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Ligand Field Theory

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Theory in Chemistry

Observable Facts (Experiments)

Chemical Language

Nonrelativistic Quantum Mechanics

Molecular Relativistic Schrödinger Equation

Density Functional Theory

Hartree-Fock Theory

Correlated Ab Initio Methods

Semiempirical Theories

Phenomenological Models

What is Ligand Field Theory ?

★ **Ligand Field Theory is:**

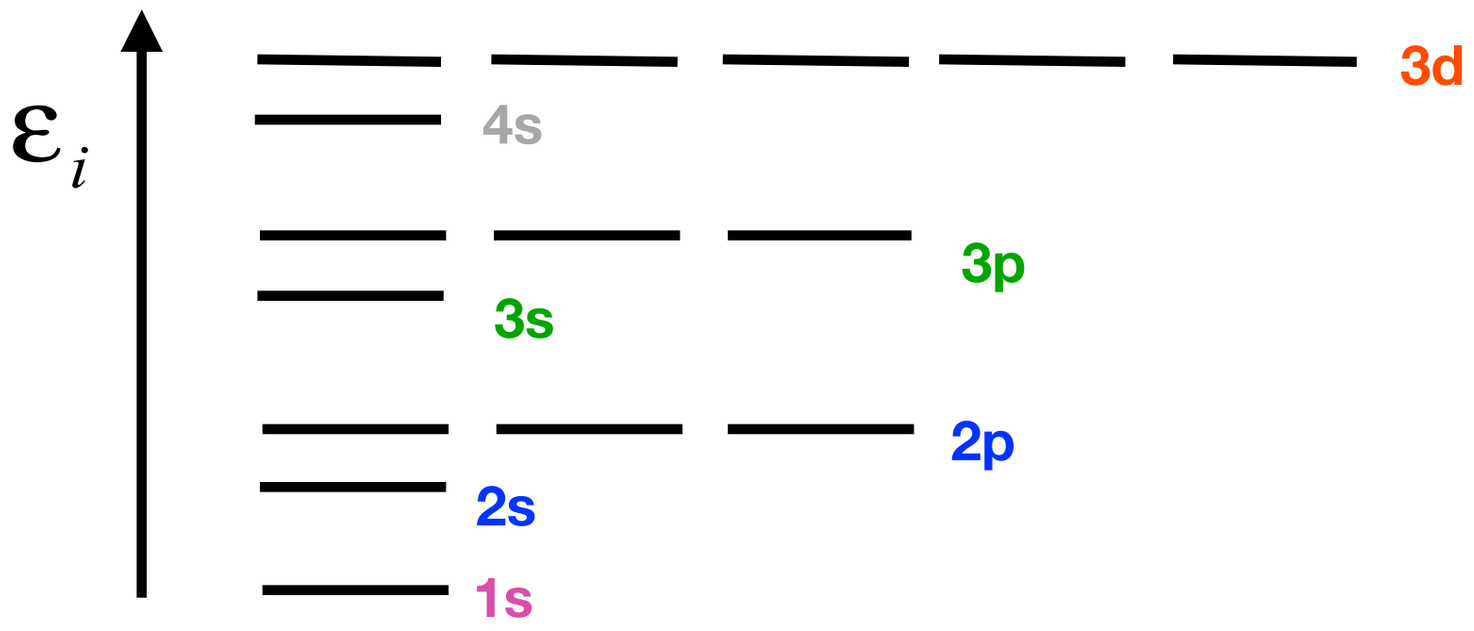
- A semi-empirical theory that applies to a **CLASS** of substances (transition metal complexes).
- A **LANGUAGE** in which a vast number of experimental facts can be rationalized and discussed.
- A **MODEL** that applies only to a restricted part of reality.

★ **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

Many Electron Atoms and the ‚Aufbau‘ Principle

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
					Mo												
					W												



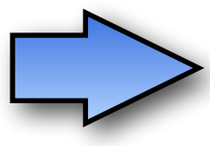
States of Atoms and Molecules

★ Atoms and Molecule exist in **STATES**

★ **ORBITALS** can NEVER be observed in many electron systems !!!

★ 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)

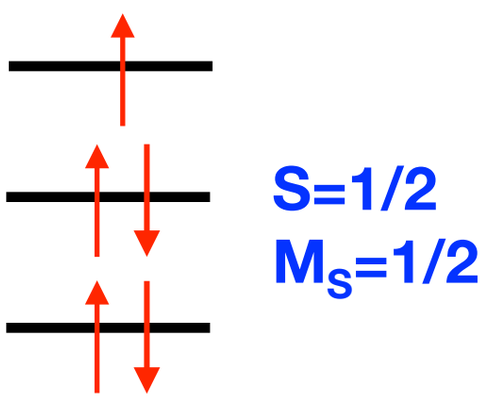


$|\mathbf{n}S_kM\Gamma M_\Gamma>$

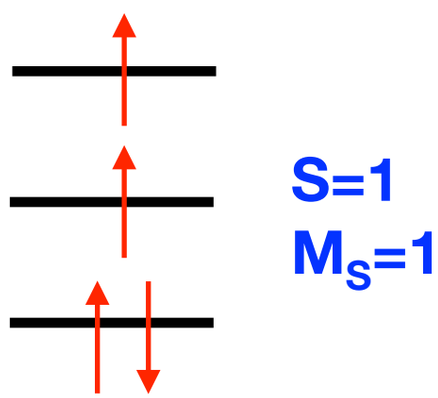
The Total Spin

For the **Total Spin** of an atom or molecule the rules apply:

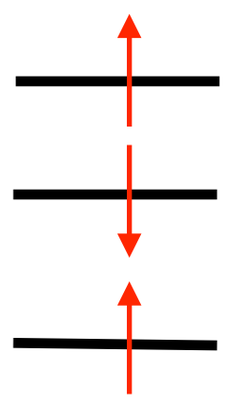
1. Doubly occupied orbitals do NOT contribute to the total Spin
2. Singly occupied orbitals can be occupied with either spin-up or spin-down electrons
3. Unpaired electrons can be coupled parallel or antiparallel to produce a final total spin S
4. For a state with total spin S there are 2S+1 ‚components' with M=S,S-1,...,-S
5. The M_S quantum number is always the sum of all individual m_s quantum numbers



S=1/2
M_S=1/2



S=1
M_S=1



S=1/2 AND 3/2
M_S=1/2

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

→ ^2D

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

→ ^6S

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

→ $^3F+^3P$

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

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

2S+1 : „Multiplicity“ = Spin Degeneracy

Γ : „Irreducible Representation“

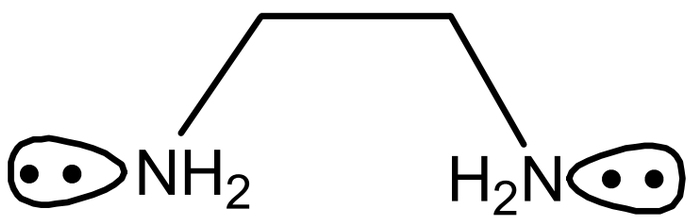
Principles of Ligand Field Theory

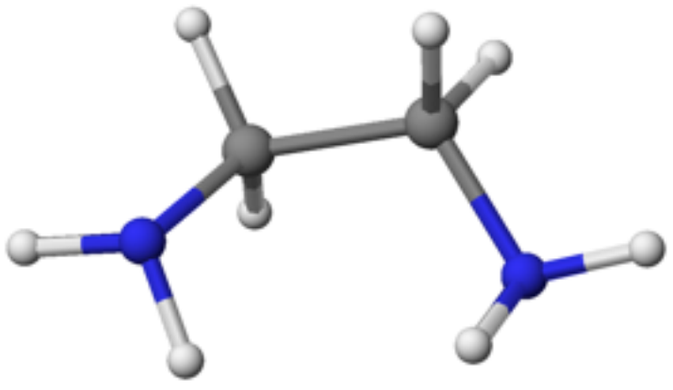
R-L| M

δ- δ+

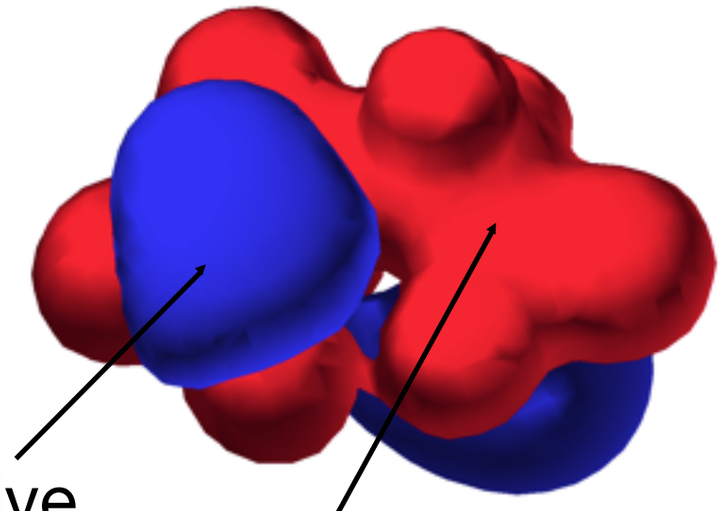
Strong Attraction

Example:





Electrostatic Potential

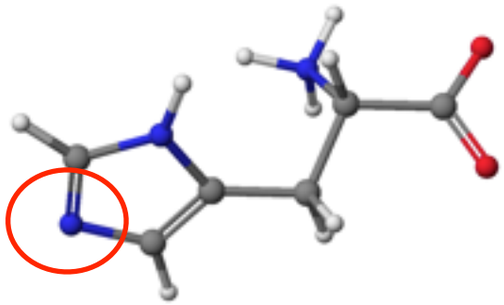


Negative

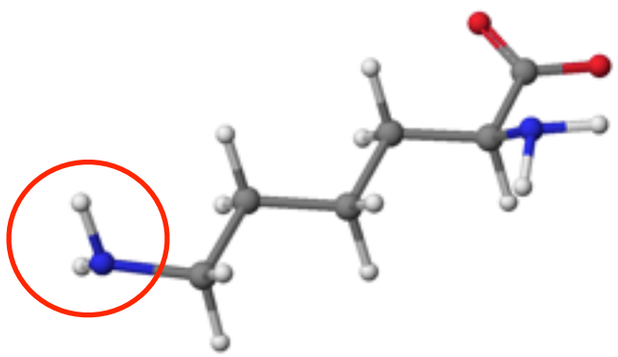
Positive

Protein Derived Ligands

N

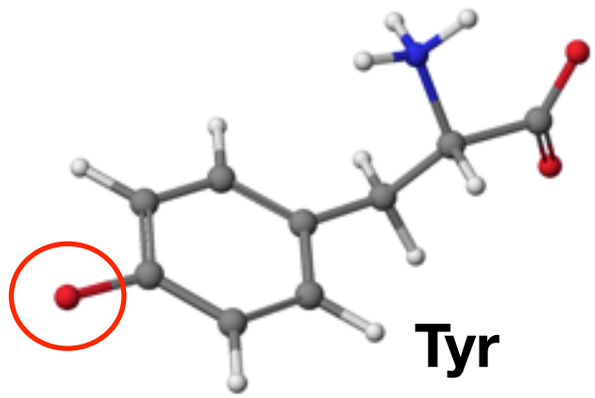


His

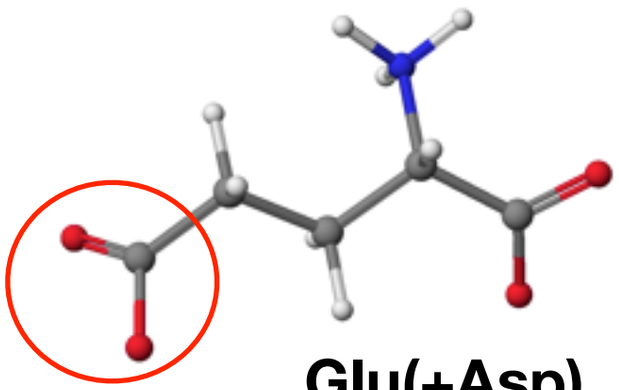


Lys

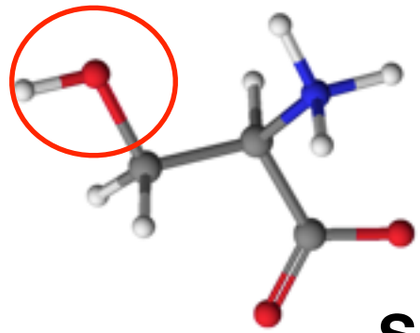
O



Tyr

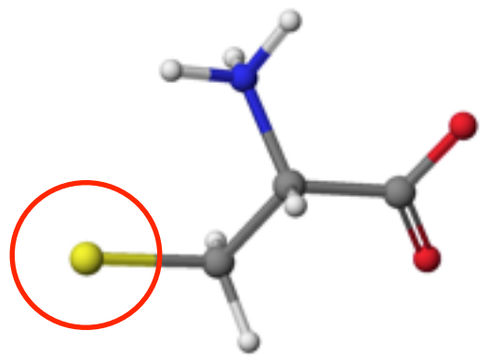


Glu(+Asp)

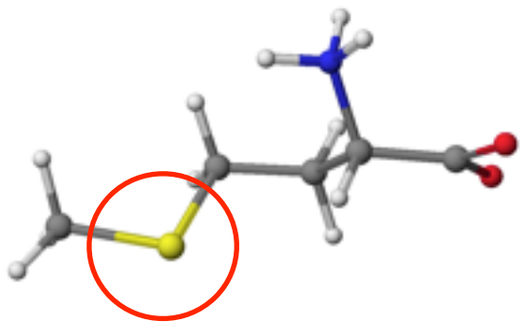


Ser

S



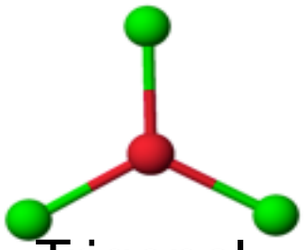
Cys



Met

Complex Geometries

3

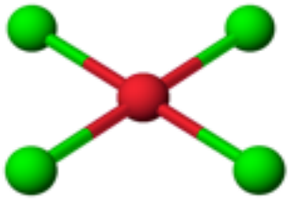


Trigonal

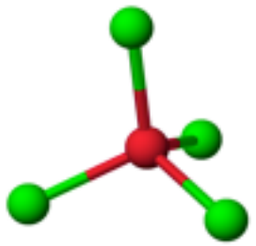
Trigonal Pyramidal

T-Shaped

4

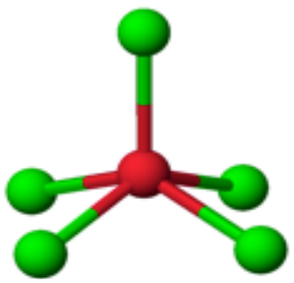


Quadratic Planar



Tetrahedral

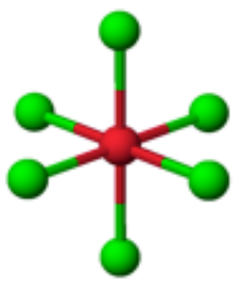
5



Quadratic Pyramidal

Trigonal Bipyramidal

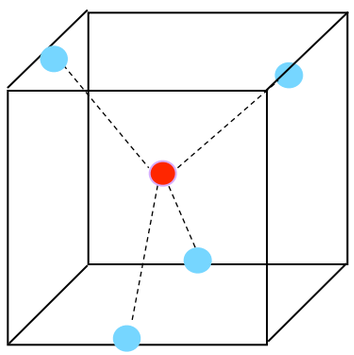
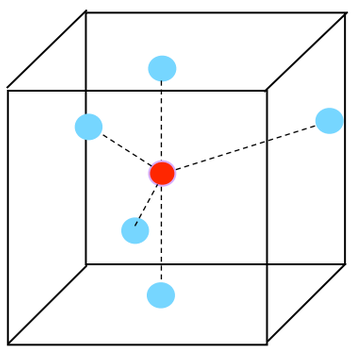
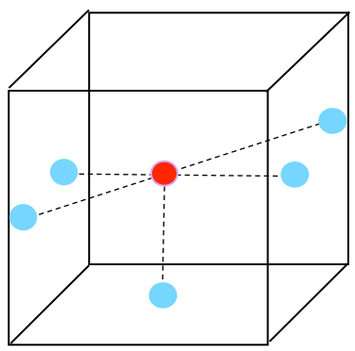
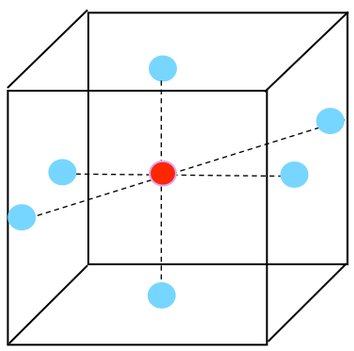
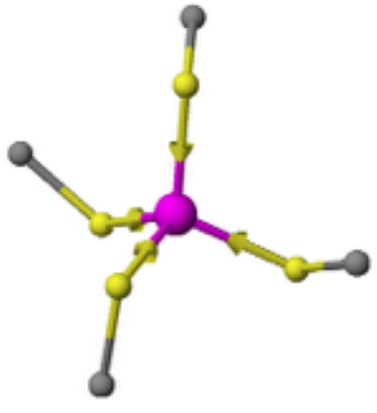
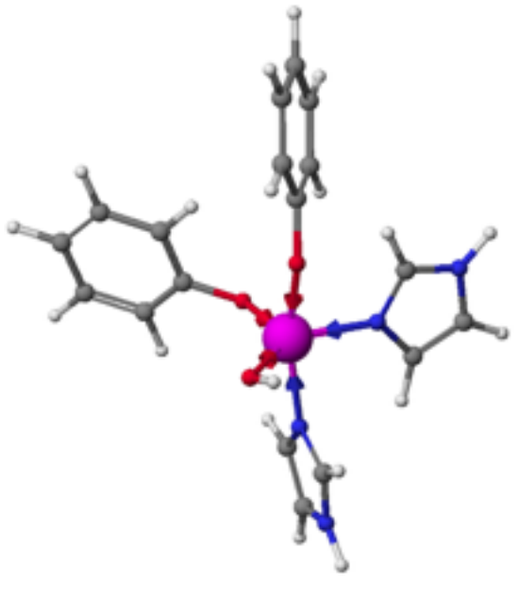
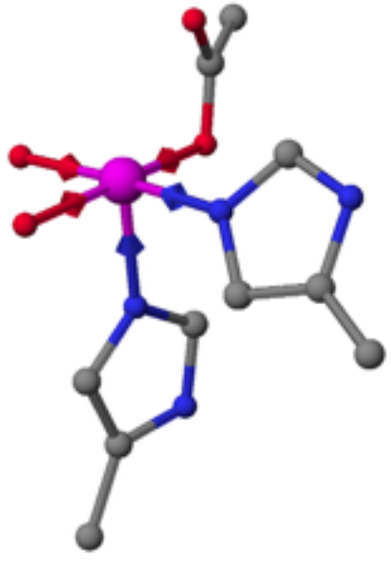
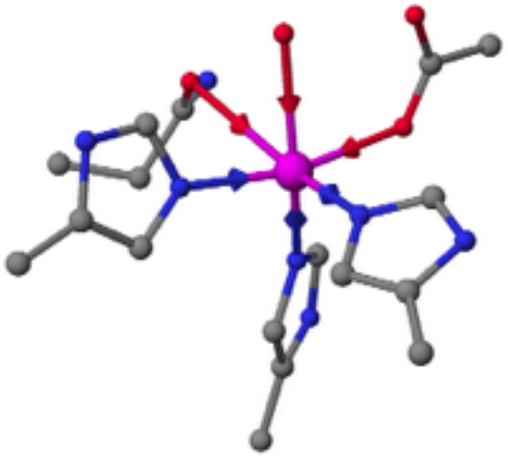
6



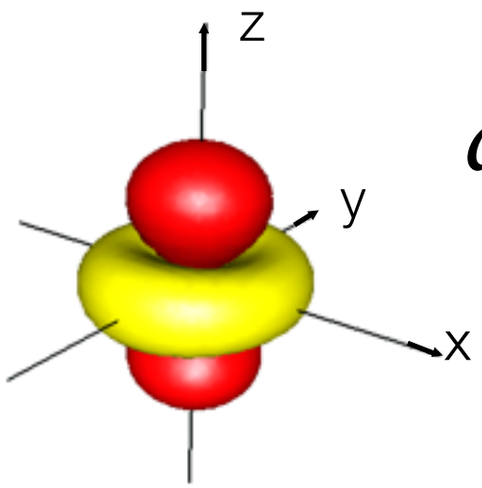
Octahedral

Coordination Geometries

- Approximate Symmetries Observed in Enzyme Active Sites -

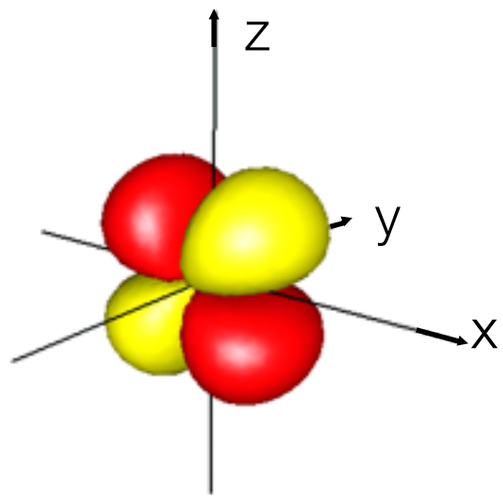
Tetrahedral	Trigonal Bipyramidal	Tetragonal Pyramidal	Octahedral
			
T_d	D_{3h}	C_{4v}	O_h
			
Rubredoxin	3,4-PCD	Tyrosine Hydroxylase	Lipoxygenase

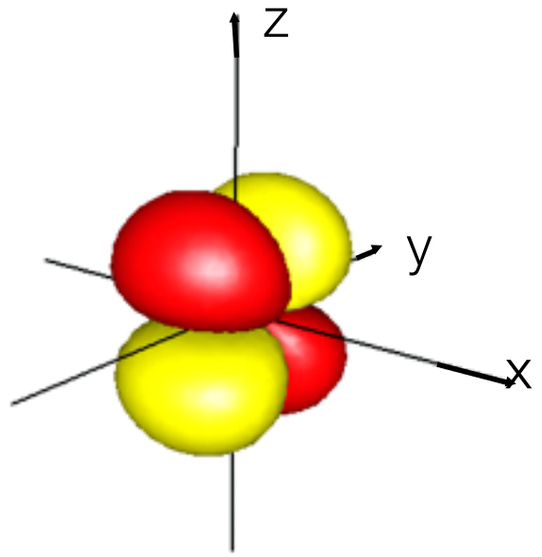
The Shape of Orbitals



$d_{z^2-r^2}$

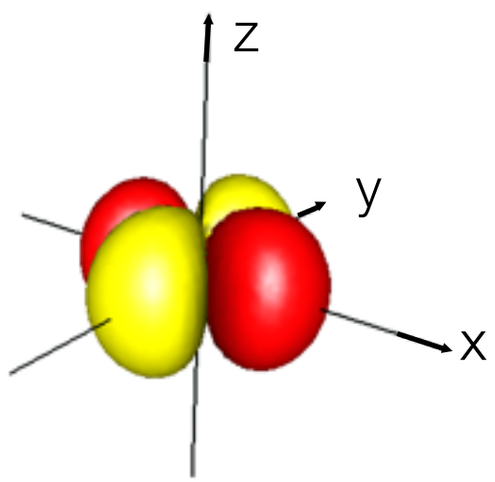
d_{xz}

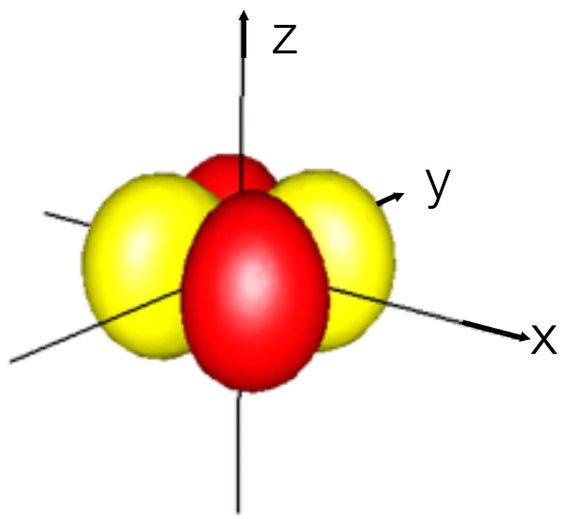




d_{yz}

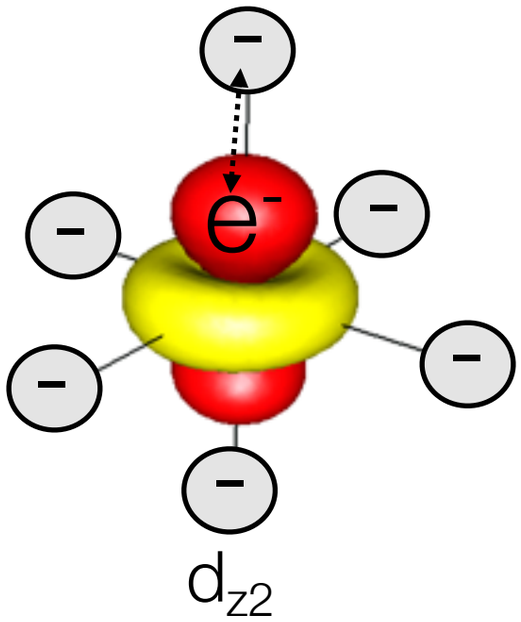
$d_{x^2-y^2}$

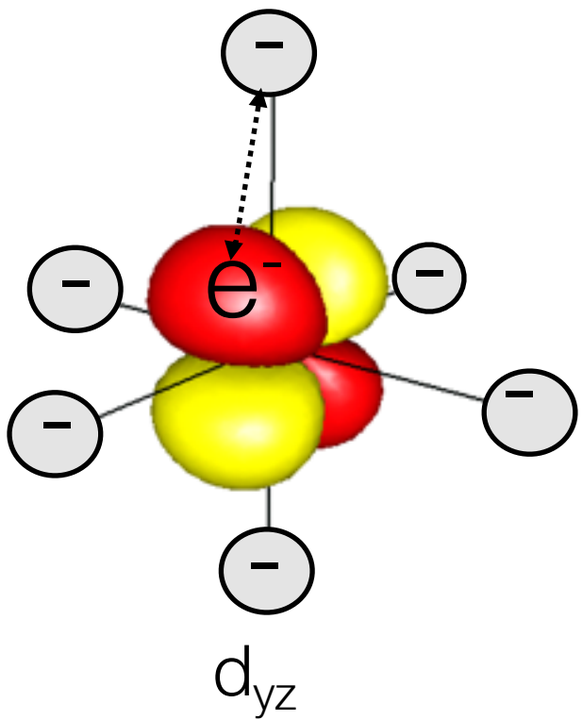




d_{xy}

A Single d-Electron in an Octahedral Field



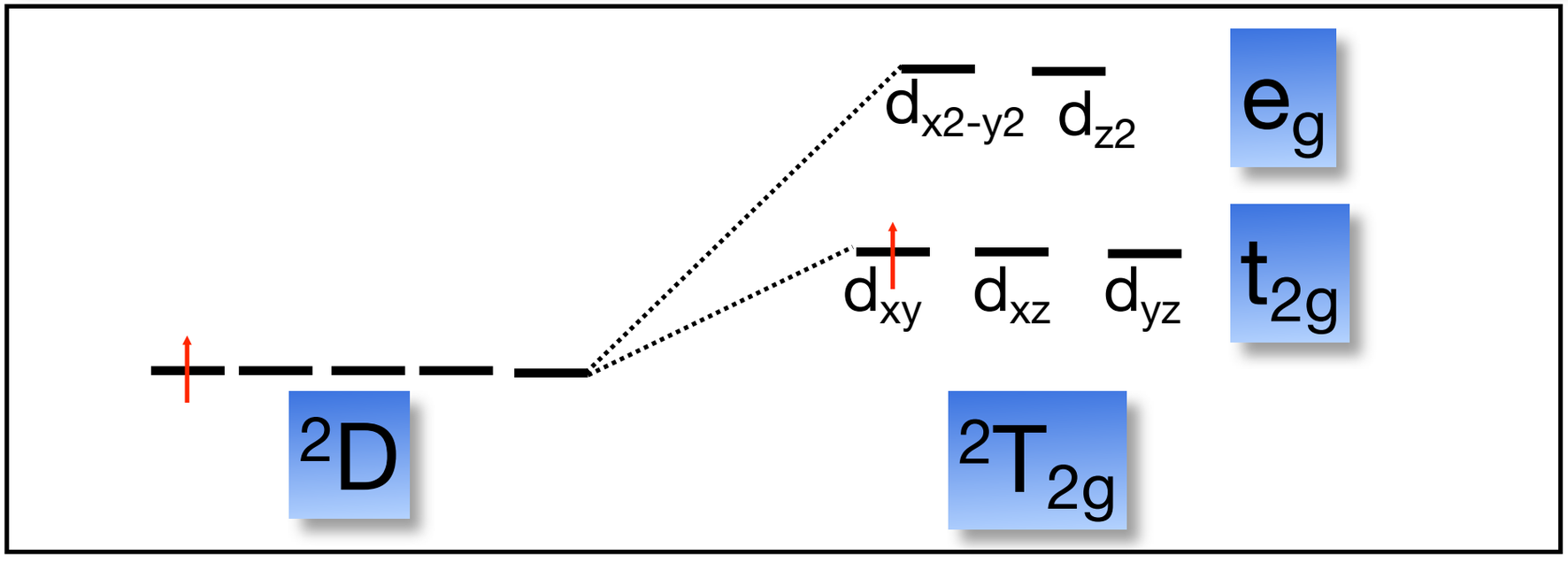


The Negatively Charged Ligands Produce an Electric Field+Potential

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: $\rho(\mathbf{R}) = \sum_{i=1}^{N_L} q_i \delta(\mathbf{R} - \mathbf{R}_{L_i})$

Ligand field potential: $V_{LF}(\mathbf{r}) = \int \frac{\rho(\mathbf{R})}{|\mathbf{R} - \mathbf{r}|} d\mathbf{R}$ 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“: $A_{lm} = \sum_{i=1}^{N_L} \frac{4\pi}{2l+1} \frac{q_i}{R_{L_i}^{l+1}} S_{lm}(\mathbf{R}_{L_i})$

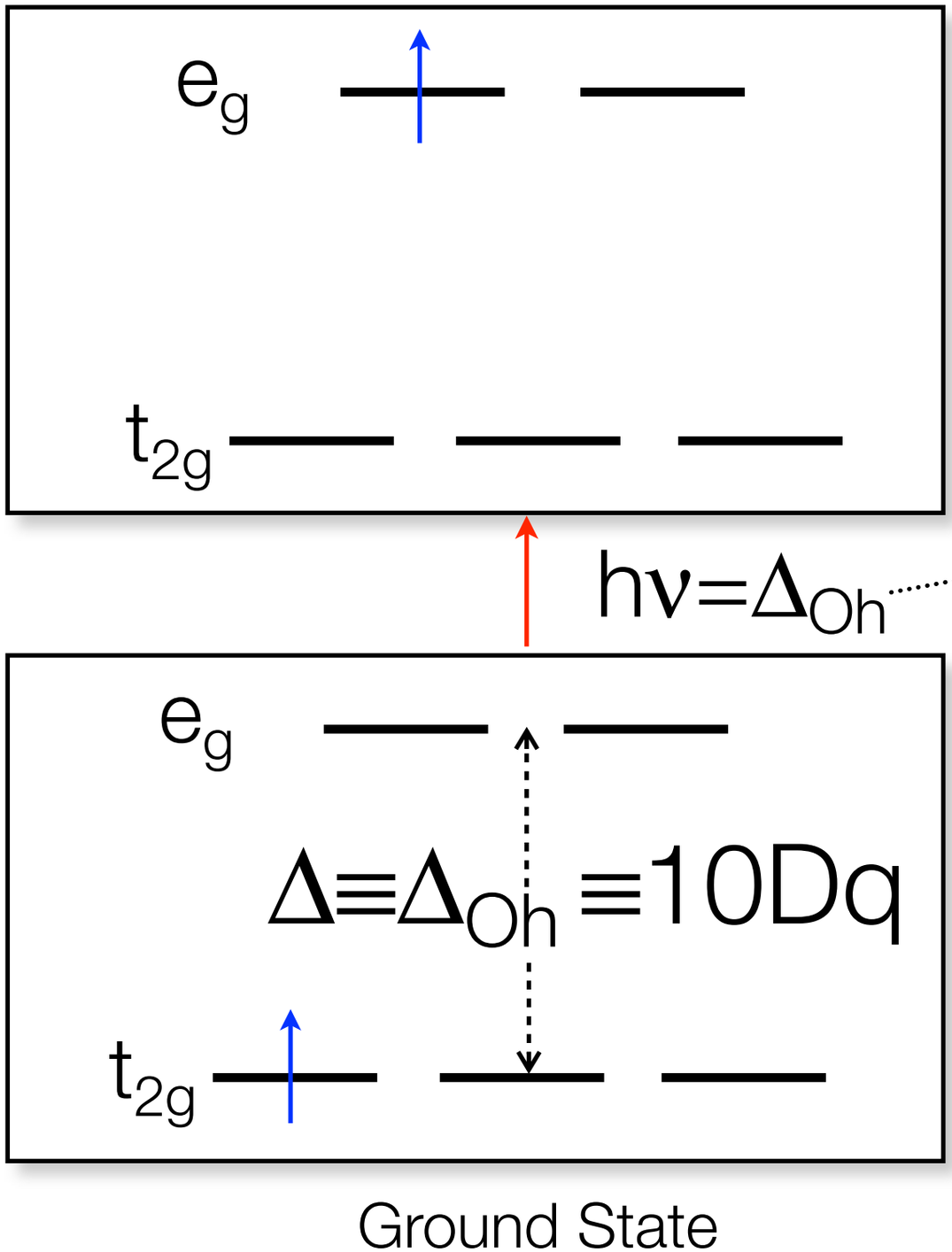
Ligand-field matrix elements: $\langle d_i | V_{LF} | d_j \rangle = -\sum_{l=0}^{\infty} \langle r^l \rangle \sum_{m=-l}^{l} A_{lm} \begin{pmatrix} l_i & l_j & l \\ m_i & m_j & m \end{pmatrix}$ $\begin{pmatrix} l_i & l_j & l \\ m_i & m_j & m \end{pmatrix}$

Ligand-field splitting in O_h: $\langle d_{e_g} | V_{LF} | d_{e_g} \rangle - \langle d_{t_{2g}} | V_{LF} | d_{t_{2g}} \rangle \equiv 10Dq = \frac{5}{3} \frac{q}{R^5} \langle d | r^4 | d \rangle$ =Gaunt Integral (tabulated)

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

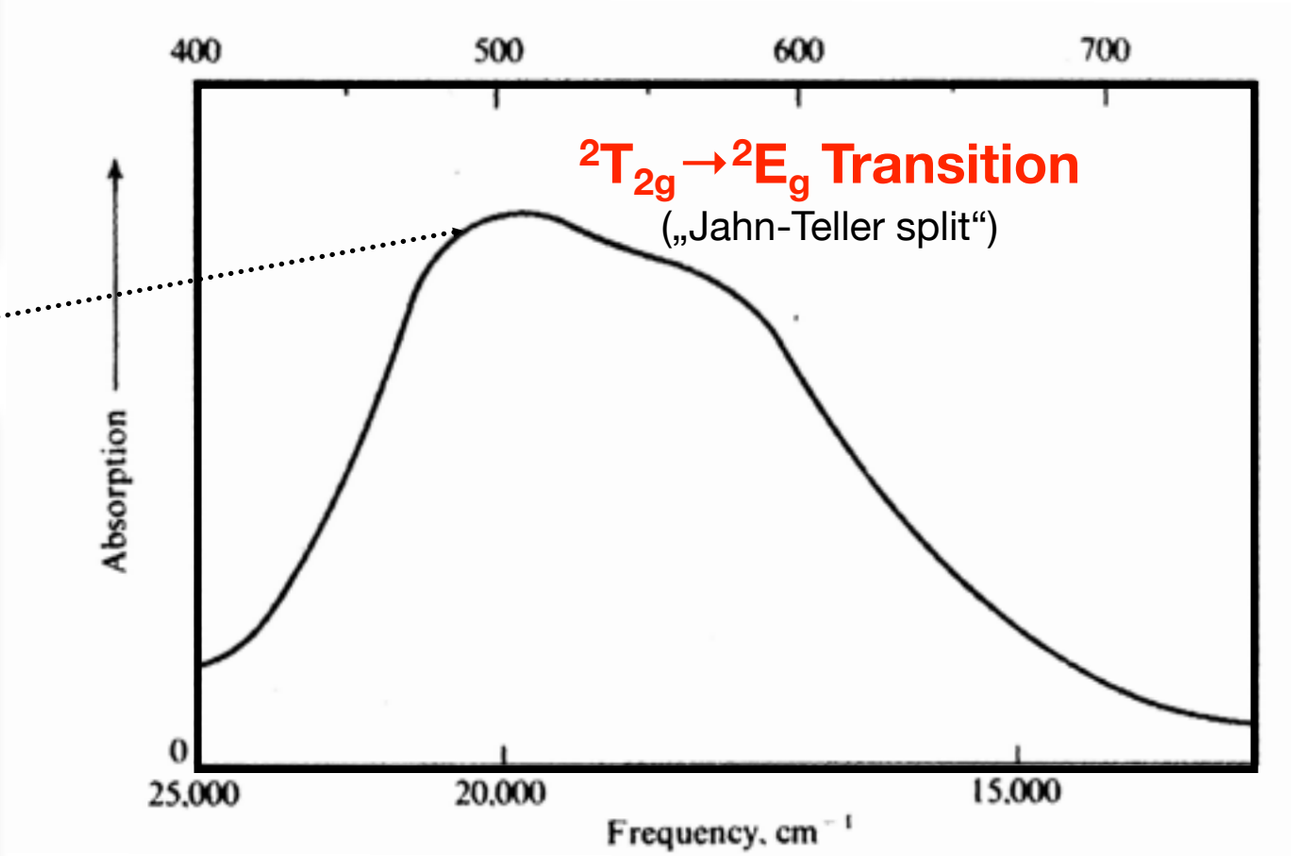
Optical Measurement of Δ: d-d Transitions

Excited State



Ground State

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



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^-

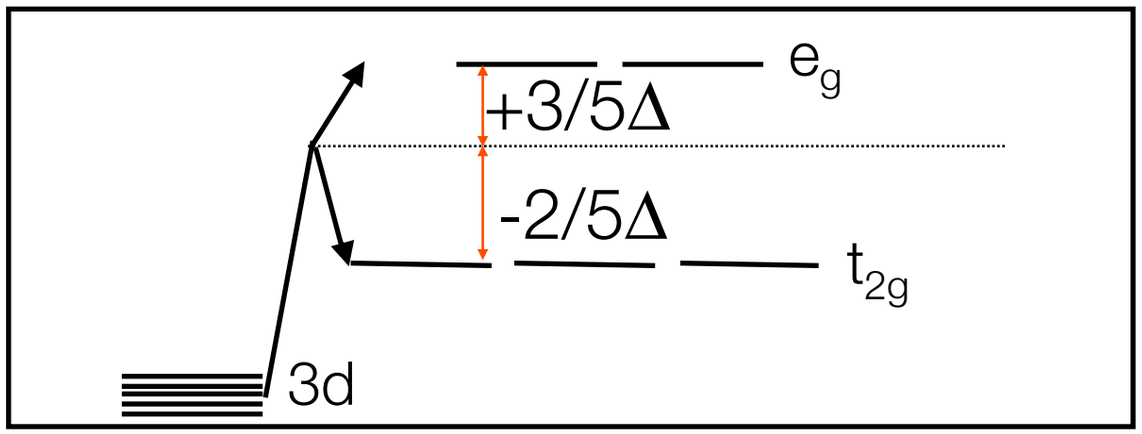
Δ SMALL

Δ LARGE

Ligand Field Stabilization Energies

Central Idea:

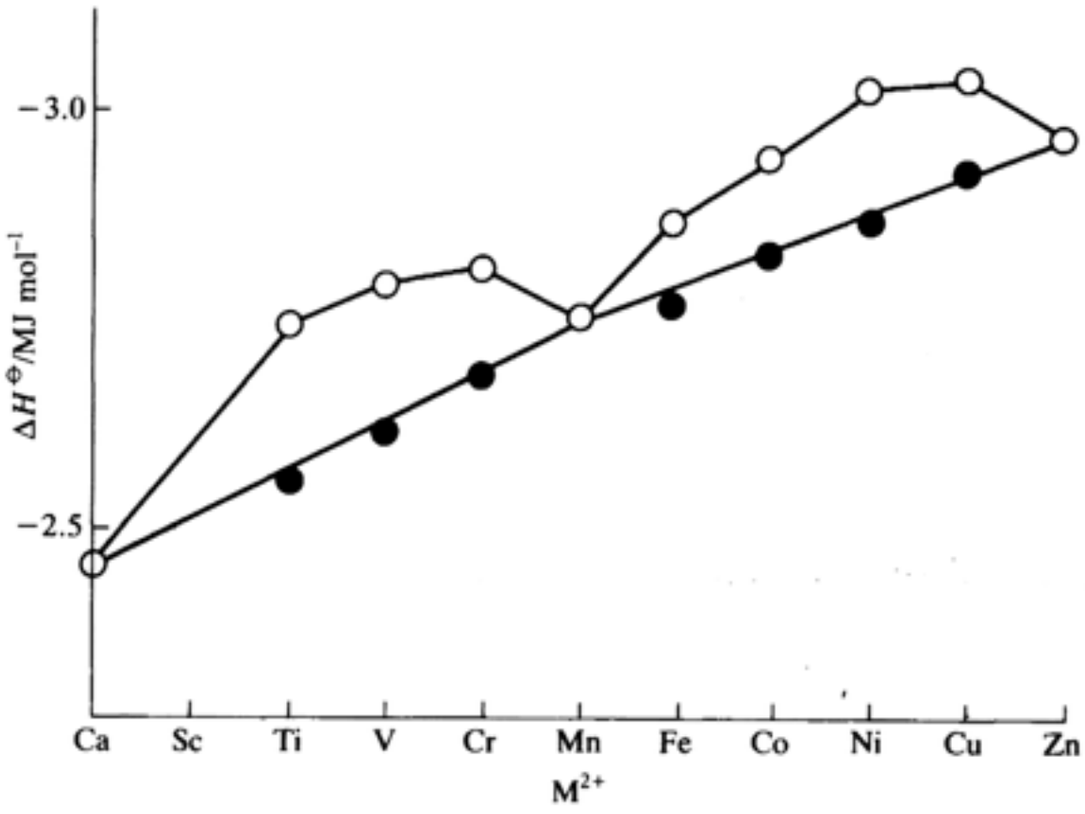
- Occupation of t_{2g} orbitals stabilizes the complex while occupation of e_g orbitals destabilizes it.
- Ligand Field Stabilization Energy (LSFE)



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

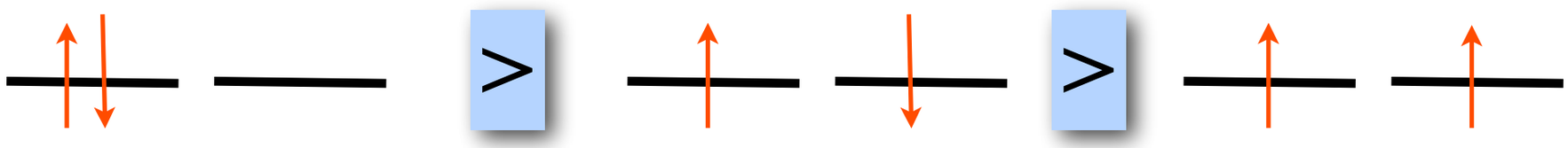
Experimental Test:

- 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:

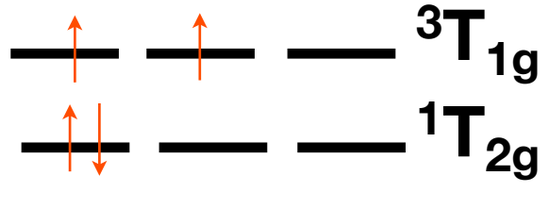
- In degenerate orbitals electrons enter first with the same spin in different orbitals (→Hund‘s Rules in atoms!)
- A given configuration produces several states with different energies

Ligand Field Theory:

- Electron repulsion can be taken care of by ONE PARAMETER: B (~1000 cm^{-1})

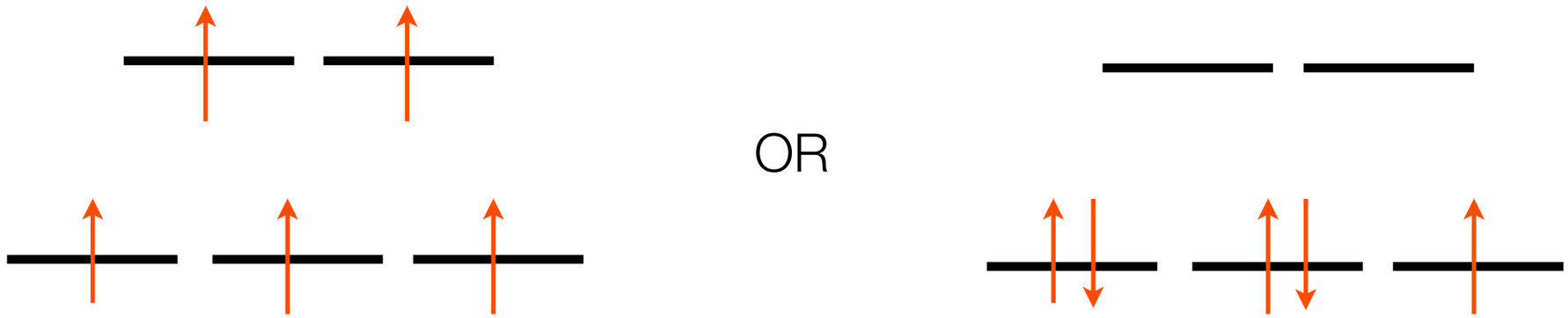
Example:

- d^2-Configuration: $\Delta E(^1T_{2g}\text{-}^3T_{1g}) \sim 4B \sim 3{,}000\text{-}4{,}000\ cm^{-1}$



High-Spin and Low-Spin Complexes

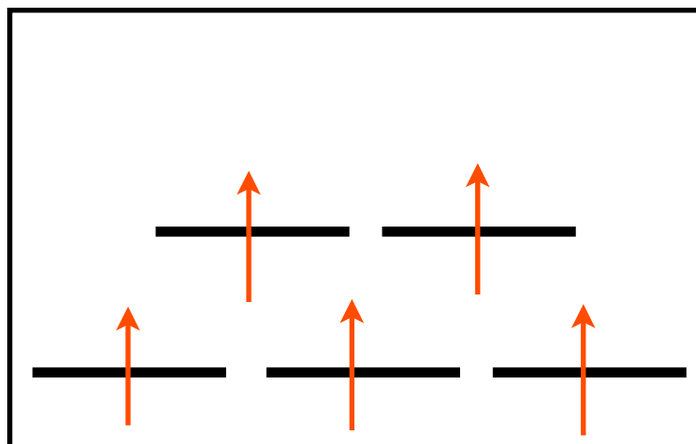
QUESTION: What determines the electron configuration?



High-Spin

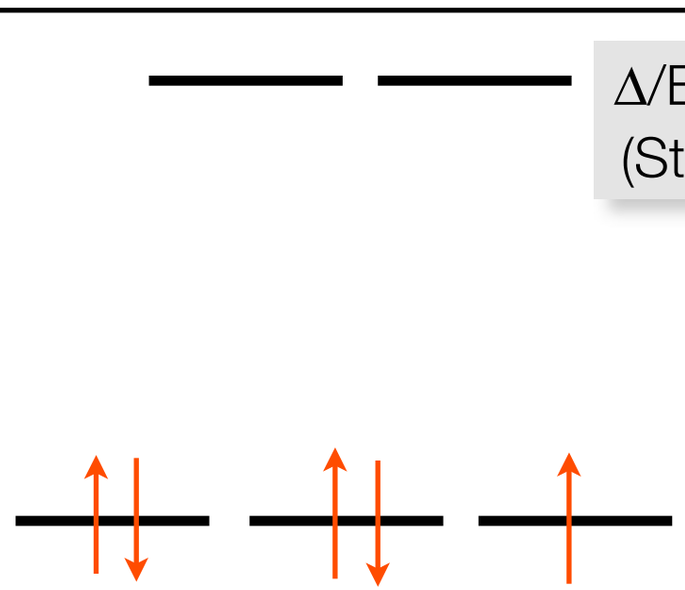
Low-Spin

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



Δ/B-SMALL
(Weak Field Ligand)

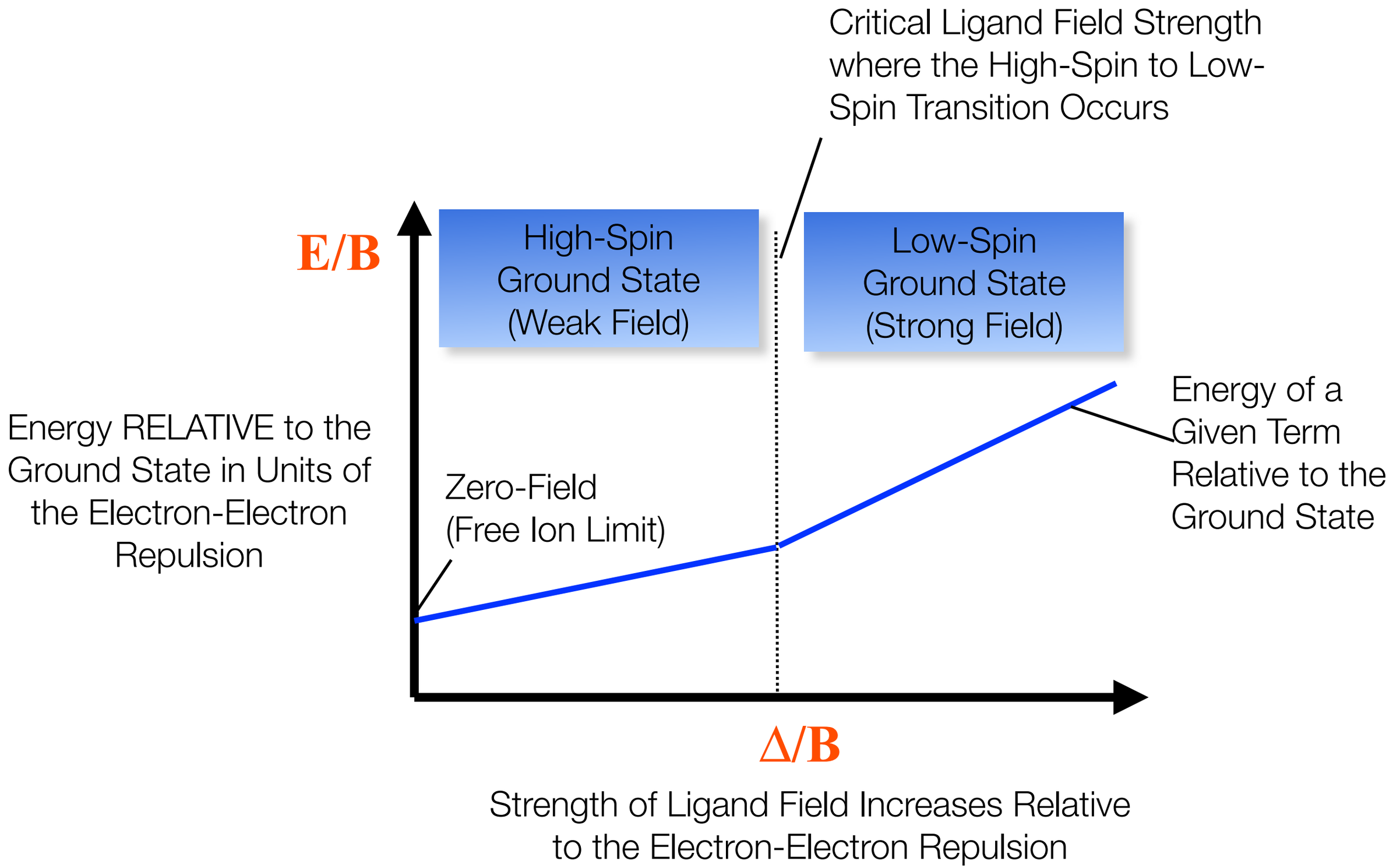
High Spin



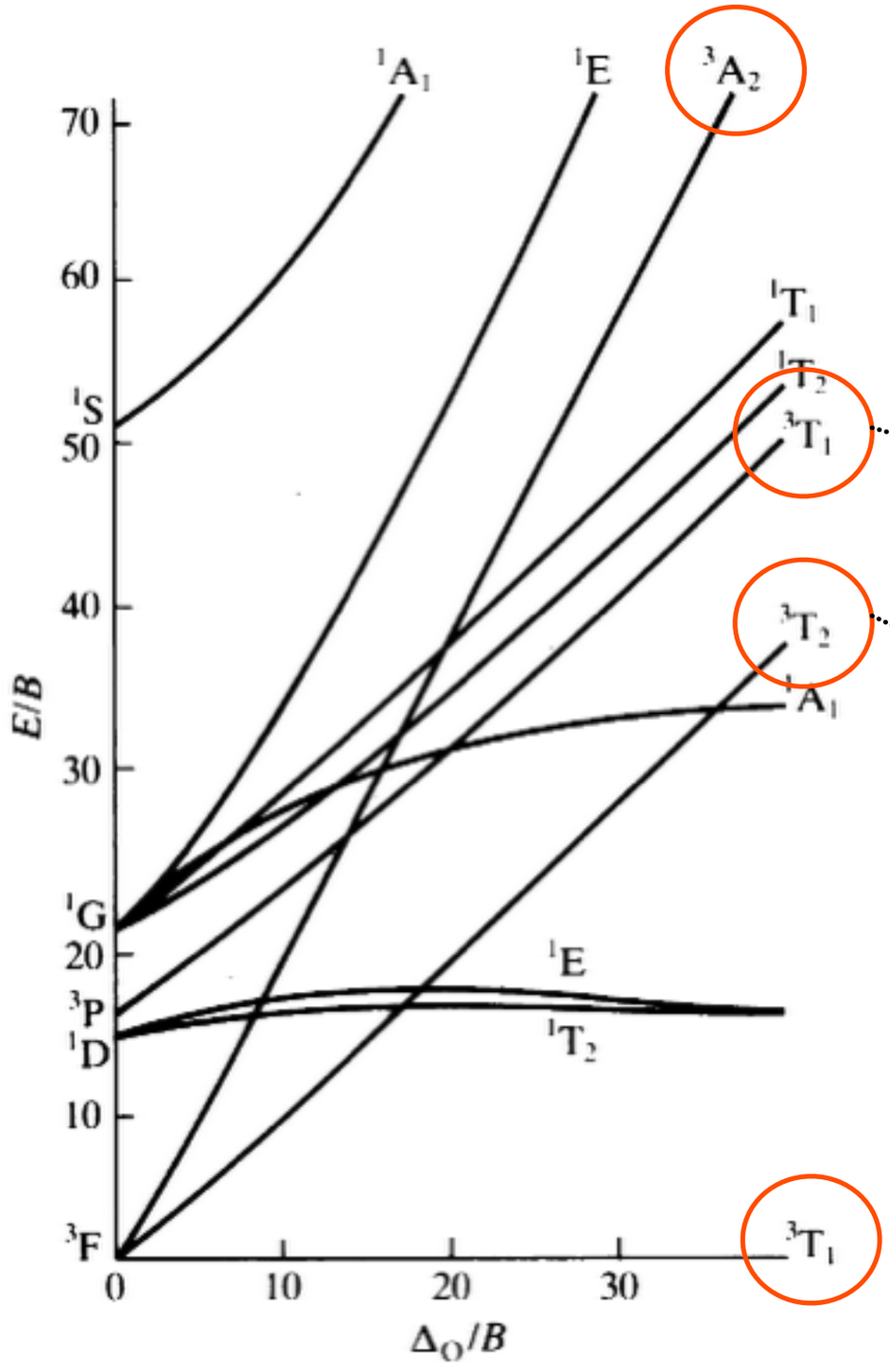
Δ/B ~20-30≡ LARGE
(Strong Field Ligand)

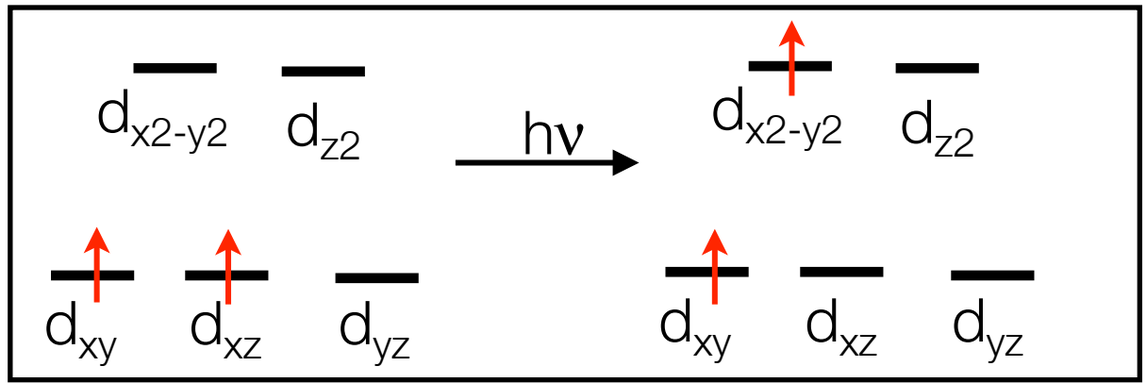
Low-Spin

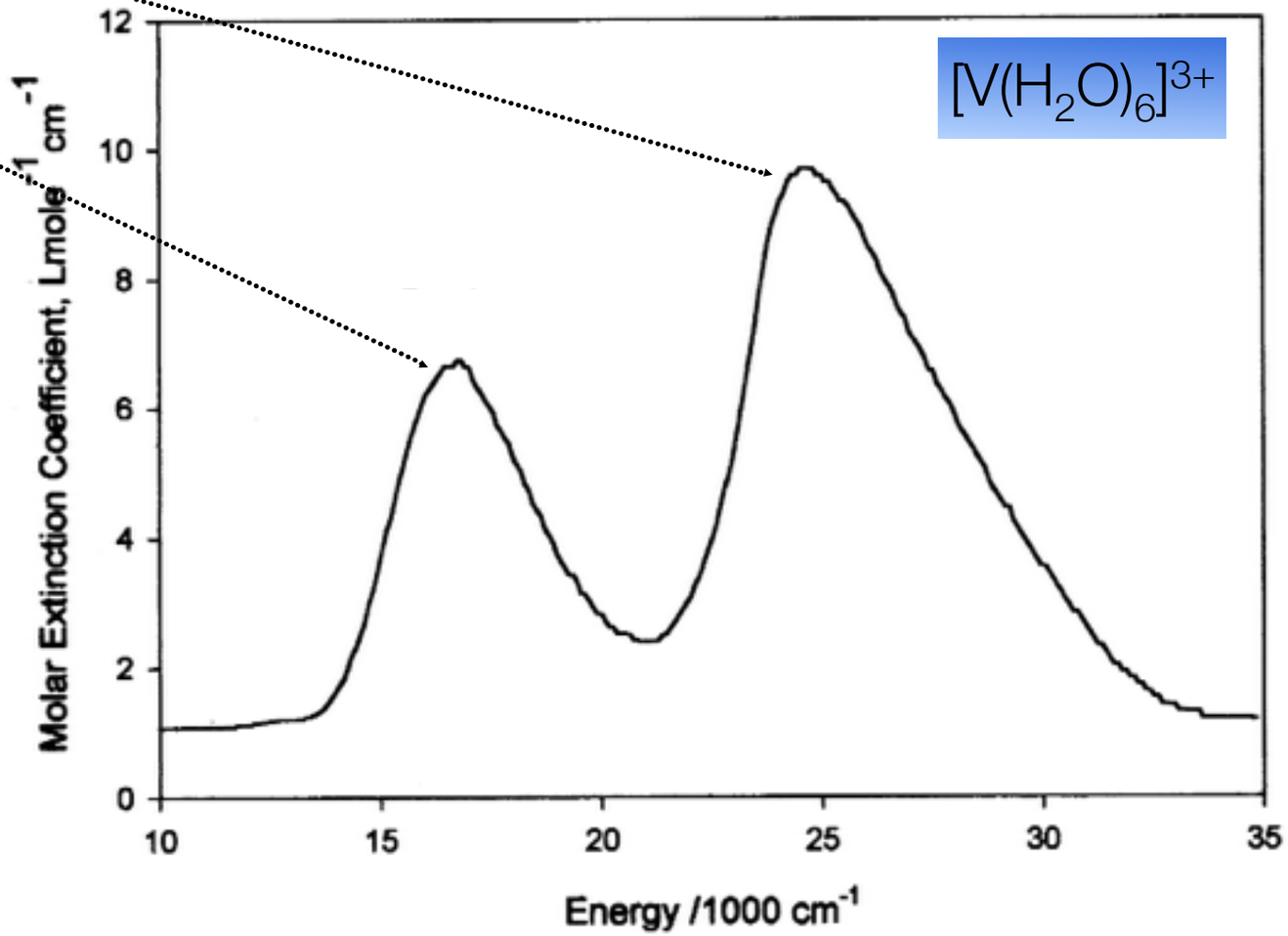
Inside Ligand Field Theory:Tanabe-Sugano Diagrams



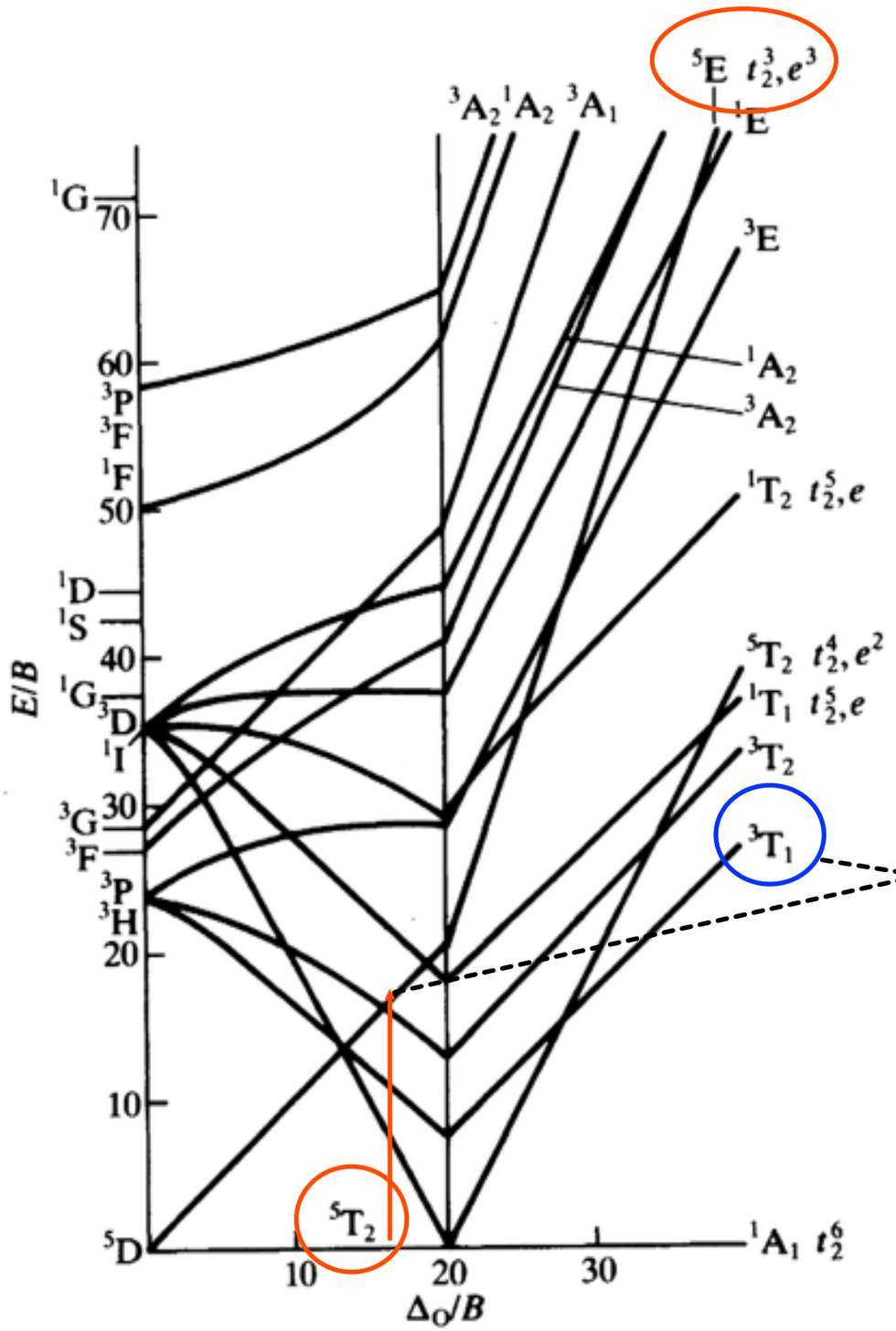
Optical Properties:d-d Spectra of d^2 Ions

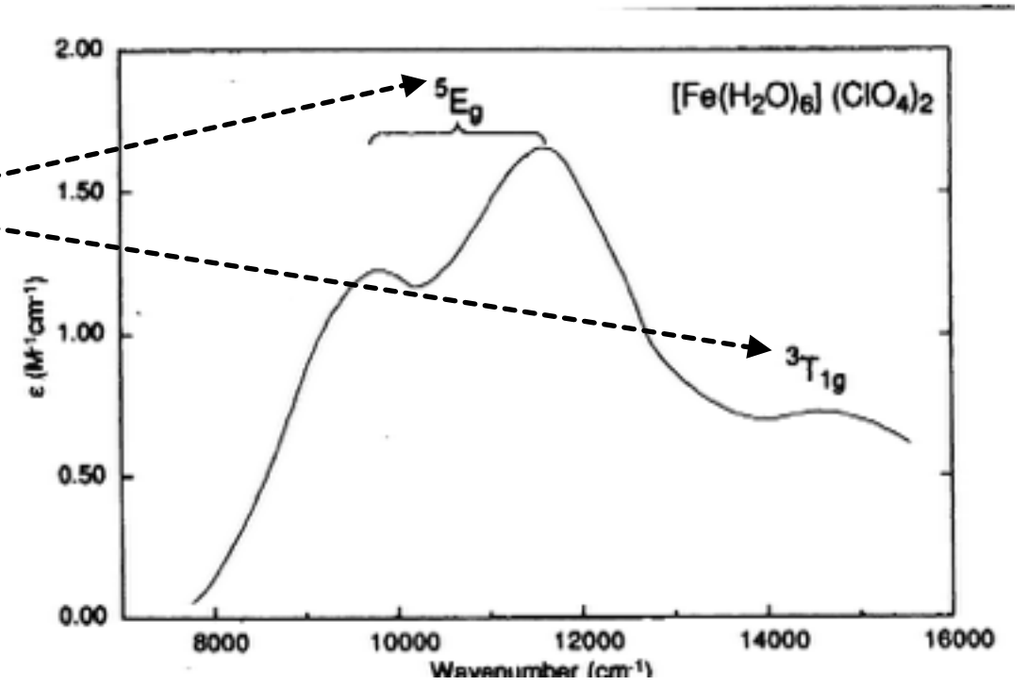




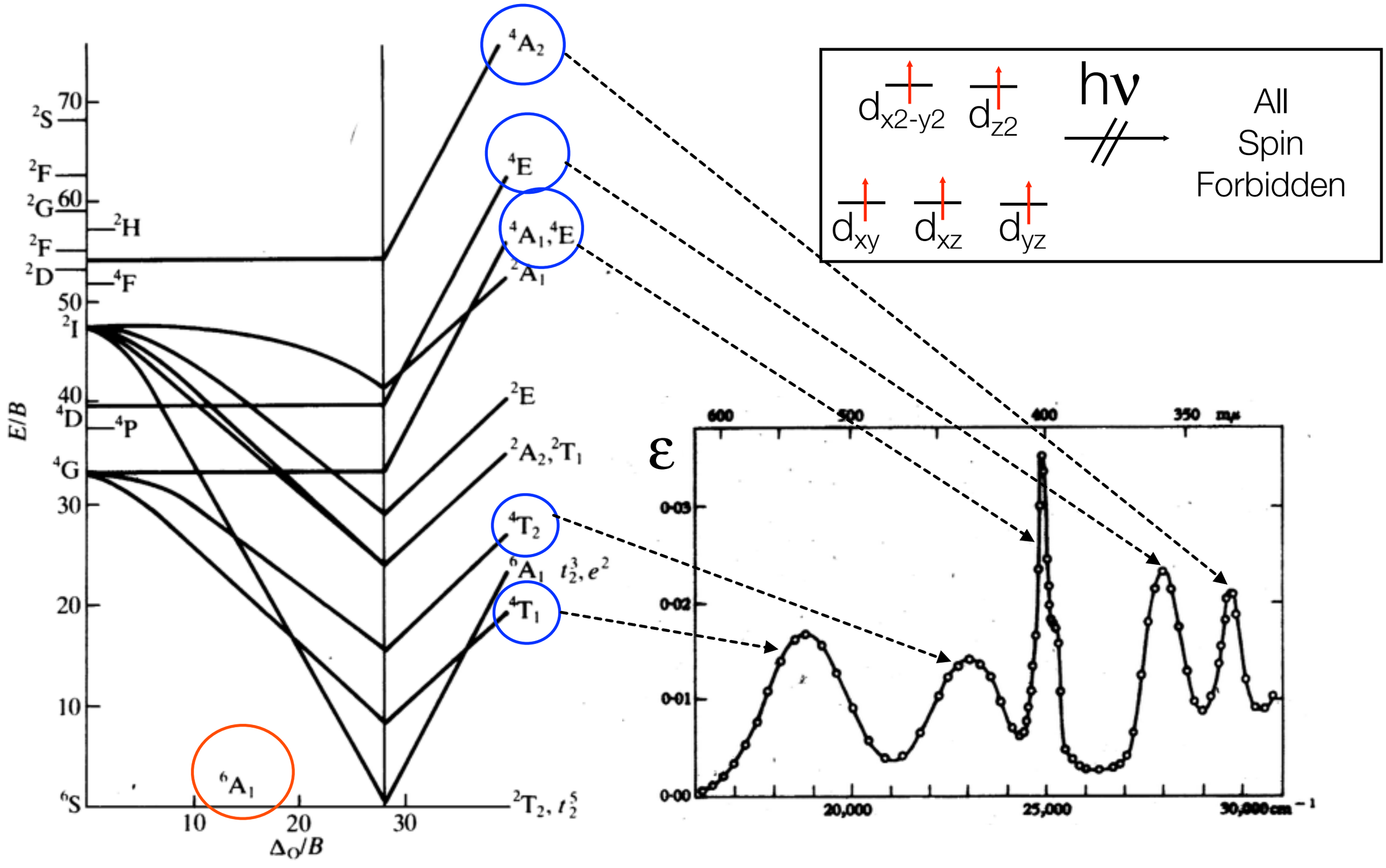


d-d Spectra of d^6 Ions (Fe^{II}, Co^{III})



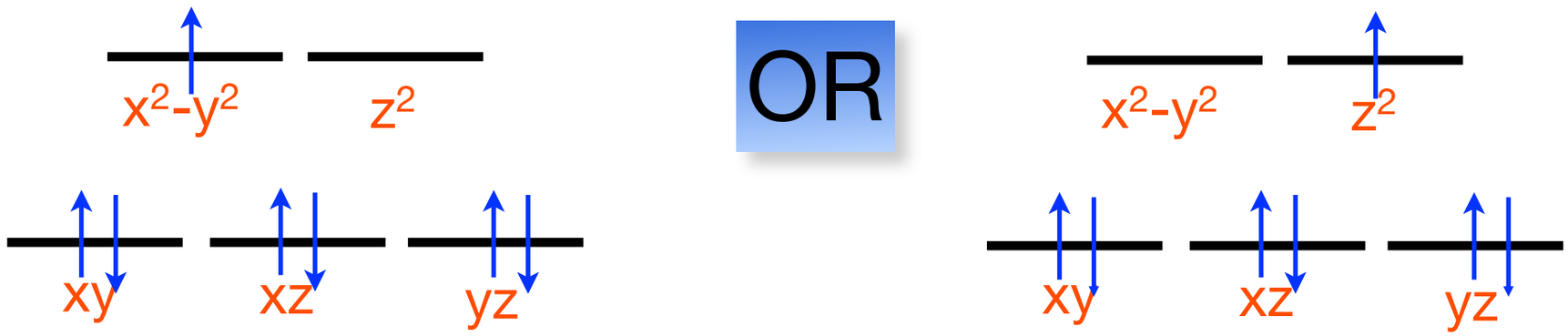


d-d Spectra of d^5 Ions (Fe^{III}, Mn^{II})

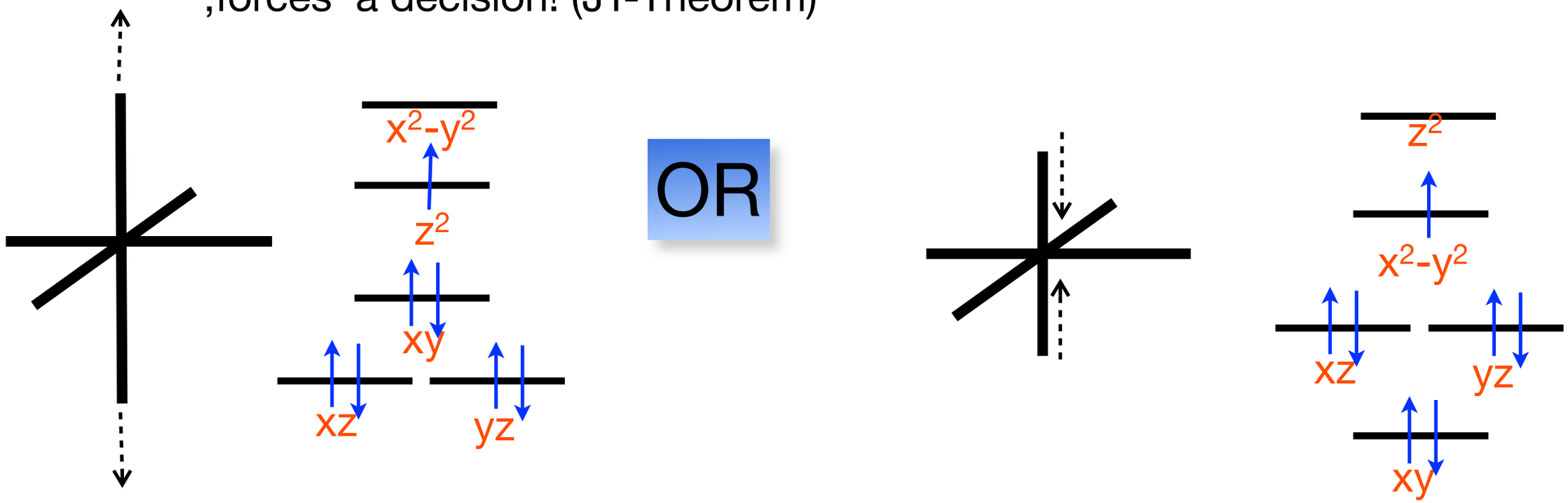


The Jahn-Teller Effect: Basic Concept

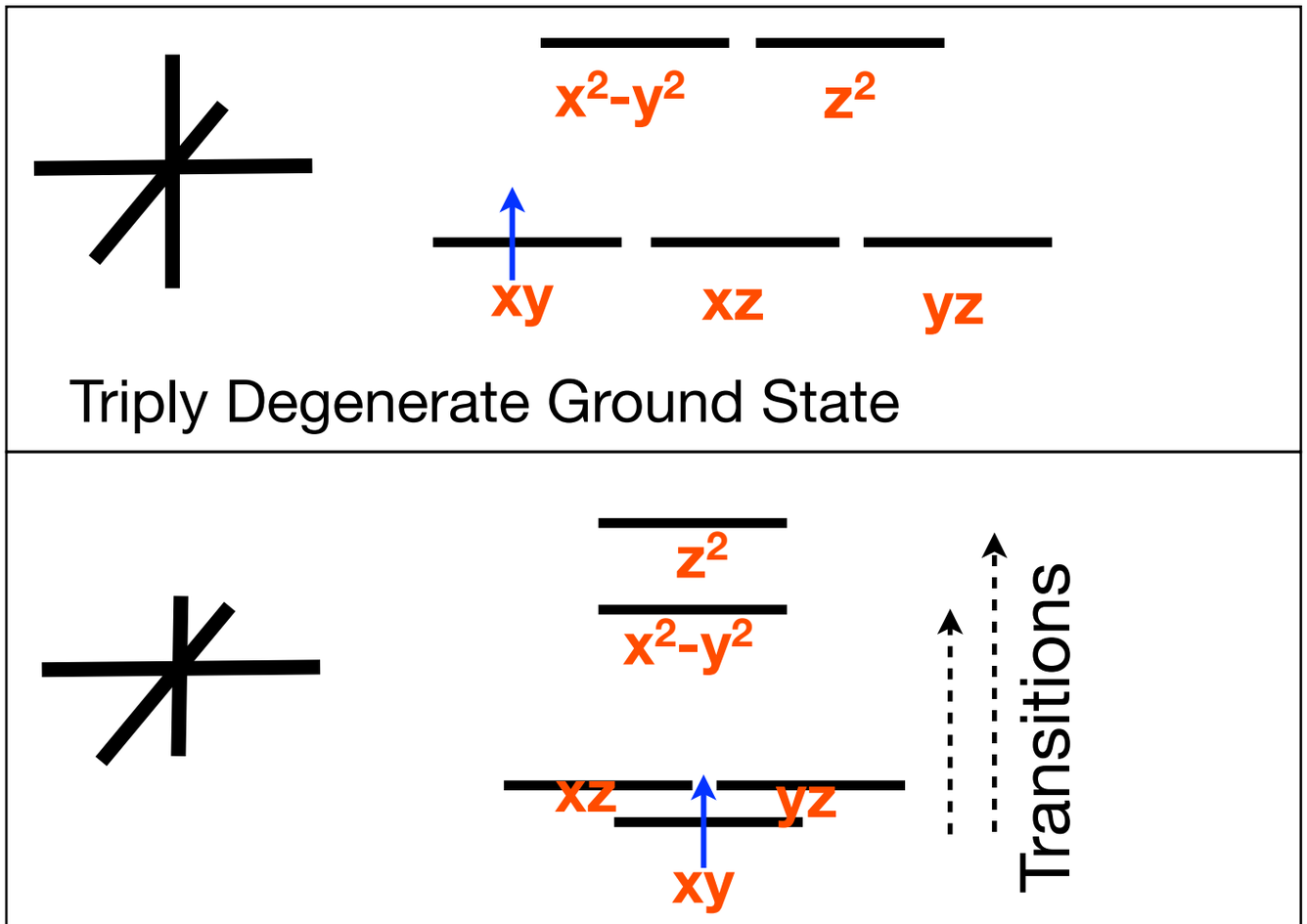
QUESTION: What happens if an electron can occupy one out of a couple of degenerate orbitals?

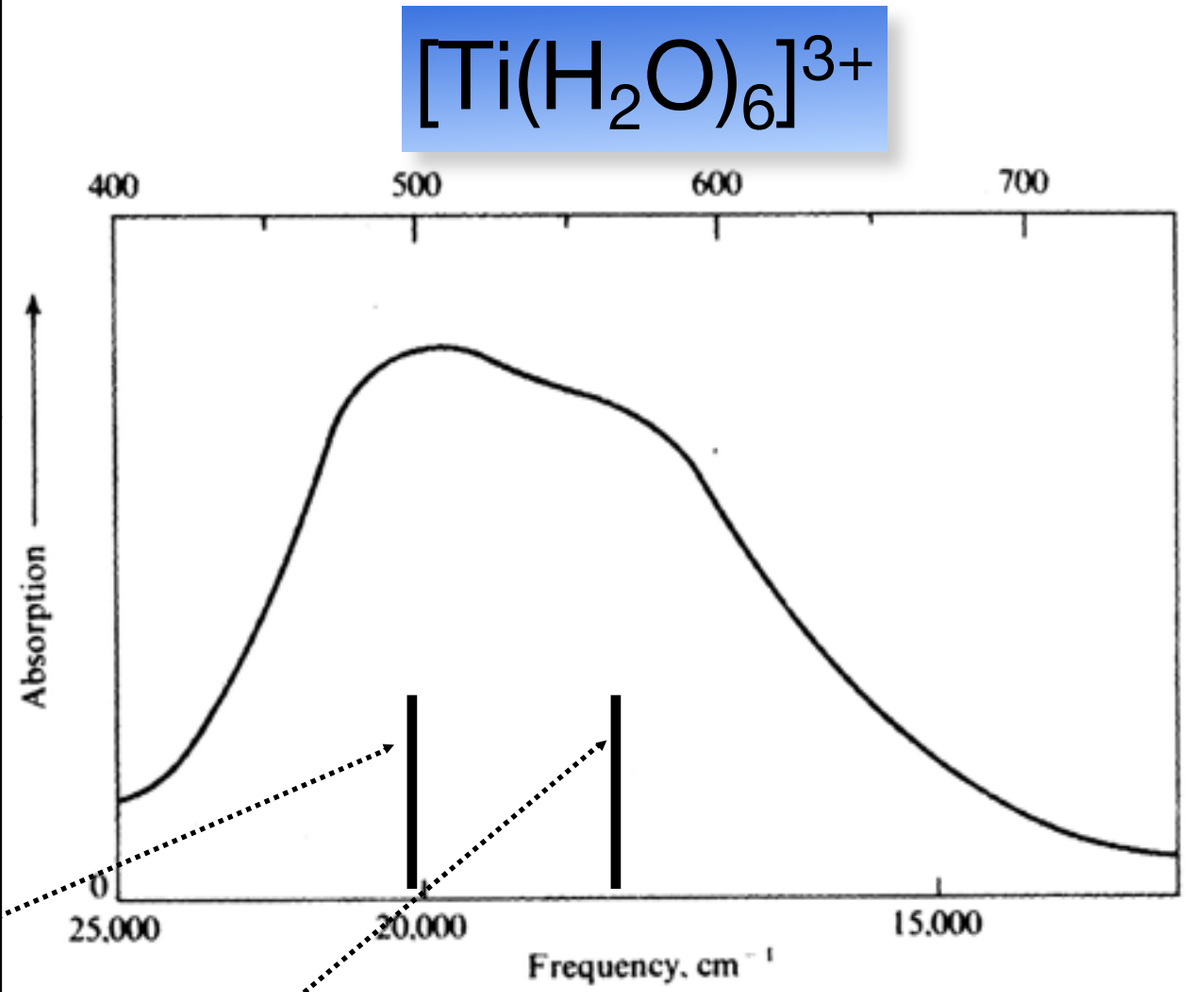


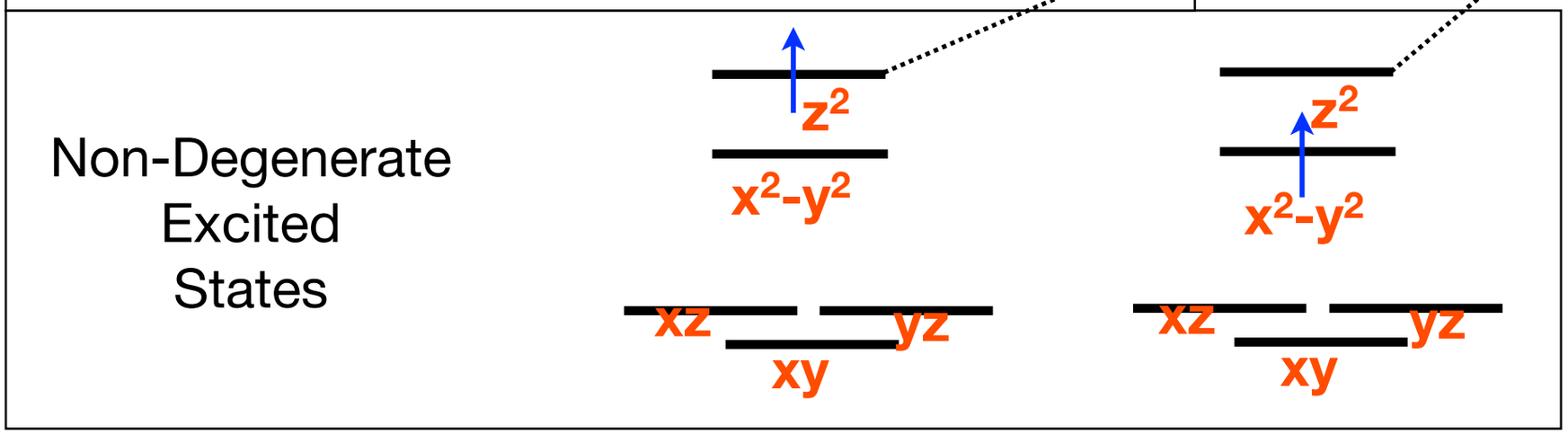
ANSWER: There is **ALWAYS** a nuclear motion that removes the degeneracy and ‚forces' a decision! (JT-Theorem)



The Jahn-Teller Effect: An Example







Ligand Field Splittings in Different Coordination Geometries

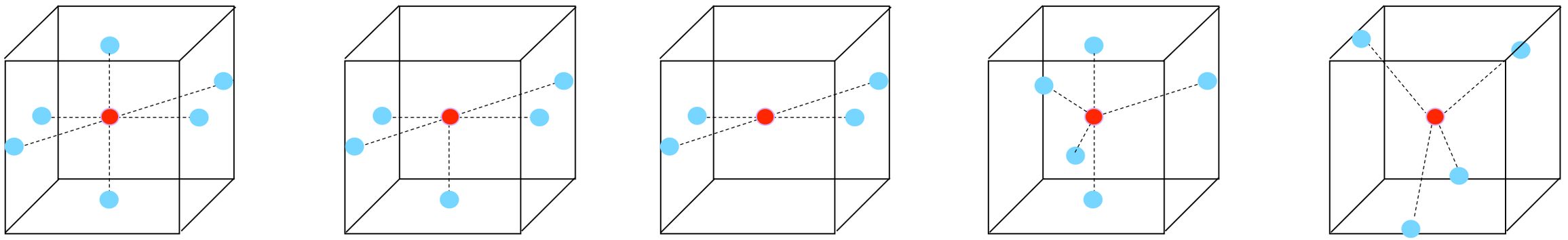
Octahedral

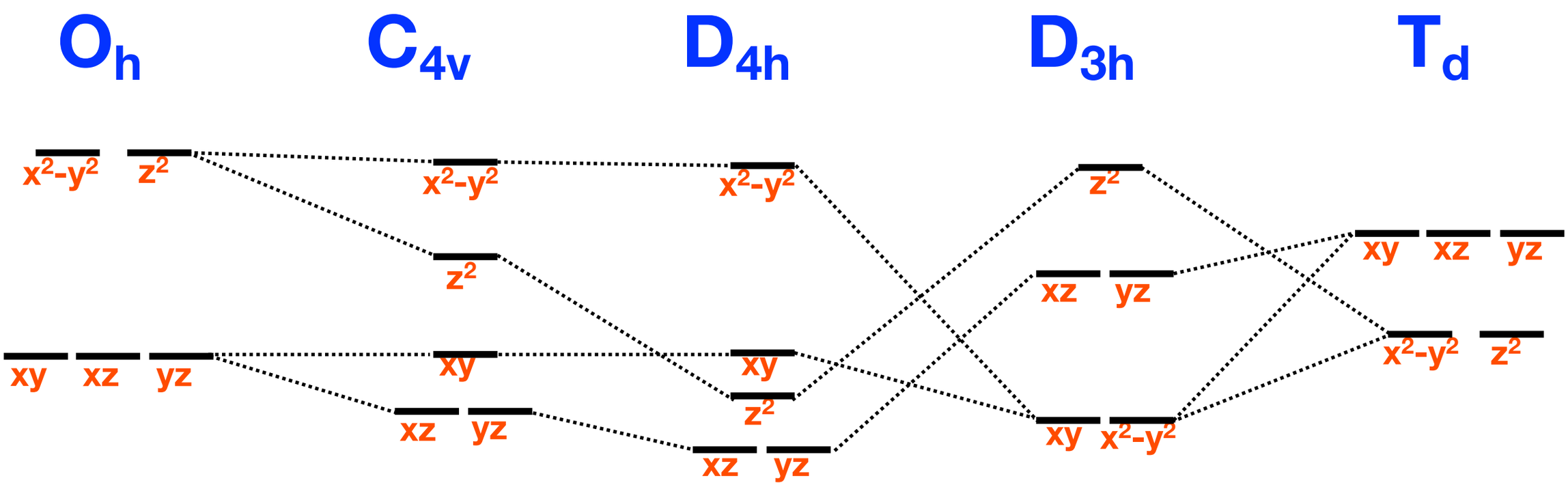
Tetragonal Pyramidal

Square Planar

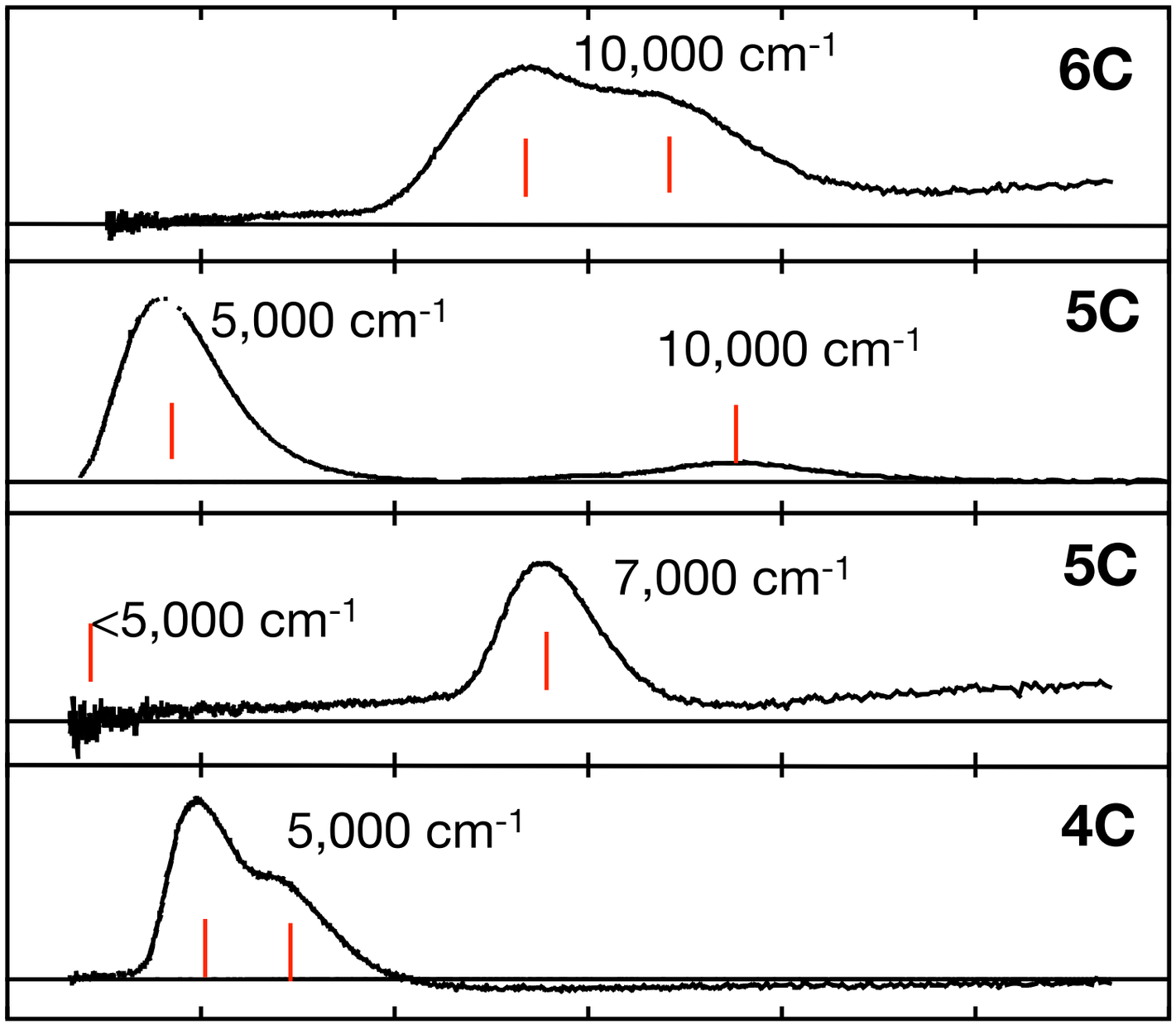
Trigonal Bipyramidal

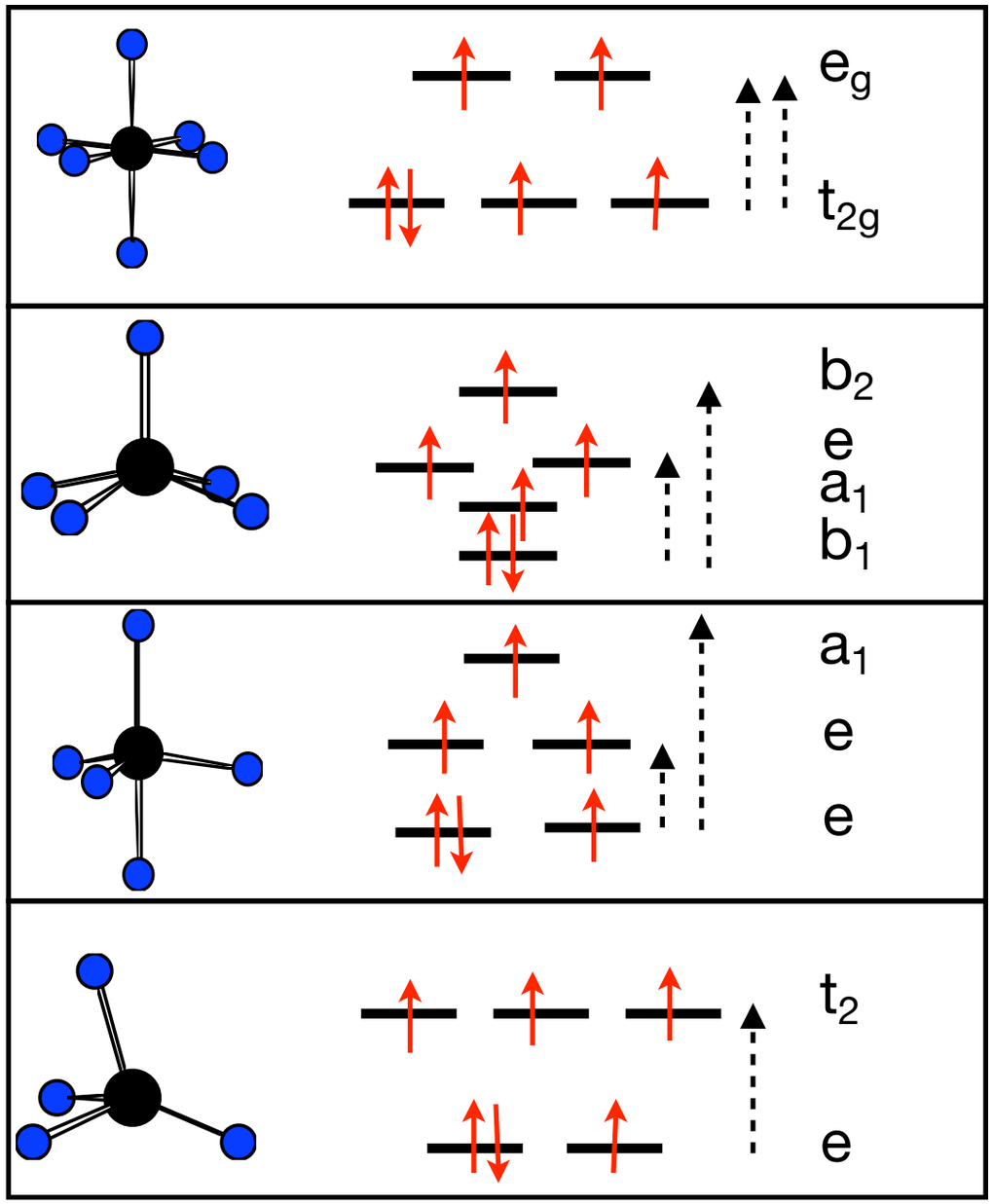
Tetrahedral





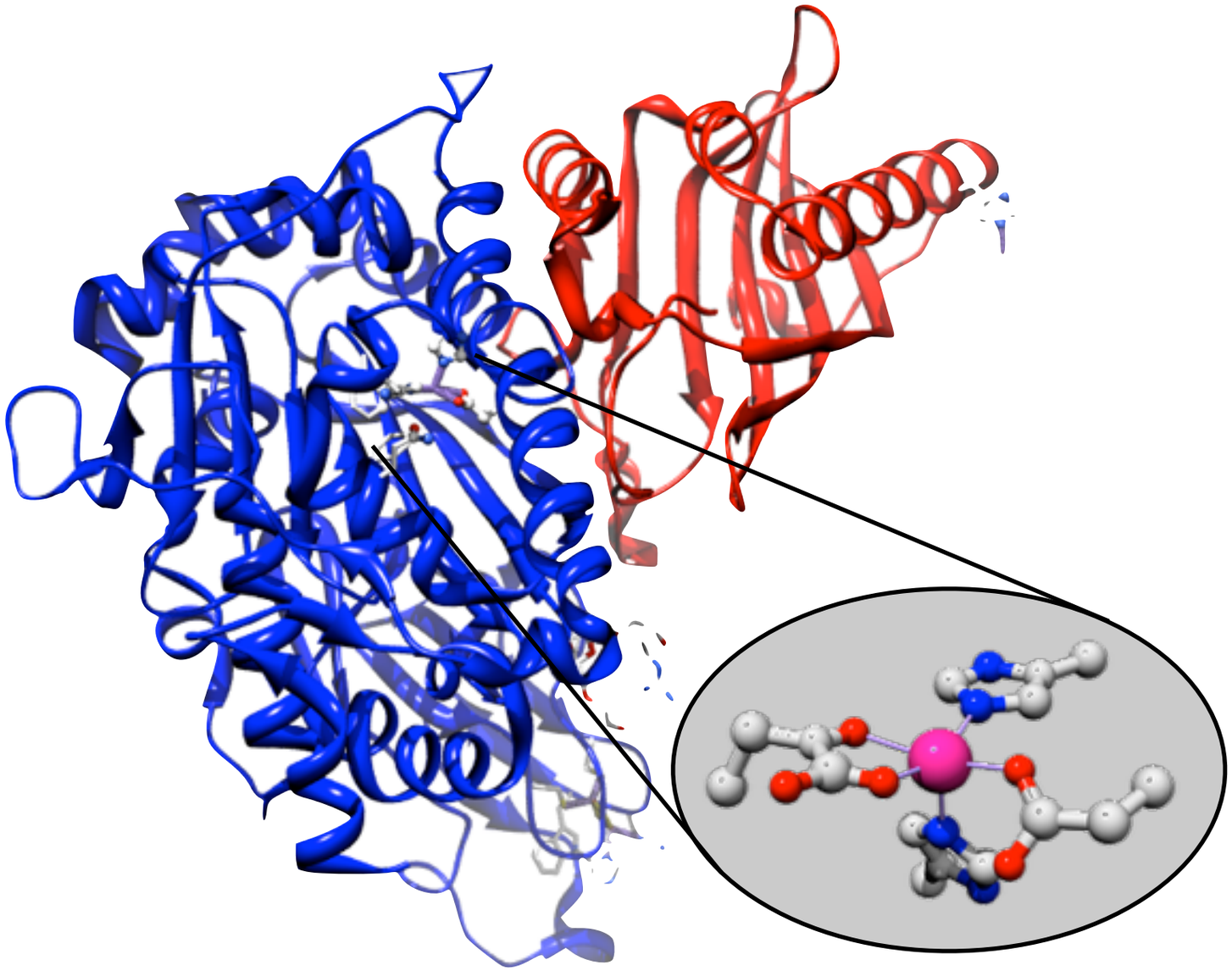
Coordnation Geometry and d-d Spectra: HS-Fe(II)

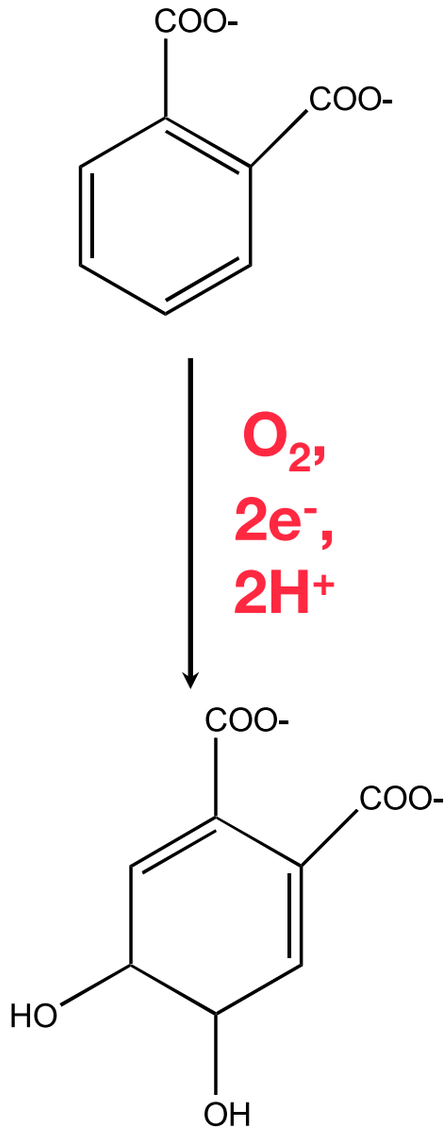




Studying Enzyme Mechanisms

Rieske-Dioxygenases



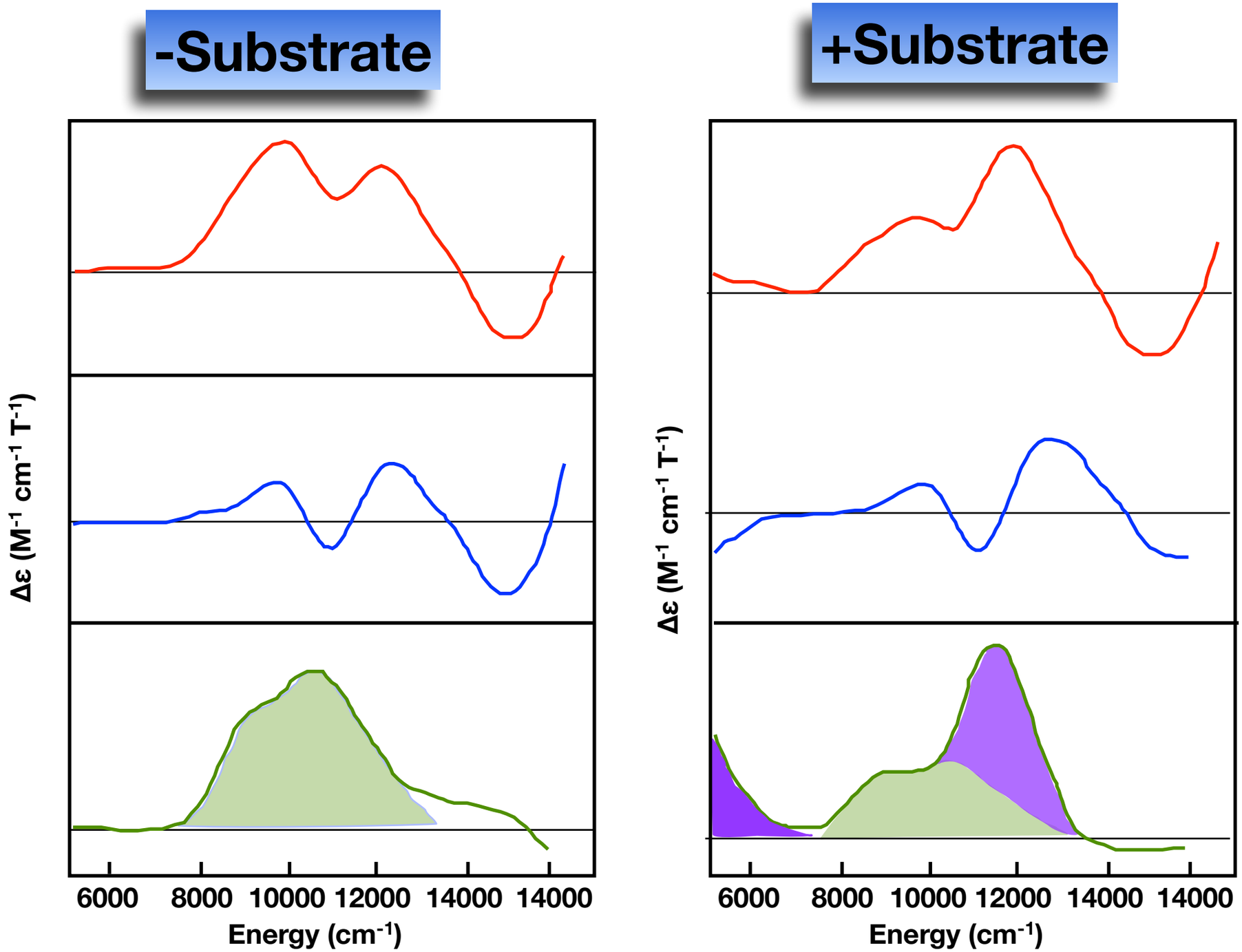


Active Site Geometry from d-d Spectra

Holoenzyme

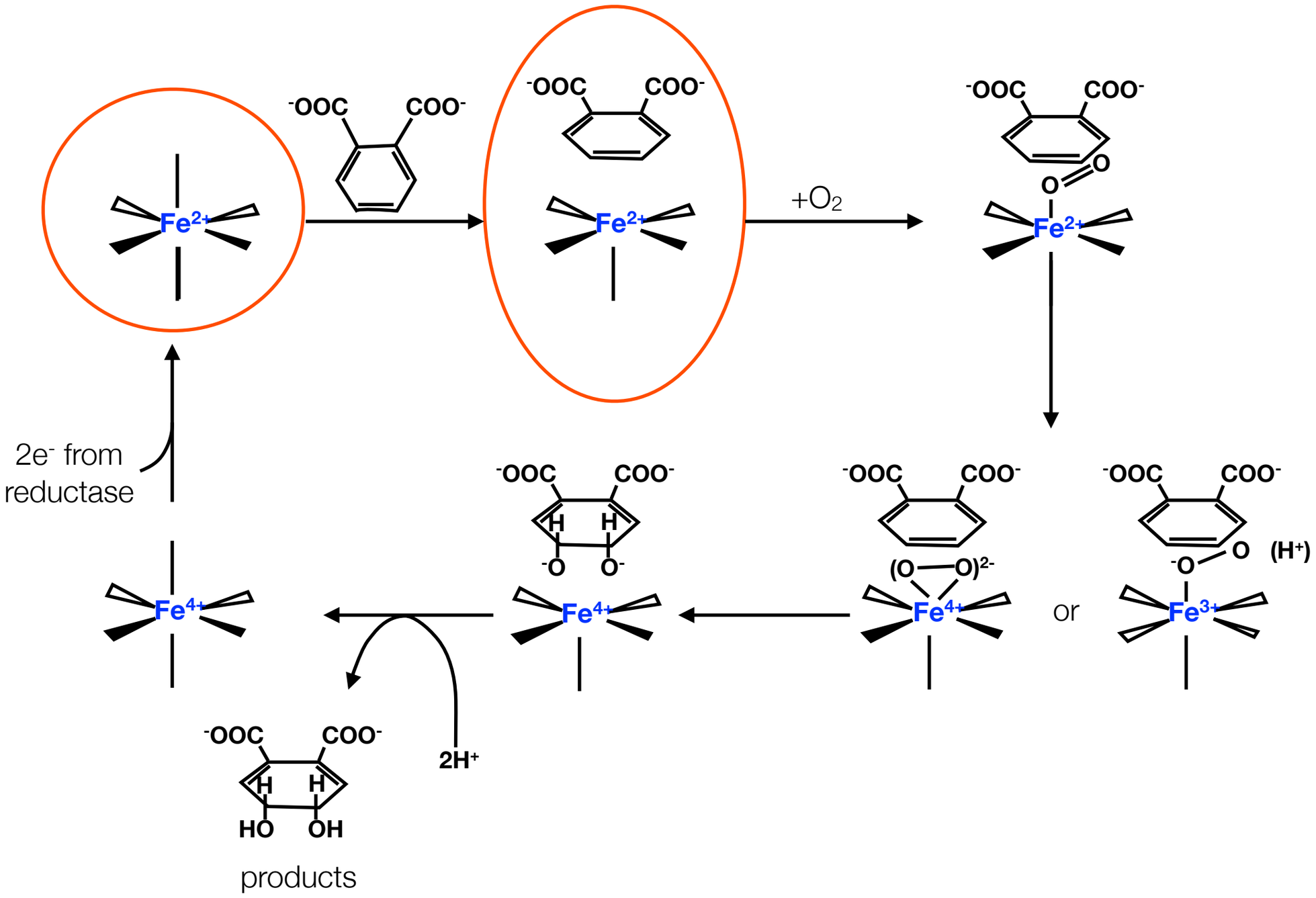
Rieske only

Difference



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

Mechanistic Ideas from Ligand Field Studies



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

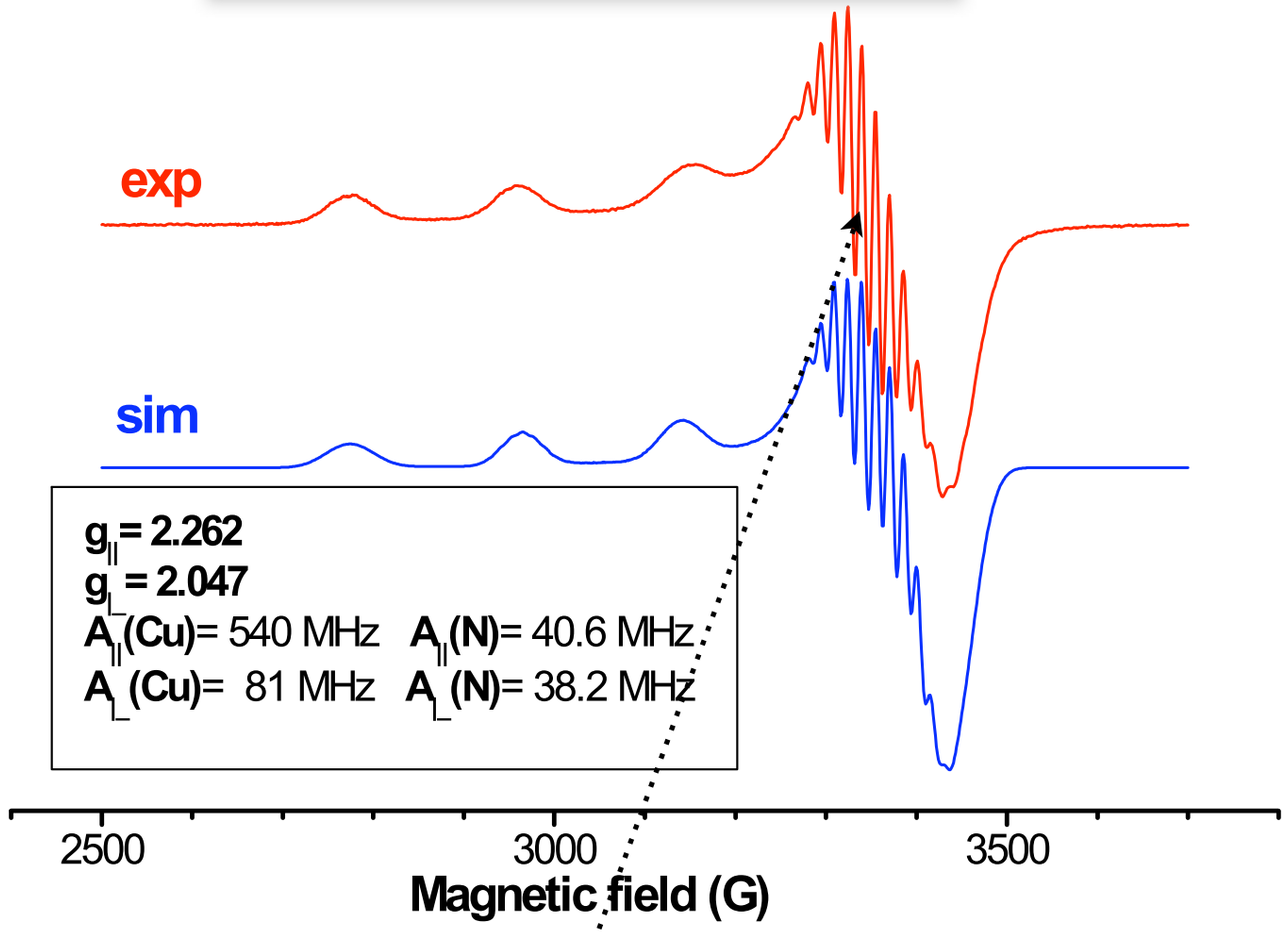
Beyond Ligand Field Theory

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

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

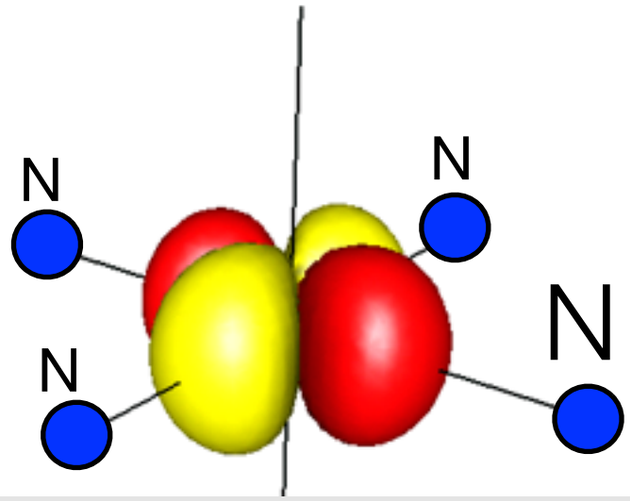
Experimental Proof of the Inadequacy of LFT

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



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

Ligand Field Picture



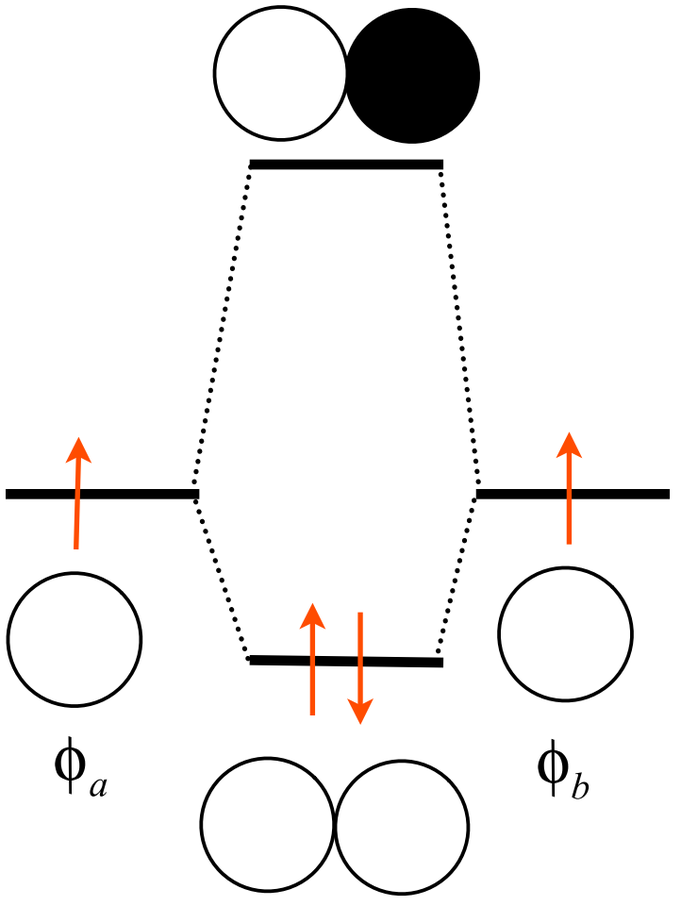
Wavefunction of the Unpaired Electron Exclusively Localized on the Metal

No Coupling Expected

Need a Refined Theory that Includes the Ligands Explicitly

Description of Bonds in MO Theory

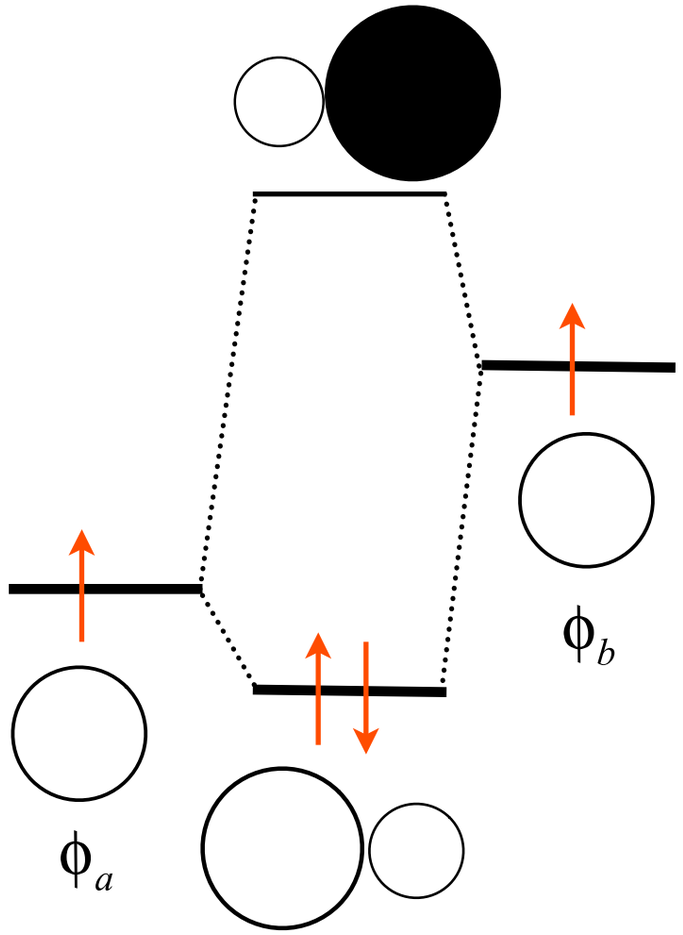
$$\frac{\phi_a - \phi_b}{\sqrt{2(1-S)}}$$



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

Homopolar Bond

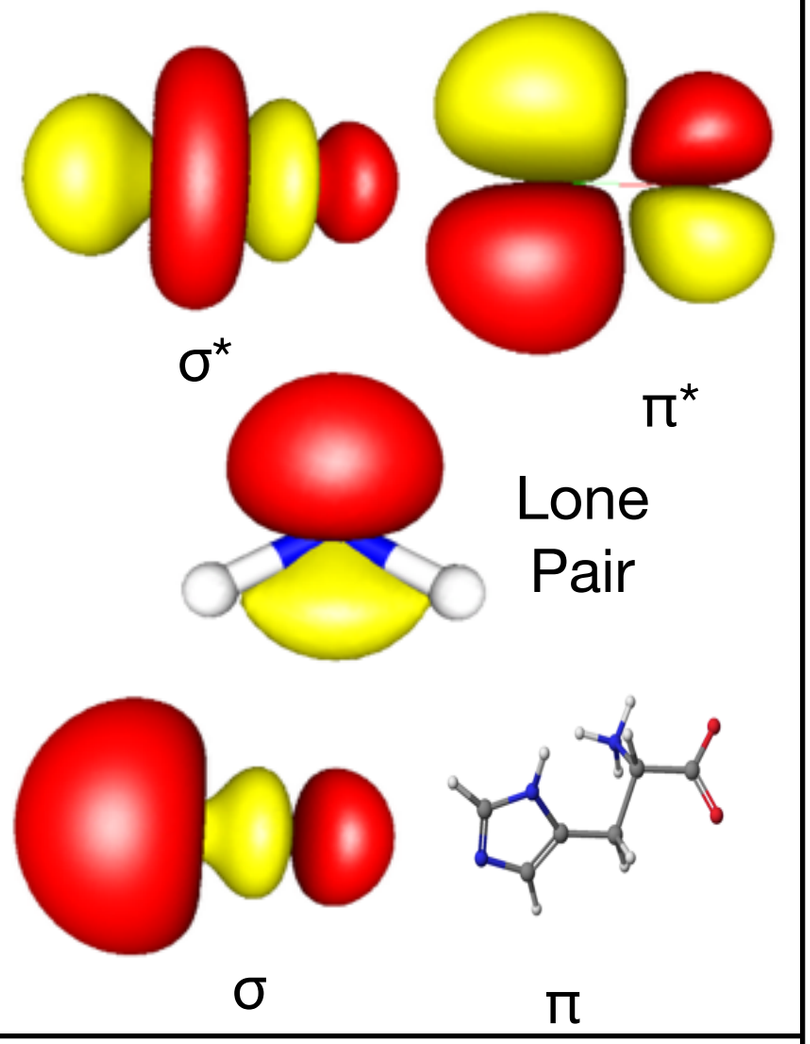
$$\frac{\lambda'\phi_a - \phi_b}{\sqrt{1+\lambda'(\lambda'-2S)}}$$



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

Heteropolar Bond

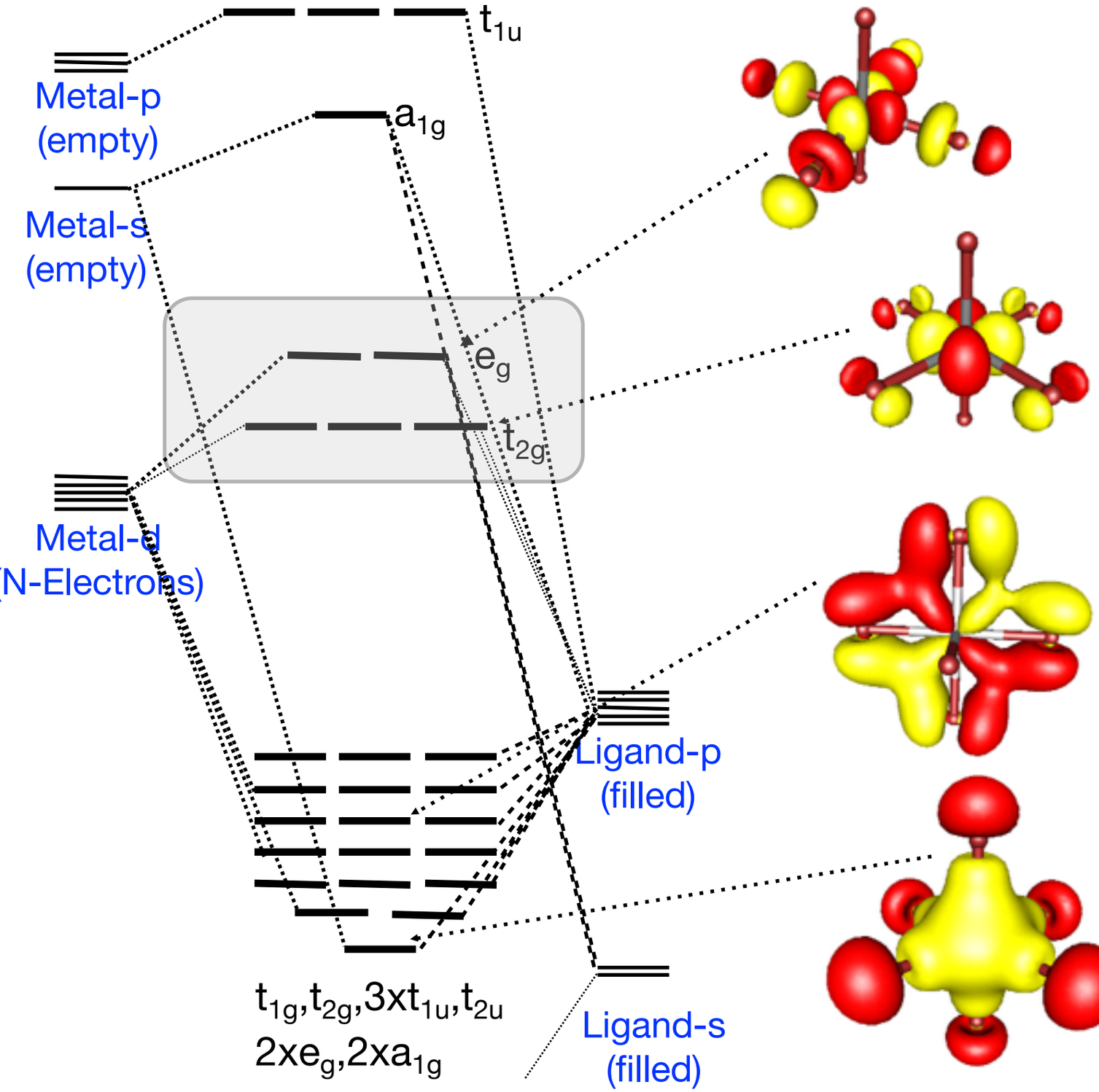
Types of MO's



Bond-Order:

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

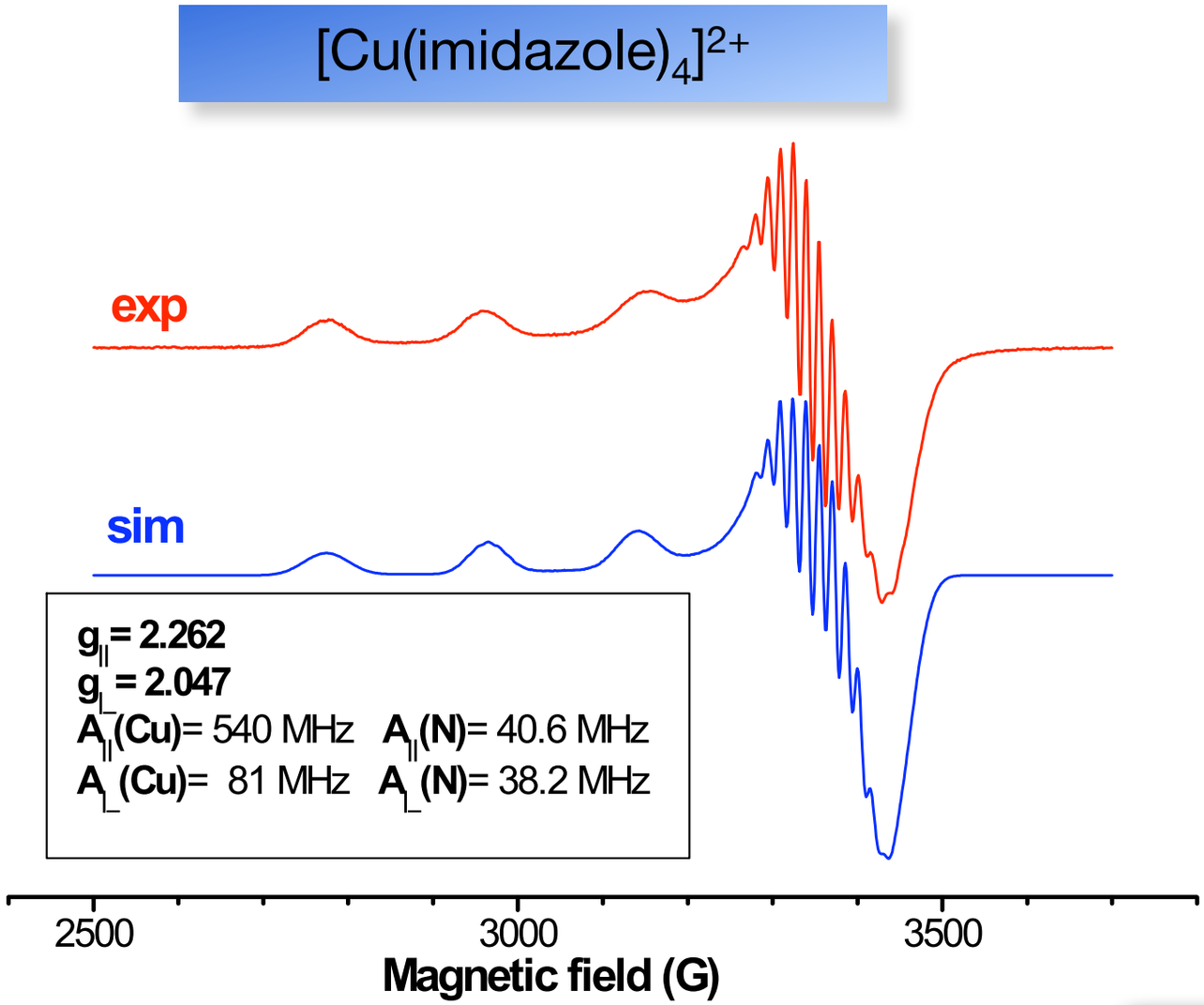
MO Theory of ML_6 Complexes

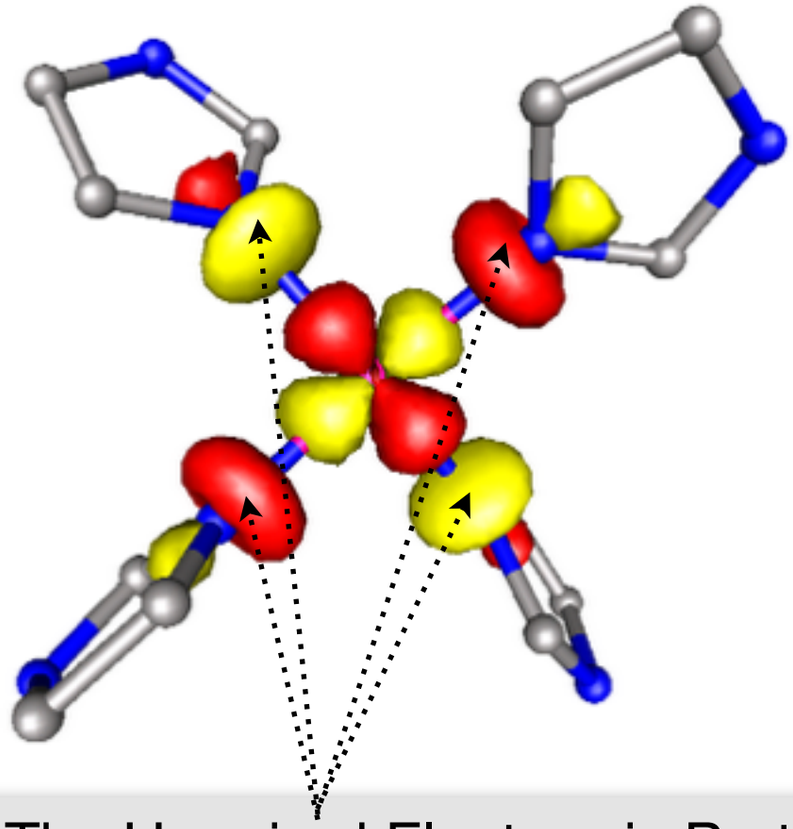


Key Points:

- 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



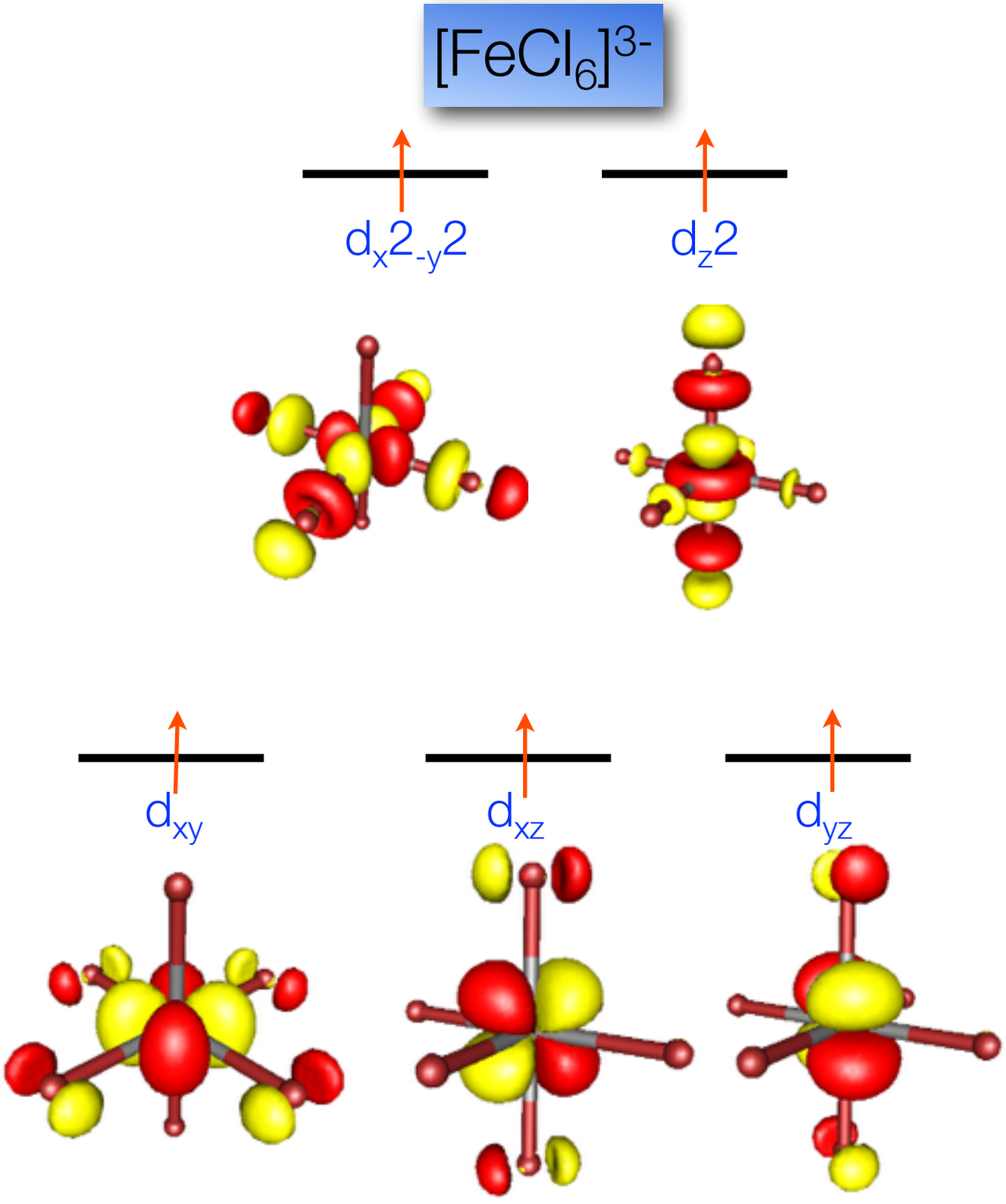


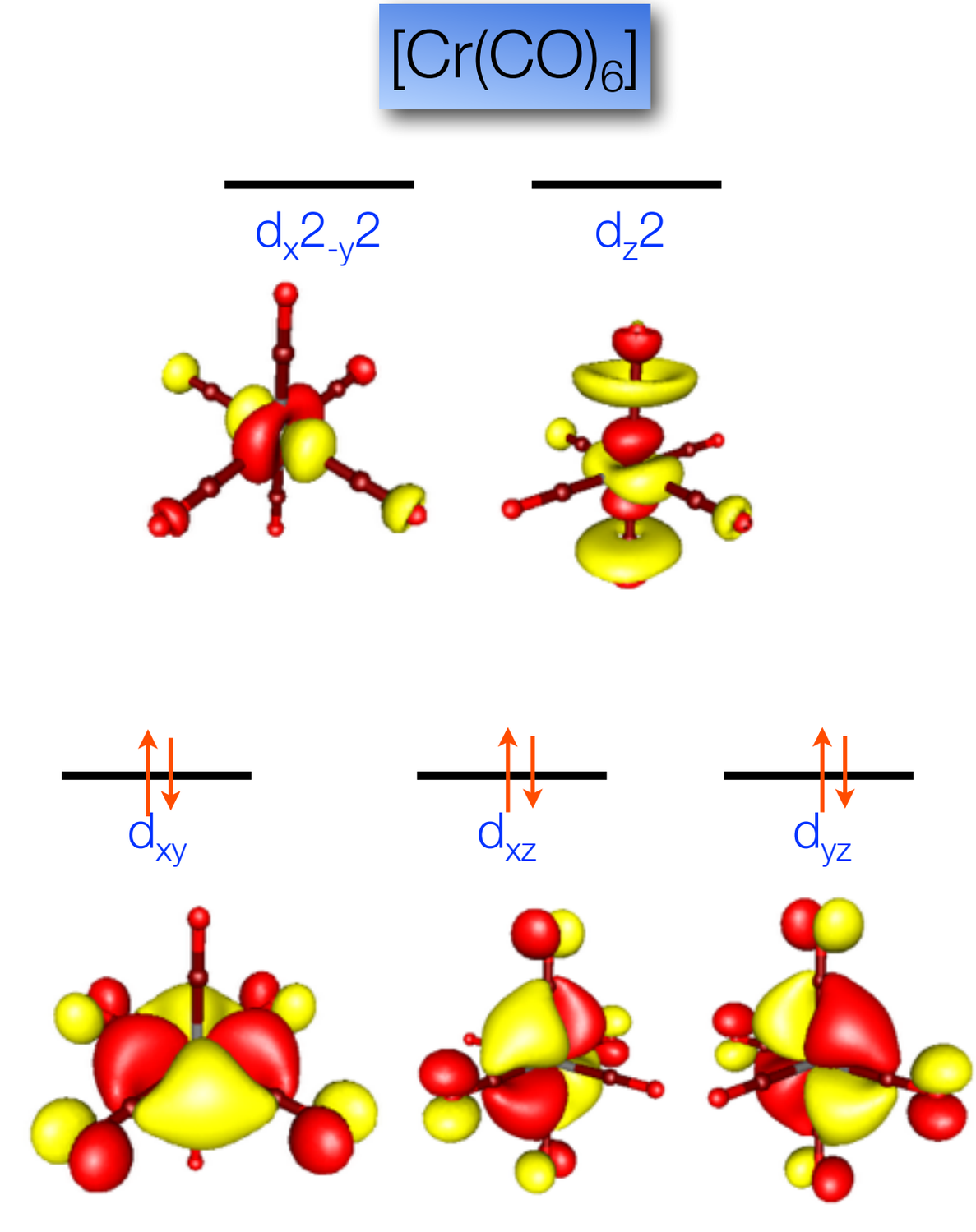
The Unpaired Electron is Partly Delocalized Onto the Ligands

Magnetic Coupling Expected

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

π-Bonding and π-Backbonding





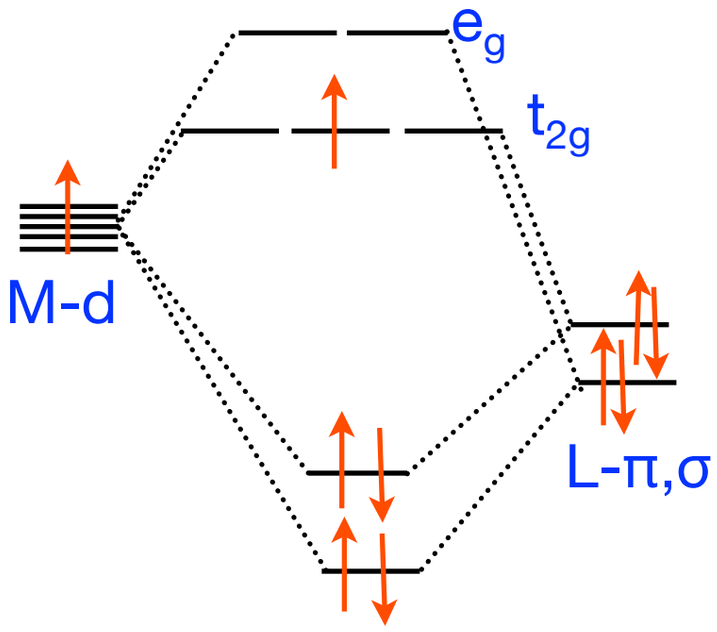
Interpretation of the Spectrochemical Series

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

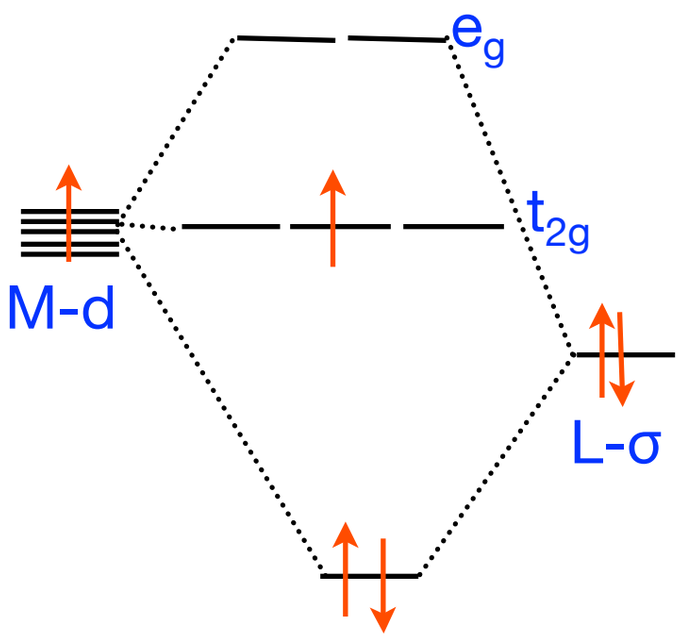
Δ SMALL

Δ LARGE

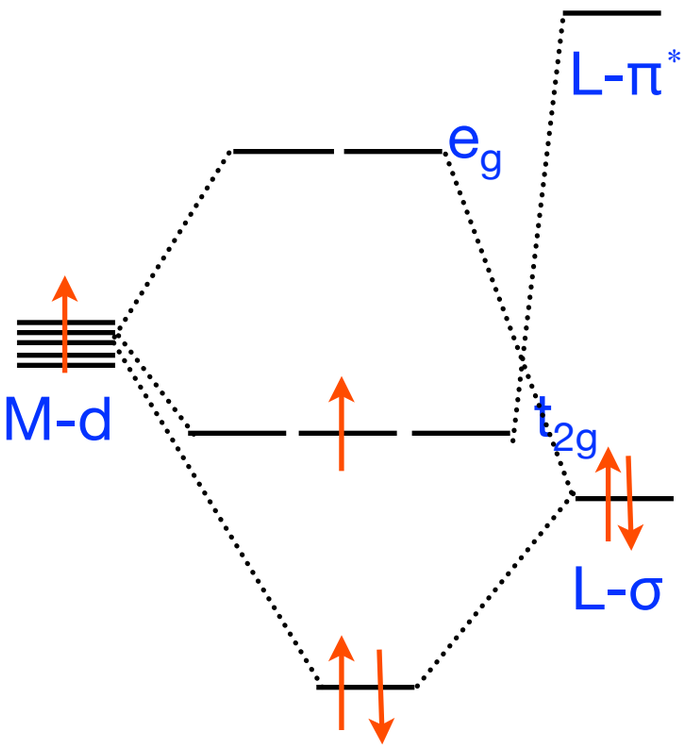
π-DONOR



π-'NEUTRAL'



π-ACCEPTOR



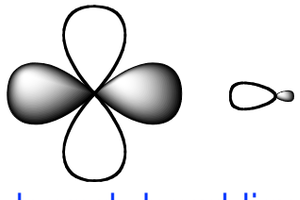
Covalency, Oxidation States and MO Theory

What is Covalency?

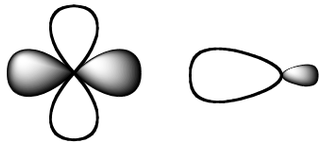
- ★ **Covalency refers to the ability of metal and ligand to share electrons** („soft“ concept with no rigorous definition)
- ★ Operationally, covalency can be defined in MO theory from the mixing coefficients of metal- and ligand orbitals

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

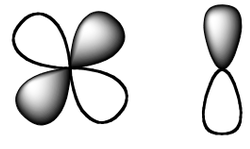
- ★ The value 1-α^2 can be referred to as „the covalency“ of the specific metal ligand bond. It is the probability of finding the electron that occupies ψ_i at the ligand
  - *The maximal covalency is 0.5, e.g. complete electron sharing*
  - *The covalency might be different in σ- and π-bonds (e.g. it 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?

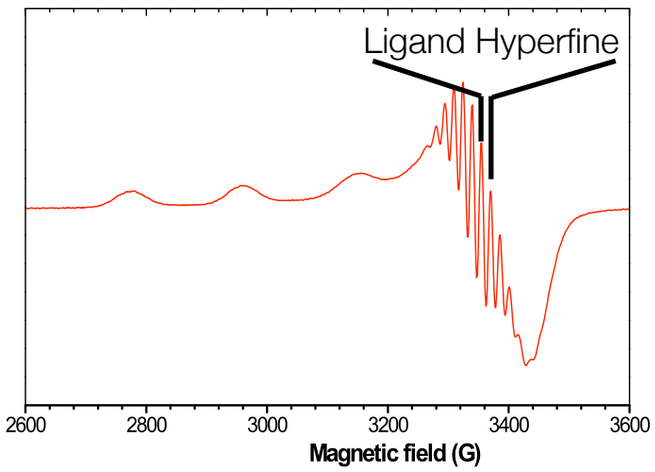
★ Can covalency be measured?

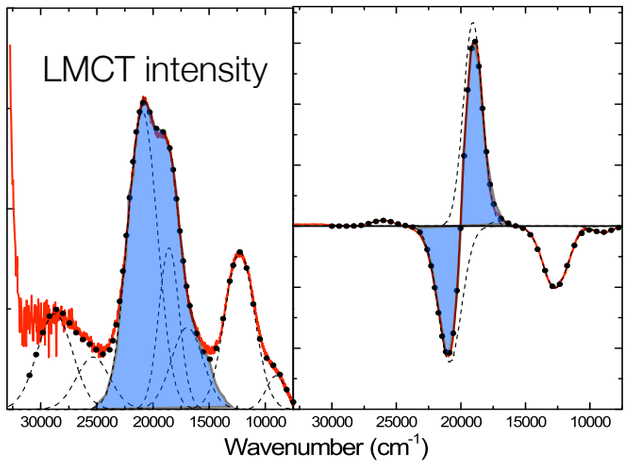
➡ Rigorously speaking: **NO**! Orbitals are not observables!

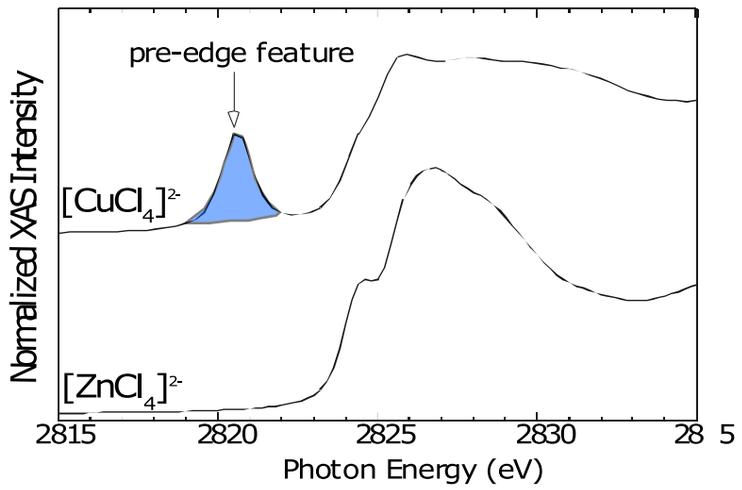
➡ On a practical level: (more or less) **YES**. Covalency can be correlated with a number of spectroscopic properties

- **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 $1-\alpha^2$

Covalency and Molecular Properties

Metal-Ligand Covalency Affects Many Chemical Properties!

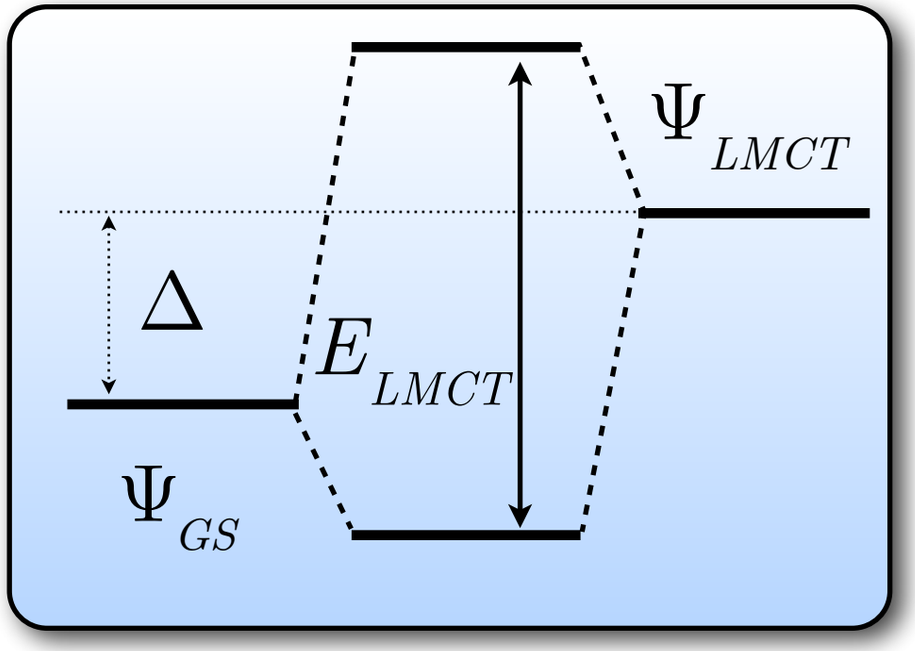
1. The **stability** of a complex increases with metal-ligand covalency
2. Covalency reflects charge-donation. The larger the charge donation the more negative the **redox potential**
3. Covalency may affect ‚**electron transfer pathways**‘
4. Covalency taken to the extreme might mean that ligands are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

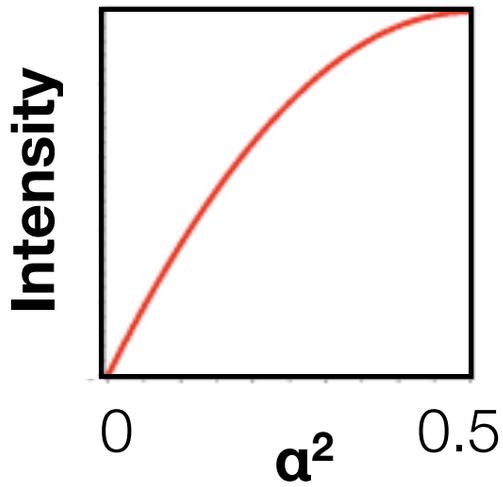
Estimating Covalency

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

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

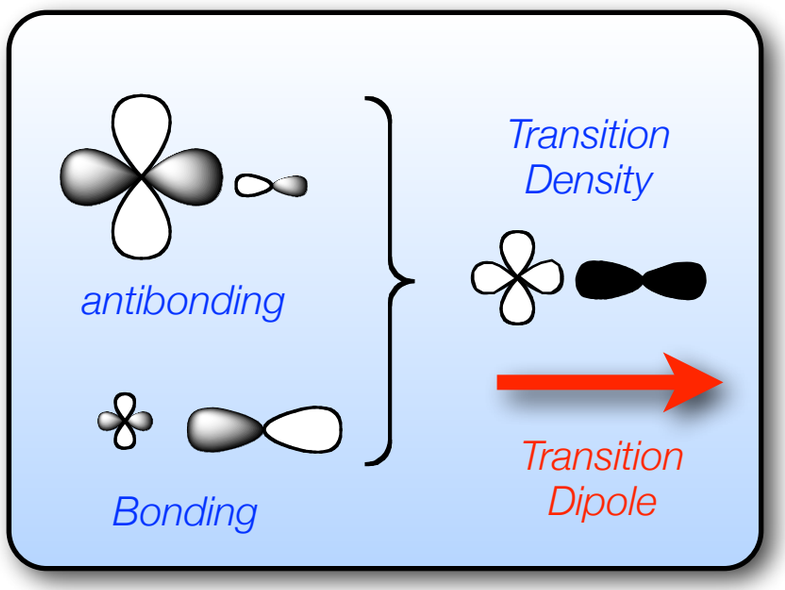
The **Transition Energy**: $E_{LMCT} = \Delta + 2\frac{\beta^2}{\Delta} - 2\frac{\beta^4}{\Delta^3} + O(\beta^6)$

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



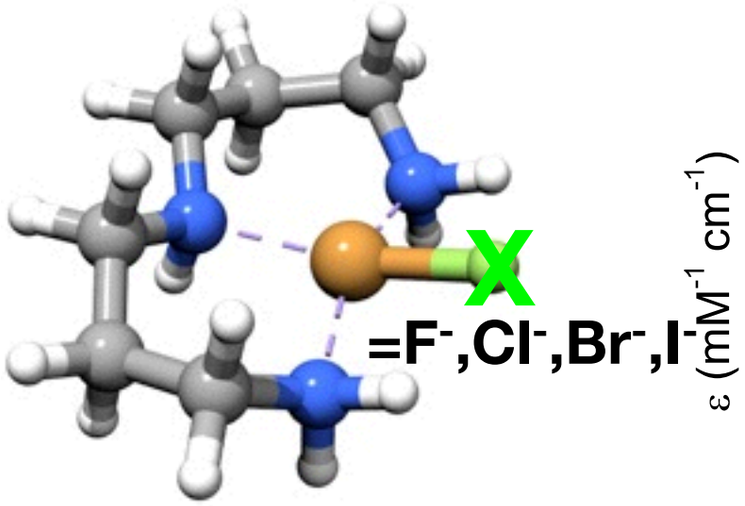
This can be turned around to obtain the model parameters from the measurable quantities: ***R*ML**, ***D*ML** and ***E*LMCT**

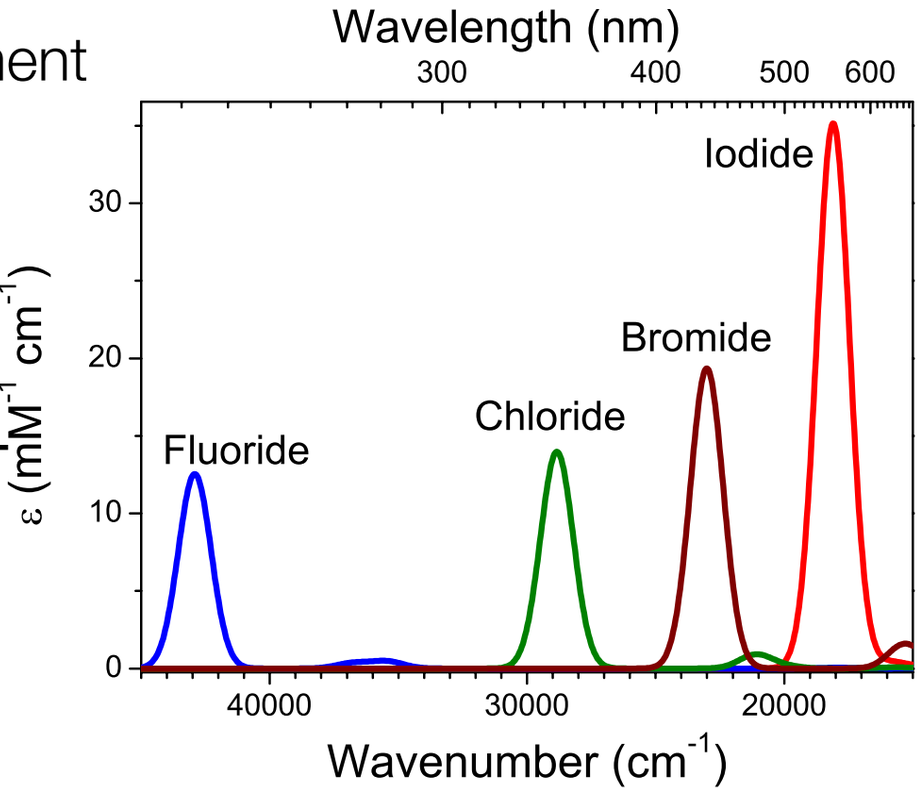
$$\beta = \pm D_{ML}\frac{R_{ML}}{R_{ML}^2 + 2D_{ML}^2}E_{LMCT} \qquad \Delta = \frac{R_{ML}^2}{R_{ML}^2 + 2D_{ML}^2}E_{LMCT}$$



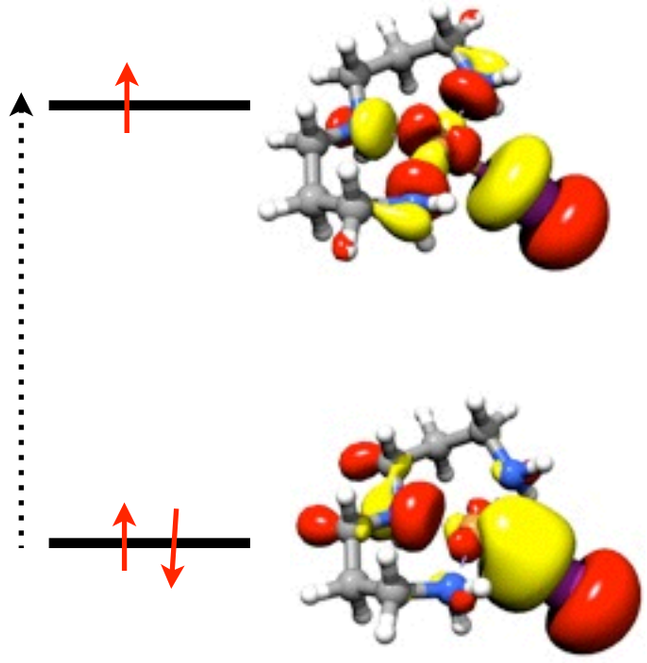
Let‘s Apply it (*in silico*)

Hypothetical Cu(II) fragment





σ-LMCT Transition



	IP/eV	**R**	**D**	**E**	**Δ**/eV	**β**/eV	**β**
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**

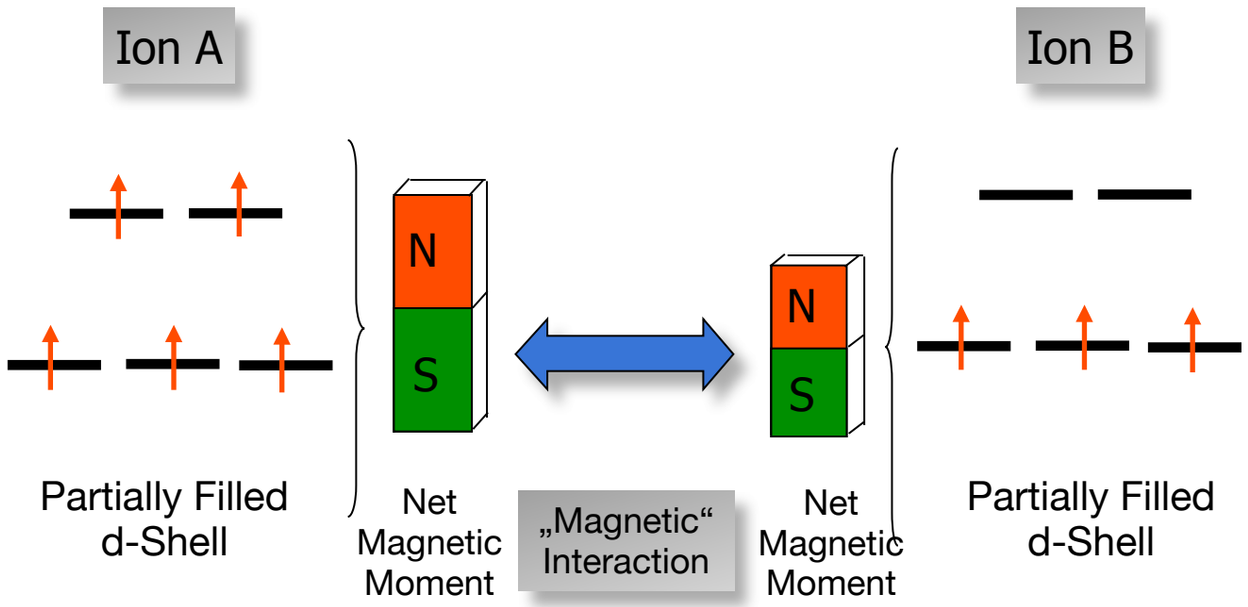
BP86/def2-sv(p) structures; State averaged CASSCF(15,8)/def-sv(p) (5d- orbitals and 3 halide orbitals) followed by uncontrated RI-MRMP2

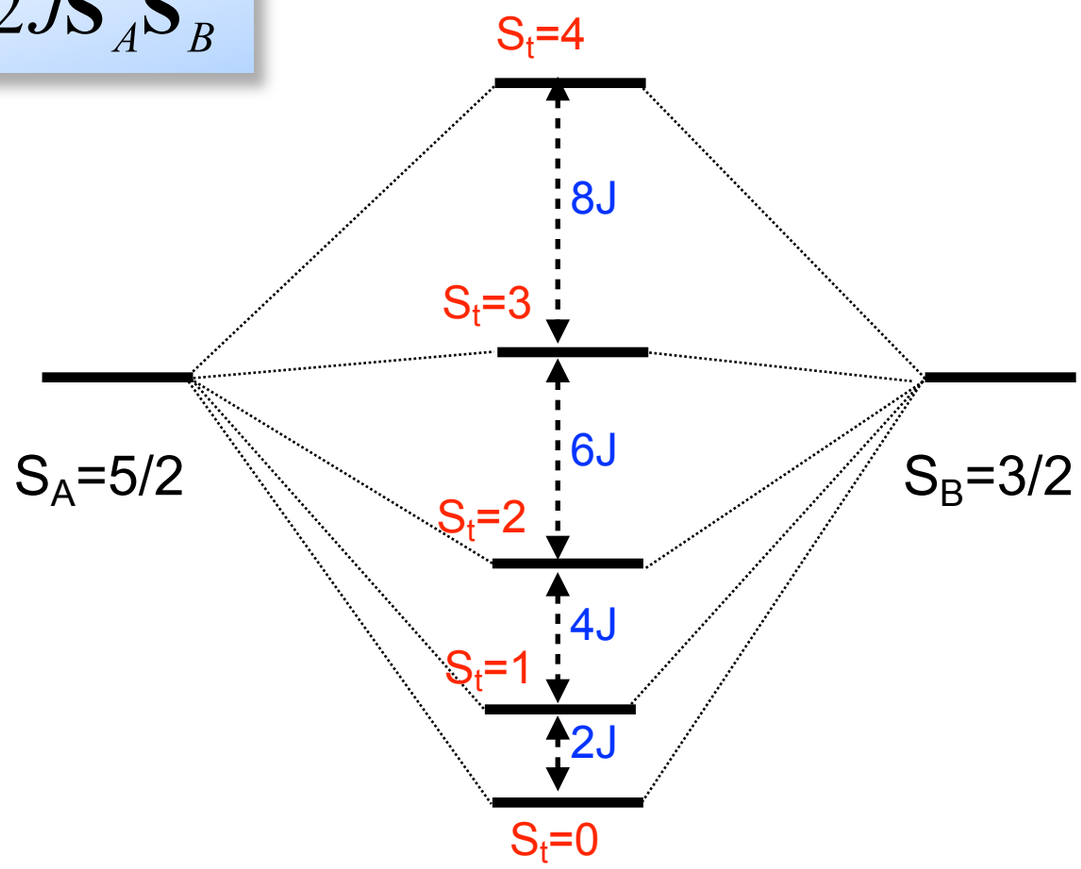
The Spin State Problem:
Exchange Coupling

What is Exchange ?

The interaction of two paramagnetic ions (or more generally fragments) leads to a „ladder“ of total spin states which are described phenomenologically by the Heisenberg-Dirac-VanVleck Hamiltonian

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





What is the origin of this „magnetic“ interaction and how do we calculate it?

With no other magnetic interactions, the energy of a given spin-state is simply: $E(J,S,S_A,S_B) = -J\left[S(S+1) - S_A(S_A+1) - S_B(S_B+1)\right]$

„Exchange Coupling“: Anderson Model

2e⁻ in 2 orbitals problem:

$$\psi_{1,2} = \frac{1}{\sqrt{2}}\left(a \pm b\right)$$

Neglect overlap for a moment

$$\left|{}^1\Psi_1\right\rangle = \left|\psi_1\,\bar{\psi}_1\right| \quad \left|{}^1\Psi_2\right\rangle = \left|\psi_2\,\bar{\psi}_2\right| \quad \left|{}^1\Psi_3\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\psi_1\,\bar{\psi}_2\right| - \left|\bar{\psi}_1\,\psi_2\right|\right)$$

3-Singlets

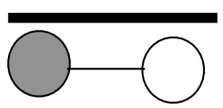
$$\left|{}^3\Psi_1\right\rangle = \left|\psi_1\,\psi_2\right|$$

1-Triplet

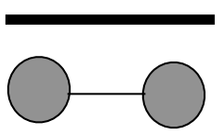
After-CI: $E\left(\left|{}^1\Psi\right\rangle\right) - E\left(\left|{}^3\Psi\right\rangle\right) \approx 2K_{ab} - \frac{4F_{ab}^2}{J_{aa} - J_{ab}} \equiv 2J_{HDvV}$

Heisenberg-Dirac-van Vleck „effective“ Exchange ($H=-2JS_AS_B$)

Orbitals

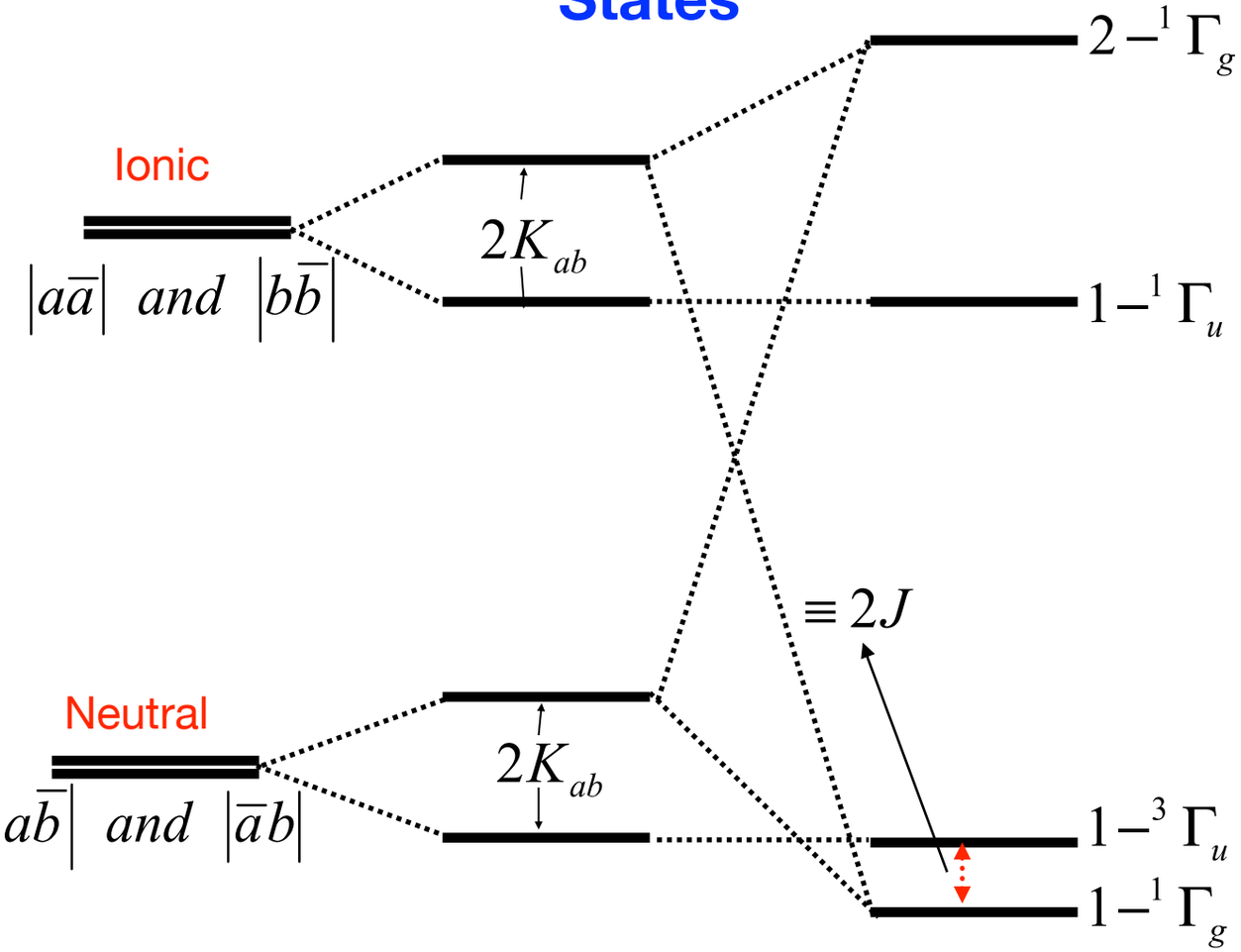


$\psi_2 \sim a - b$



$\psi_1 \sim a + b$

States



Integrals

$$J_{aa} = J_{bb} = \left(a(1)a(1) \mid r_{12}^{-1} \mid a(2)a(2)\right)$$

On-Site Coulomb Integral

$$J_{ab} = \left(a(1)a(1) \mid r_{12}^{-1} \mid b(2)b(2)\right) \propto R_{ab}^{-1}$$

Inter-Site Coulomb Integral

$$K_{ab} = \left(a(1)b(1) \mid r_{12}^{-1} \mid a(2)b(2)\right) \propto \mathrm{e}^{-\alpha R_{ab}}$$

Inter-Site Exchange Integral

$$F_{ab} = h_{ab} + \left(a(1)a(1) \mid r_{12}^{-1} \mid a(2)b(2)\right) + \left(b(1)b(1) \mid r_{12}^{-1} \mid a(2)b(2)\right)$$

Fock Like „Transfer“ Integral