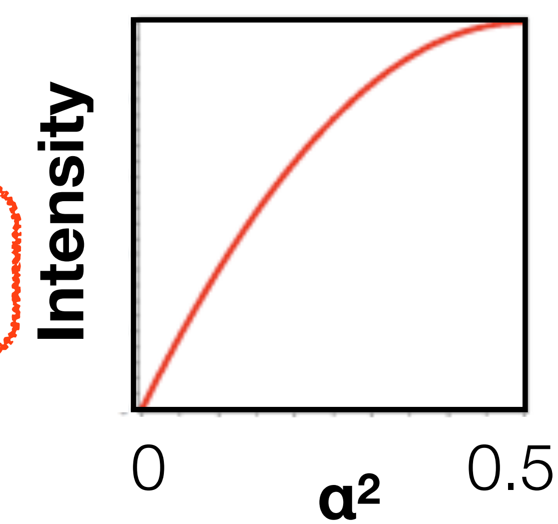
Estimating Covalency

From the little valence bond model, we can obtain the two eigenstates as:

$$\left|\Psi'_{GS}\right\rangle = \alpha\left|\Psi_{GS}\right\rangle + \sqrt{1-\alpha^2}\left|\Psi_{LMCT}\right\rangle \qquad \left|\Psi'_{LMCT}\right\rangle = \sqrt{1-\alpha^2}\left|\Psi_{GS}\right\rangle - \alpha\left|\Psi_{LMCT}\right\rangle$$

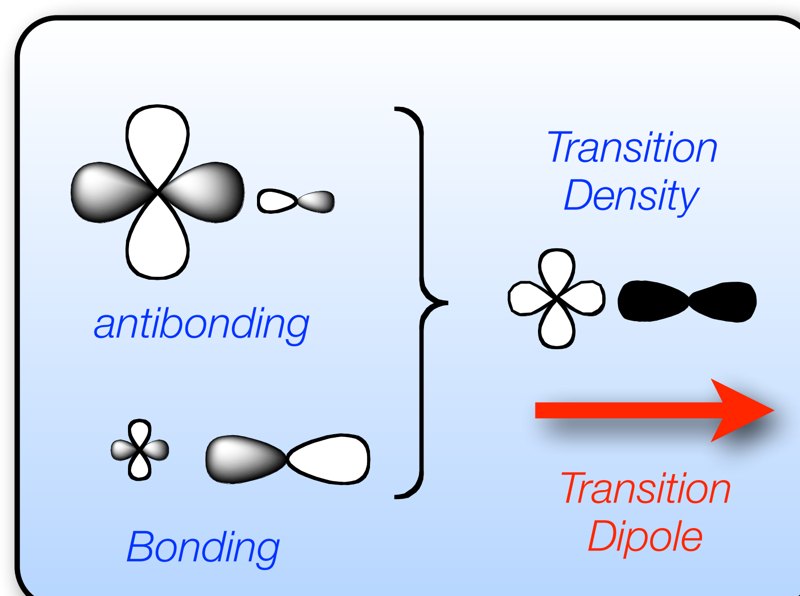
The **Transition Energy**: $E_{LMCT} = \Delta + 2\dfrac{\beta^2}{\Delta} - 2\dfrac{\beta^4}{\Delta^3} + O(\beta^6)$

The **Transition Intensity:** $\left|\left\langle \Psi'_{GS} \mid \vec{\mu} \mid \Psi'_{LMCT}\right\rangle\right|^2 \equiv \boxed{D_{ML}^2 \approx \alpha^2(1-\alpha^2)R_{ML}^2 \approx \dfrac{\beta^2}{\Delta^2}R_{ML}^2}$



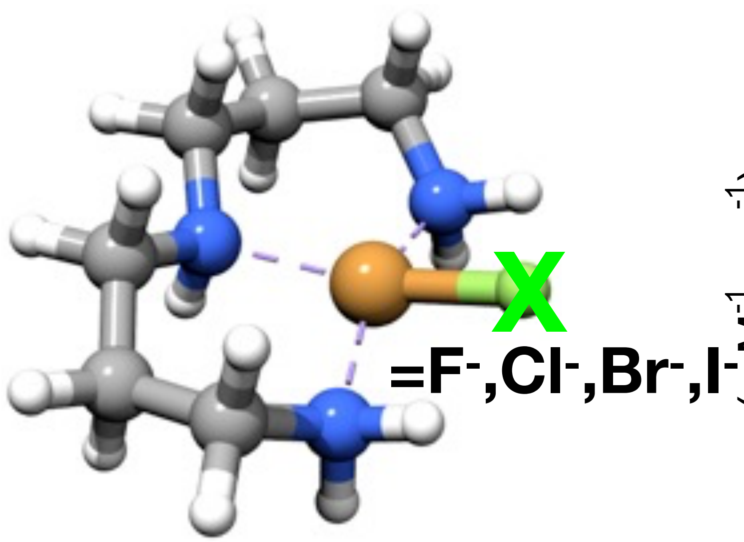
This can be turned around to obtain the model parameters from the measurable quantities: ***R*$_{ML}$*,* *D*$_{ML}$** and ***E*$_{LMCT}$**

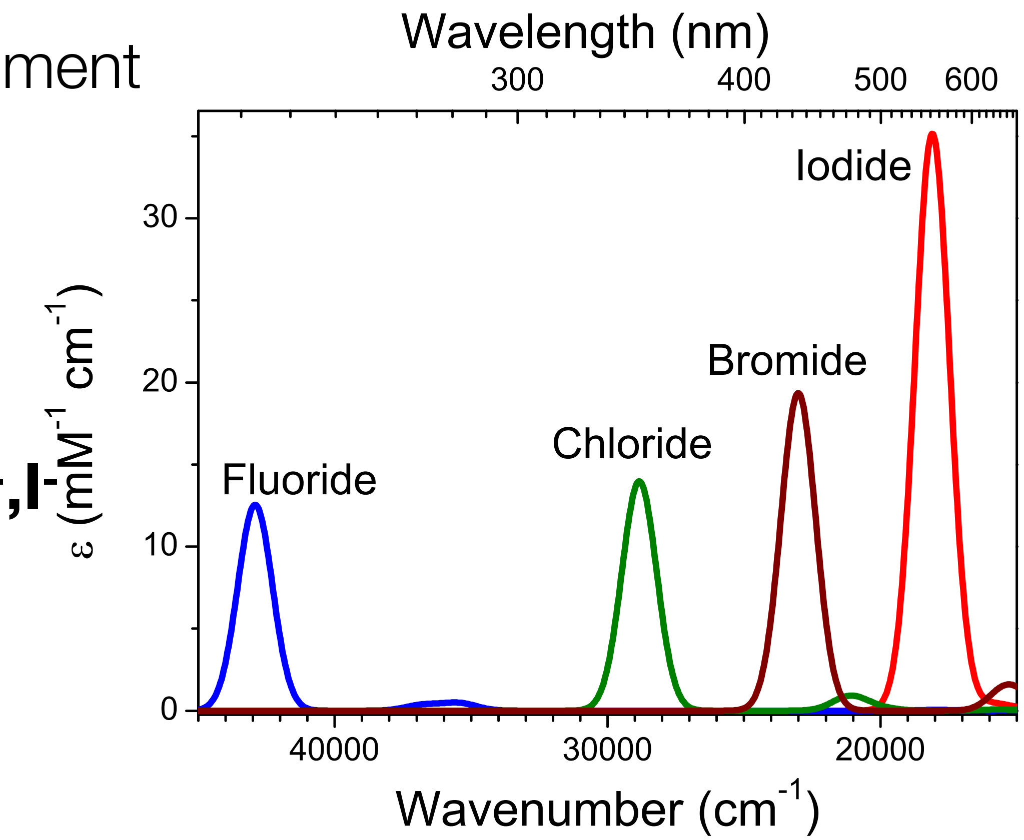
$$\beta = \pm D_{ML}\frac{R_{ML}}{R_{ML}^2 + 2D_{ML}^2}E_{LMCT} \qquad \Delta = \frac{R_{ML}^2}{R_{ML}^2 + 2D_{ML}^2}E_{LMCT}$$



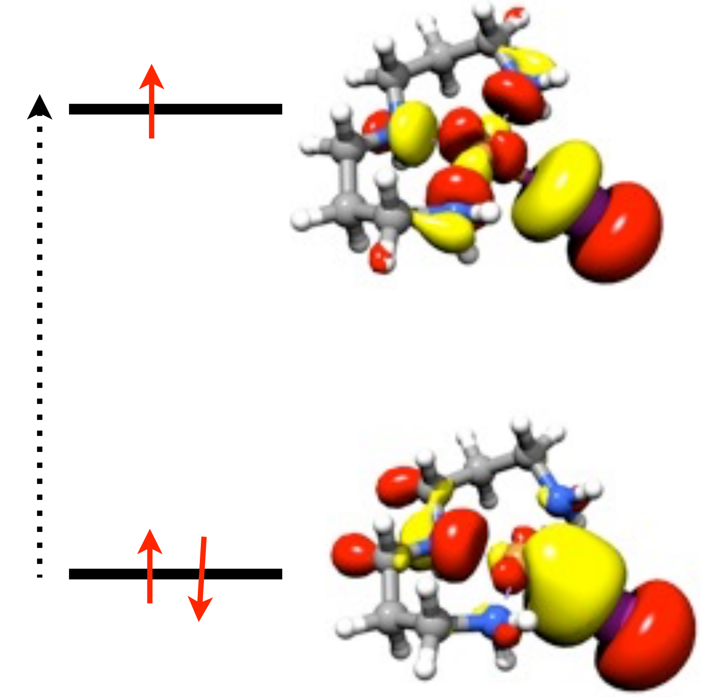
Let‘s Apply it (*in silico*)

Hypothetical Cu(II) fragment





σ-LMCT Transition



	IP/eV	**R_{ML}**/A	**D_{ML}^2**/D^2	**E_{LMCT}**/cm^{-1}	**Δ**/eV	**β**/eV	**$β^2/Δ^2$**
F^-	2,8	1,818	4,29	42918	**4,79**	**1,12**	**0,05**
Cl^-	3,2	2,228	7,12	28340	**3,13**	**0,77**	**0,06**
Br^-	3,4	2,373	12,35	23010	**2,41**	**0,73**	**0,09**
I^-	3	2,644	28,53	18096	**1,67**	**0,69**	**0,17**

BP86/def2-sv(p) structures; State averaged CASSCF(15,8)/def-sv(p) (5d- orbitals and 3 halide orbitals) followed by uncontrated RI-MRMP2