

3. Lecture: Basics of Magnetism: Local Moments

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Content

1. Local moments of magnetic ions
2. Hund's rules
3. Magnetic moments of transition metal ions
4. Crystal field splitting
5. Magnetic moments of rare earth ions



1. Local moments of magnetic ions

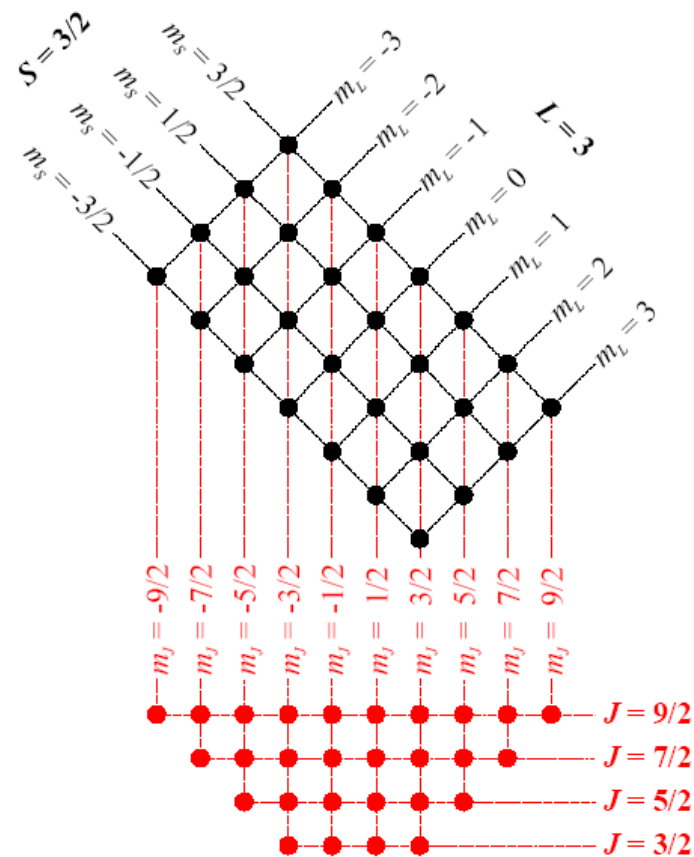
Orbital moment \vec{L} and spin \vec{S} combine to different total moment \vec{J}

The z-components m_j may take any value from $|L-S|$ to $|L+S|$, each $2J+1$ fold degenerate. The total number of combinations is:

$$\sum_{J=|L-S|}^{L+S} (2J+1) = (2L+1)(2S+1)$$

Example: $L = 3, S=3/2$

- m_j may take the values from $|L-S| = 3/2$ to $|L+S| = 9/2$
- 28 Possible combinations are shown in the graph.
- **Which J corresponds to the ground state?**
⇒ Hund's rule.





2. Hund's Rules

Hund's rules help to find the ground state. The empirical rules fulfill Pauli principle and should be followed in the sequence from more important to less important:

1. First Hund's rule

Maximize \vec{S} without violating Pauli principle

2. Second Hund's rule

The states with largest m_L are filled first

3. Third Hund's rule

Because of spin orbit coupling J takes the following values:

$$J = L - S \quad \text{for shells less than half filled}$$

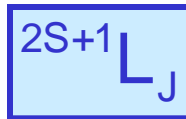
$$J = L + S \quad \text{for shells more than half filled}$$

This is referred to as the Russell-Saunders-coupling scheme. It works only for weak LS – coupling, for stronger LS – coupling, i.e. for heavier elements, the j-j coupling dominates



Nomenclature for spectroscopic terms

The ground state is written in the form



J and S are expressed in numbers. For L capital letter are used:

$$\begin{aligned} L = |\Sigma L_z| &= 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \\ &= S \quad P \quad D \quad F \quad G \quad H \quad I \end{aligned}$$

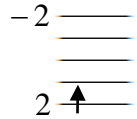
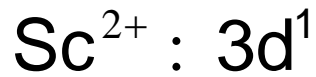
The spin is expressed by its multiplicity (2S+1).

g_j - value is calculated according to:

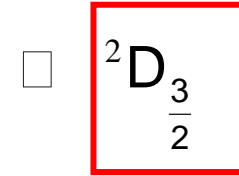
$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$



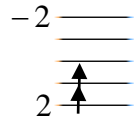
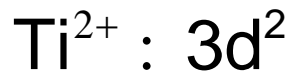
Examples



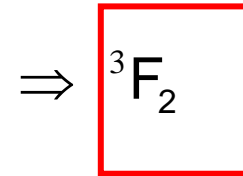
$$\left\{ \begin{array}{l} S = 1/2 \\ L = 2 \\ J = L - S = 3/2 \end{array} \right.$$



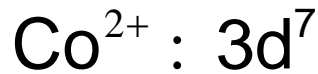
$$g_J = 0.8$$



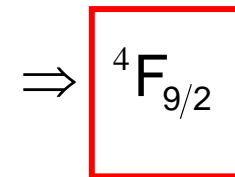
$$\left\{ \begin{array}{l} S = 1 \\ L = 2 + 1 = 3 \\ J = L - S = 2 \end{array} \right.$$



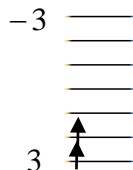
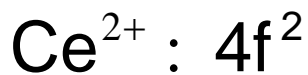
$$g_J = 0.66$$



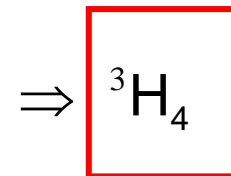
$$\left\{ \begin{array}{l} S = 3/2 \\ L = 4 + 2 - 1 - 2 = 3 \\ J = L + S = 9/2 \end{array} \right.$$



$$g_J = 1.33$$



$$\left\{ \begin{array}{l} S = 1 \\ L = 3 + 2 = 5 \\ J = L - S = 4 \end{array} \right.$$



$$g_J = 0.8$$

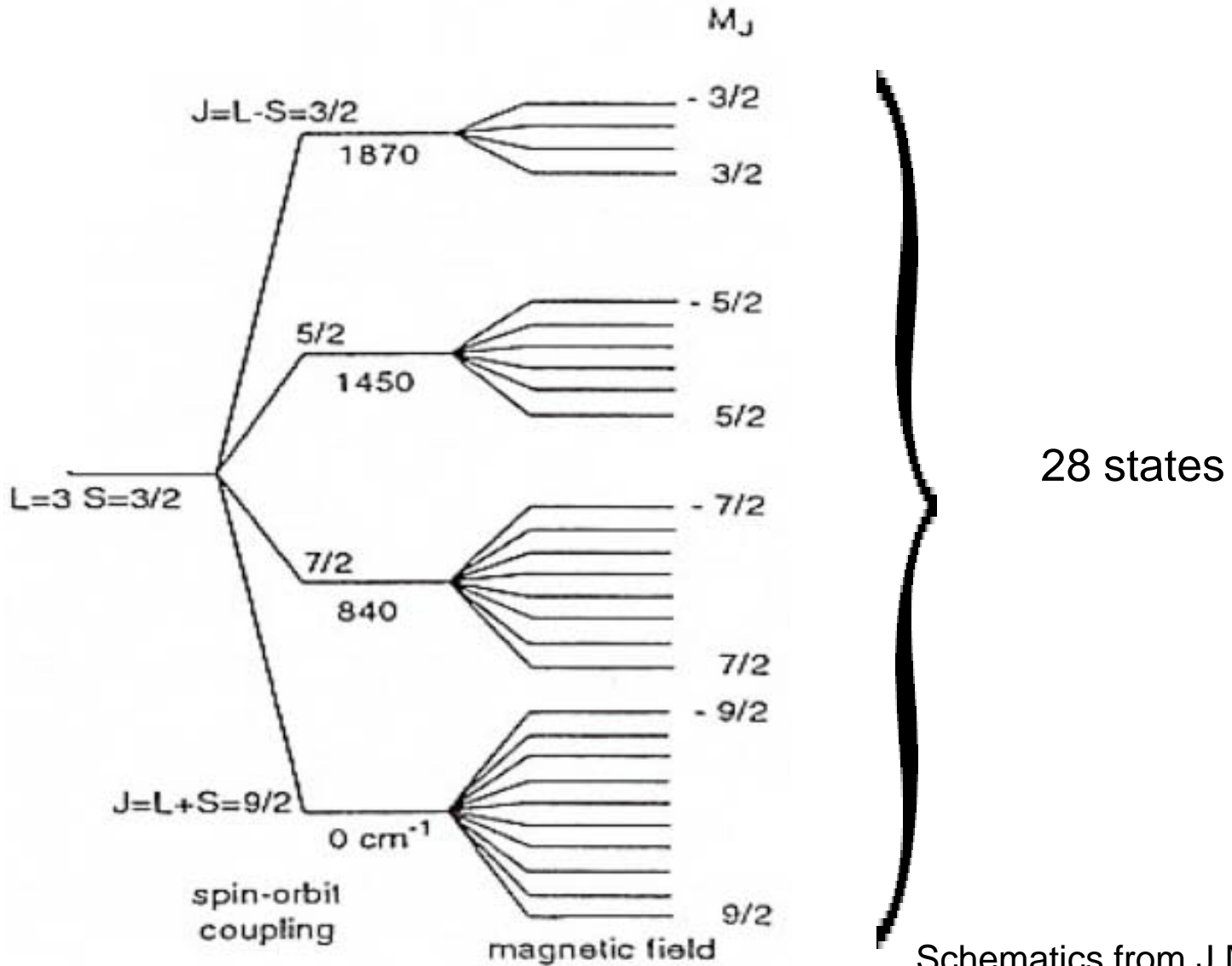


Overview of 3d-metal ions

d-Schale (L=2)											
n	$m_L =$	2	1	0	-1	-2	S	$L= \sum L_z $	J	Symbol	
1		↓					1/2	2	3/2	} $J= L-S $	${}^2D_{3/2}$
2		↓	↓				1	3	2		3F_2
3		↓	↓	↓			3/2	3	3/2		${}^4F_{3/2}$
4		↓	↓	↓	↓		2	2	0		5D_0
5		↓	↓	↓	↓	↓	5/2	0	5/2		${}^6S_{5/2}$
6		↓↑	↓	↓	↓	↓	2	2	4	5D_4	
7		↓↑	↓↑	↓	↓	↓	3/2	3	9/2	} $J=L+S$	${}^4F_{9/2}$
8		↓↑	↓↑	↓↑	↓	↓	1	3	4		3F_4
9		↓↑	↓↑	↓↑	↓↑	↓	1/2	2	5/2		${}^2D_{5/2}$
10		↓↑	↓↑	↓↑	↓↑	↓↑	0	0	0		1S_0



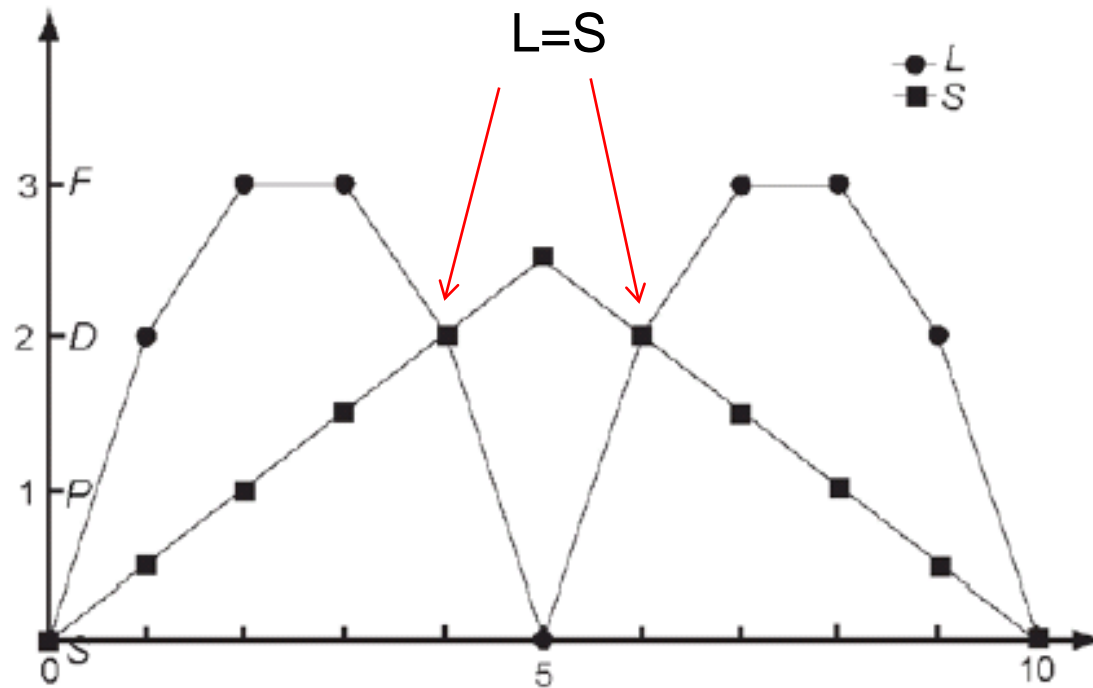
Splitting of energy states for $L=3, S=3/2$



Schematics from J.M.D. Coey



L and S according to Hund's Rule in 3d shell

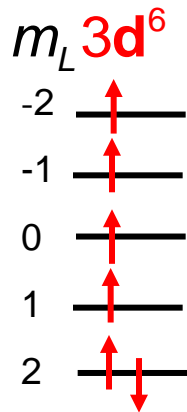




4. Magnetic moments for transition metal ions

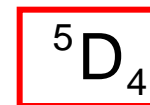
Metal ions in salts : Example: FeCl_2 with an ionic state: Fe^{2+}

- For atomic Fe the electronic configuration is $3d^6 4s^2$
- The s-electron go into the ionic bond, remaining $3d^6$, i.e. 6 electrons in the d-shell
- Level scheme according to Hund's rule:



$$\left. \begin{array}{l} S = 4 \cdot \frac{1}{2} = 2 \\ L = 2 \\ J = L + S = 4 \end{array} \right\}$$

Spectroscopic term:



- Expected g_J value:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} = \frac{3}{2} \text{ for } S=L$$



Calculated effective magnetic moment

$$p^J = g_J \sqrt{J(J+1)} = \frac{3}{2} \sqrt{4(4+1)} = \frac{3}{2} \sqrt{20} = 6.7$$

If we consider spin only:

$$p^S = g_S \sqrt{S(S+1)} = 2\sqrt{2 \cdot 3} = 4.89$$

Experimentally determined: $p^{\text{exp}} = 5.4$

The experimentally determined value is closer to p^S than to p^J



In most cases of transition metal ions the orbital momentum appears to be quenched.

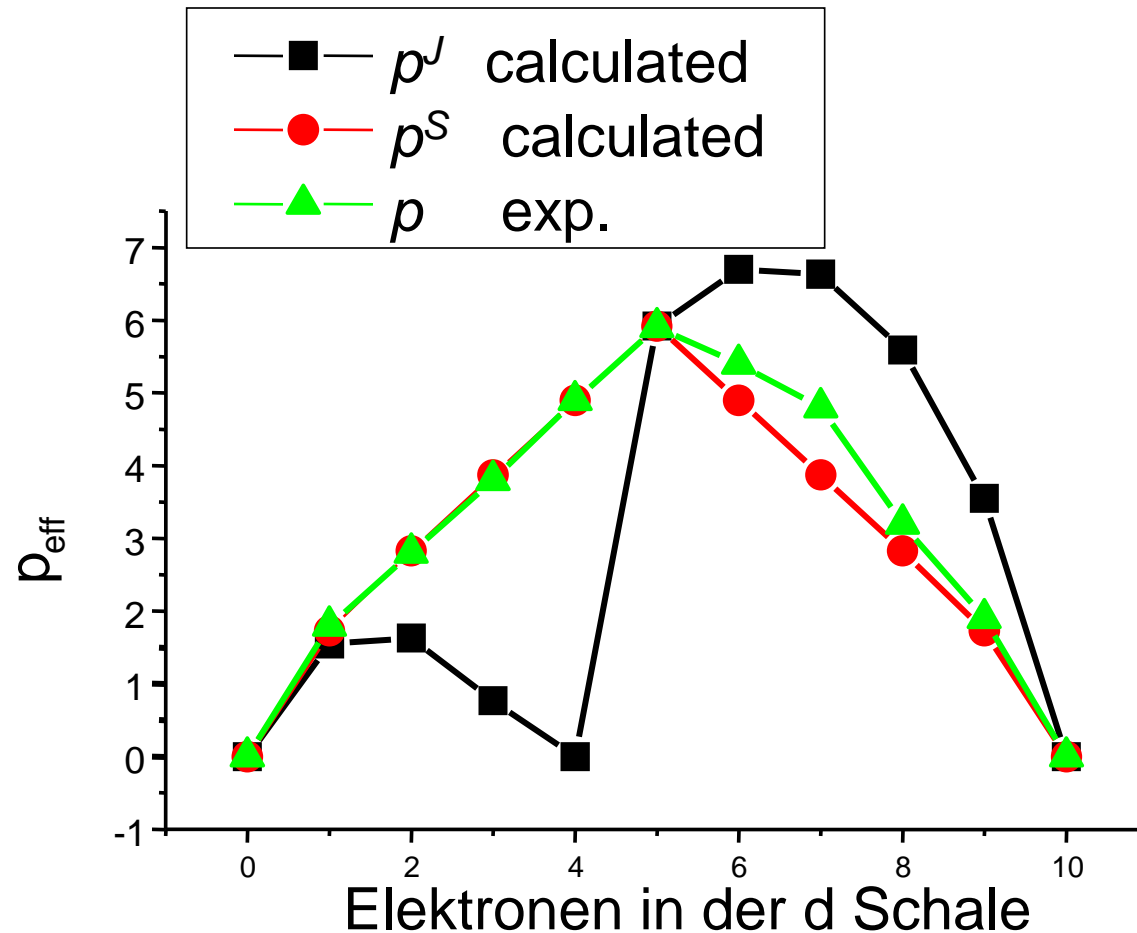


Examples for 3d metal - ions

Ion	configuration	Ground level	$p^J = g_J \sqrt{J(J+1)}$	$p^S = g_S \sqrt{S(S+1)}$	p^{exp}
Ti ³⁺ , V ⁴⁺	3d ¹	² D _{3/2}	1.55	1.73	1.8
V ³⁺	3d ²	² F ₂	1.63	2.83	2.8
Cr ³⁺ , V ²⁺	3d ³	² F _{3/2}	0.77	3.87	3.8
Mn ³⁺ , Cr ²⁺	3d ⁴	² D ₀	0	4.90	4.9
Fe ³⁺ , Mn ²⁺	3d ⁵	² S _{5/2}	5.92	5.92	5.9
Fe ²⁺	3d ⁶	² D ₄	6.70	4.90	5.4
Co ²⁺	3d ⁷	² F _{9/2}	6.63	3.87	4.8
Ni ²⁺	3d ⁸	² F ₄	5.59	2.83	3.2
Cu ²⁺	3d ⁹	² D _{5/2}	3.55	1.73	1.9



Magnetic moments of 3d-transition metal ions as a function of the number of electrons in the d-shell

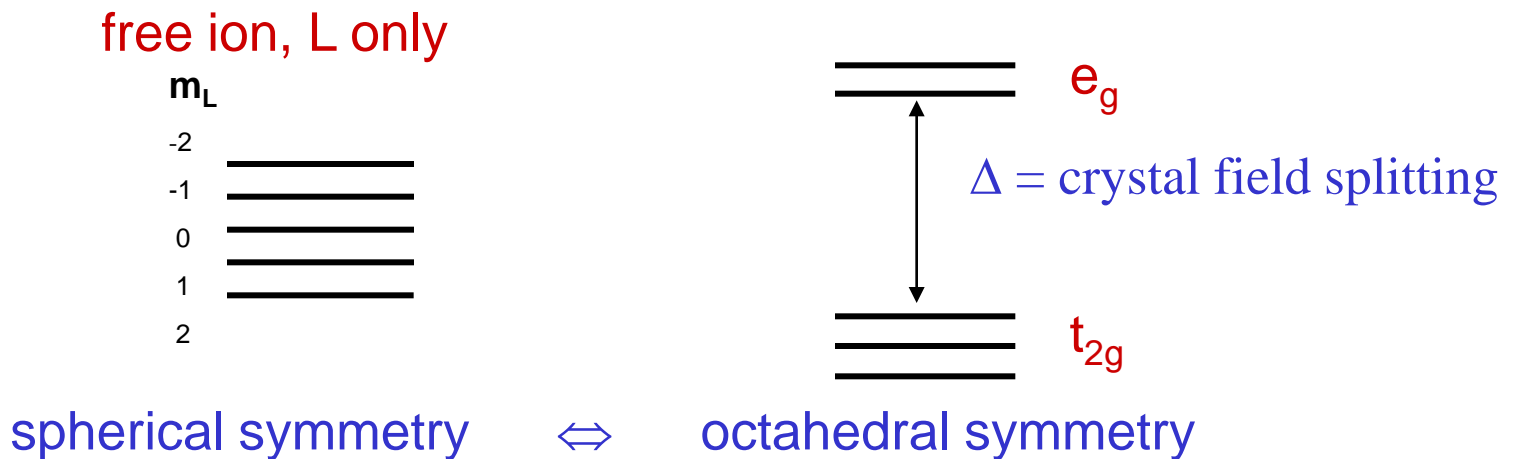


The experimental values are closer to the calculated p^S values than to the calculated p^J -values



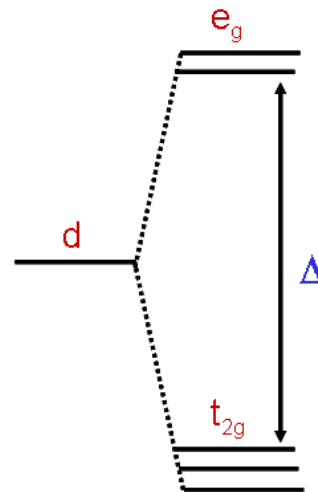
5. Crystal electrical field splitting

- 3d-electrons take part in the chemical binding, not only the 4s electrons (example: in $\text{FeCl}_2, \text{FeF}_3, \dots$)
- The 3d-shell is exposed to strong inhomogeneous electrical fields, the crystal electric fields from the neighbors cause internal Stark-effect
- The crystal electrical fields lifts the $2L + 1$ degeneracy of the d-electrons
- The m_L levels are split into two parts
- Octahedral environment: t_{2g} (ground level, three fold degenerate) and e_g (upper level, doubly degenerate)





Crystal electrical field splitting

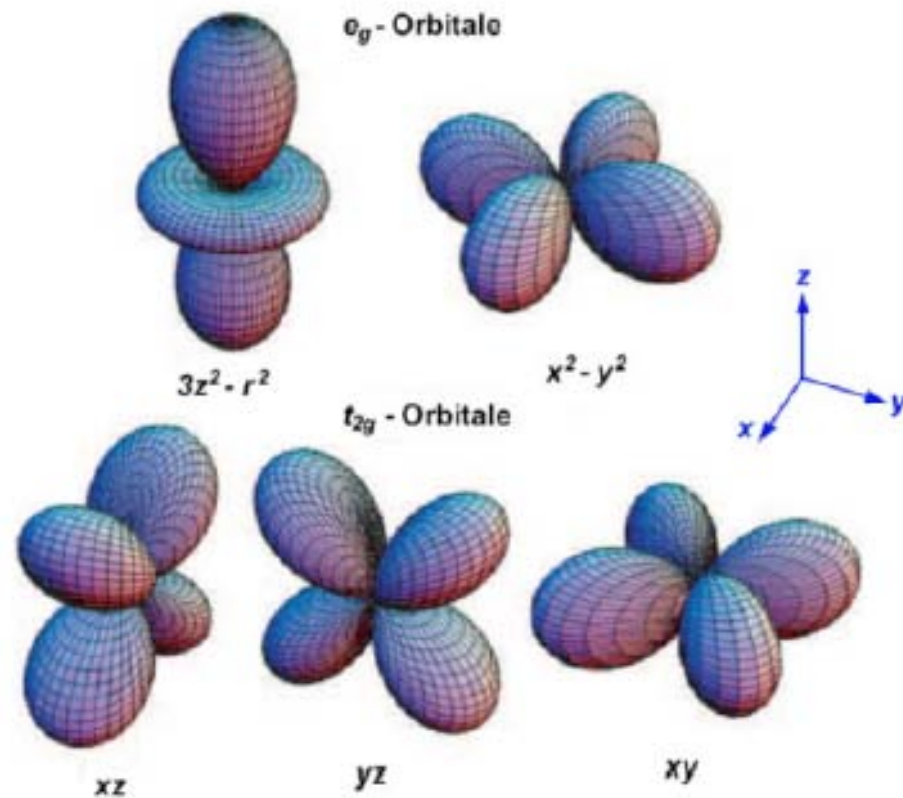
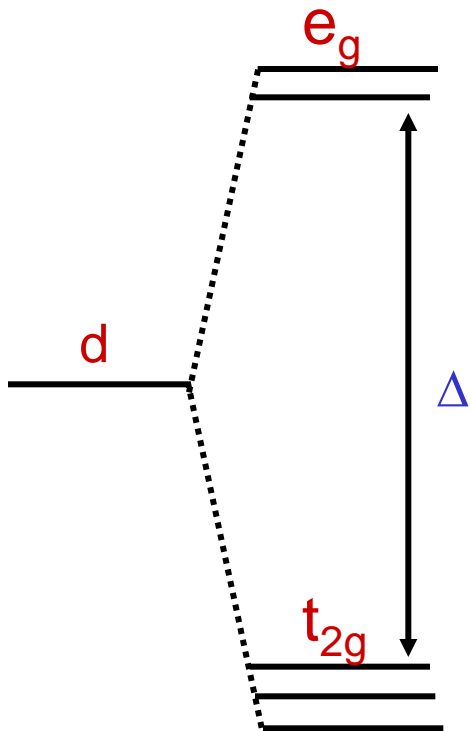


- Δ is the crystal field splitting between orbitals of different symmetry
- Orbital moments of non-degenerate levels have no fixed phase relationship, orbital moments are not fixed and vary in time.
- **→** time average of the orbital moment $\langle L \rangle = 0$
- L^2 and L_z are no longer good quantum numbers.
- Hund's rules do not apply for a non-spherical environment.



Crystal electrical field splitting with octahedral symmetry

5 orthogonal wave functions of the d-shell

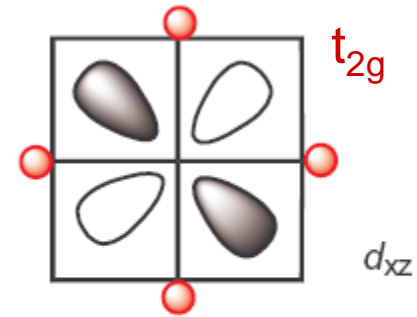
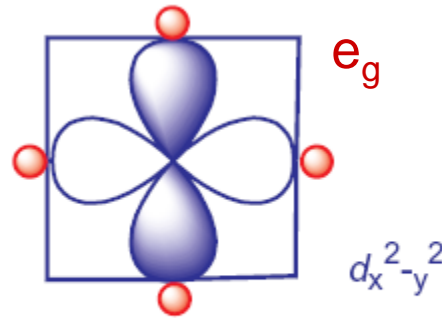
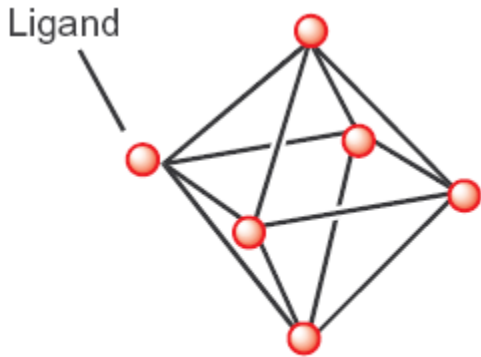




Octahedral crystal field

Max. probability density in direction of neighbors

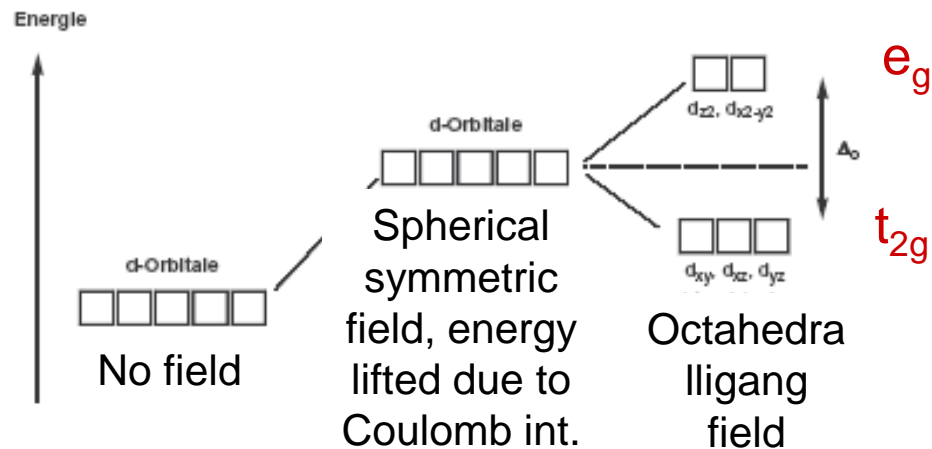
Low overlap with neighbors



Repulsion, increase of energy, e_g

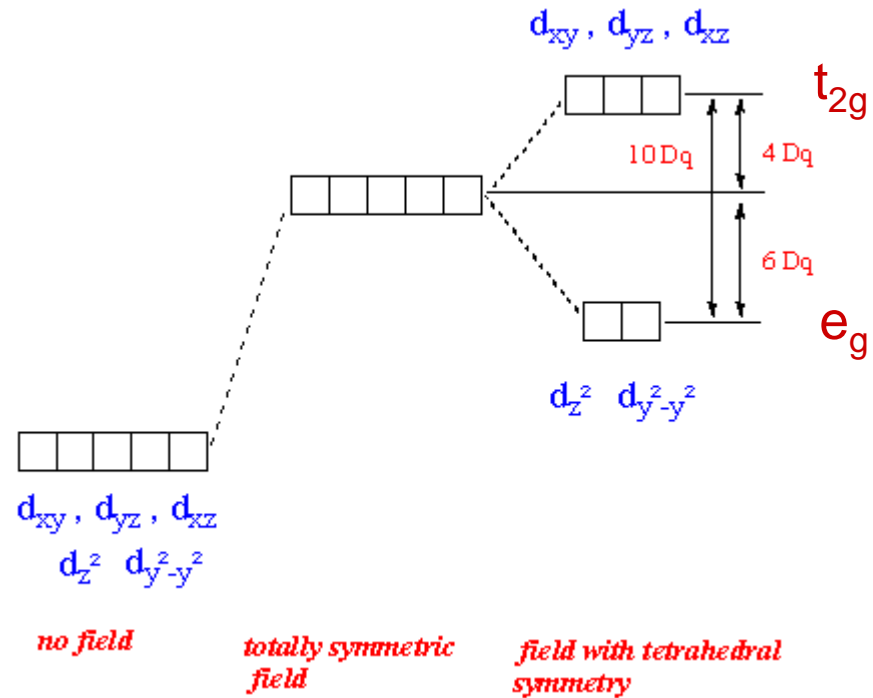
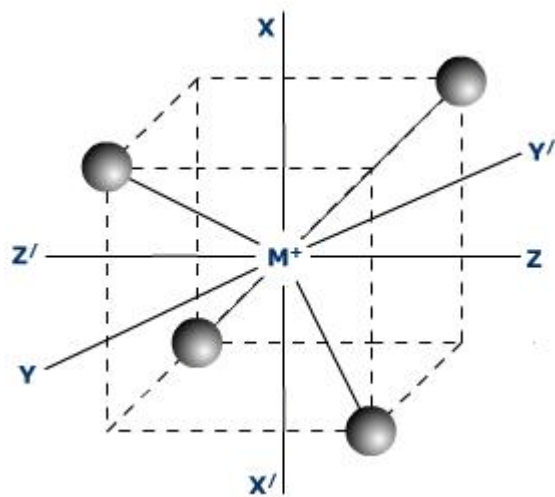
Less repulsion, lowering of energy, t_{2g}

Result:
2 sets of d-orbitals





Tetrahedral crystal field



In tetrahedrally coordinated systems, e_g and t_{2g} exchange their role, e_g has the lower energy.

The energy splitting is on the order of 1-10 μeV .



Adding all energy terms

$$\mathcal{H}_i = \mathcal{H}_0 + \mathcal{H}_{so} + \mathcal{H}_{CF} + \mathcal{H}_Z$$

Coulomb interactions $|L,S\rangle$

spin-orbit interaction $\lambda \vec{L} \cdot \vec{S}$

Zeeman interaction $\mu_0 m_{z,J} H_z$

Crystal field interaction $\int \rho_0(\mathbf{r}) \varphi_{cf}(\mathbf{r}) d^3r$

	ion	Δ
3d ¹	Ti ³⁺	124
3d ²	Ti ²⁺	88
3d ³	V ²⁺	82
3d ⁴	Cr ²⁺	85
3d ⁶	Fe ²⁺	-164
3d ⁷	Co ²⁺	-272
3d ⁸	Ni ²⁺	-493

4f ¹	Ce ³⁺	920
4f ²	Pr ³⁺	540
4f ³	Nd ³⁺	430
4f ⁵	Sm ³⁺	350
4f ⁸	Tb ³⁺	-410
4f ⁹	Dy ³⁺	-550
4f ¹⁰	Ho ³⁺	-780
4f ¹¹	Er ³⁺	-1170
4f ¹²	Tm ³⁺	-1900
4f ¹³	Yb ³⁺	-4140

	\mathcal{H}_0	\mathcal{H}_{so}	\mathcal{H}_{cf}	\mathcal{H}_Z in 1 T
3d	1 - 5 10 ⁴	10 ² - 10 ³	10 ⁴	1
4f	1 - 6 10 ⁵	1 - 5 10 ³	≈ 3 10 ²	1

adapted from J.M.D. Coey



Energy scales for CF and SO - splitting

3d metals:

- SO splitting is an order of magnitude smaller, i.e. 50 meV
- CF is on the order of 500 meV

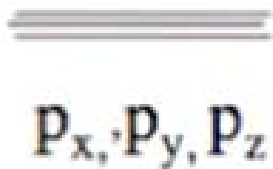
RE-materials:

- SO-splitting on the order of 250 meV,
In some cases SO splitting can be as low as 25 meV, in which case higher states mix with ground states at RT.
- CF-splitting is on the order of 10-15 meV or on the order of RT

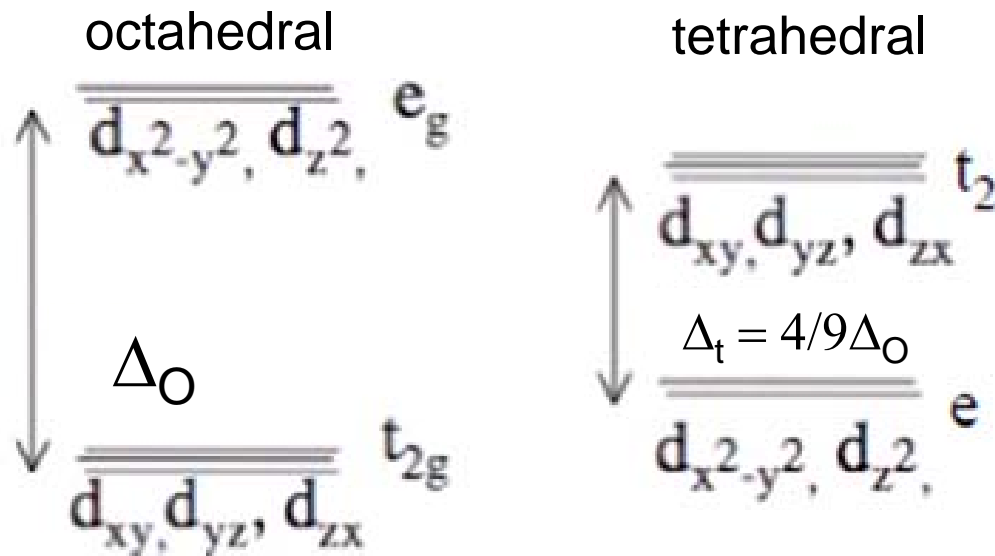


Degeneracies in crystal fields

p-levels
No effect of
crystal field
Independent of
oct. or tetr.
environment



Splitting of d-levels depends on symmetry
of environment



adapted from J.M.D. Coey



Occupation of sublevels

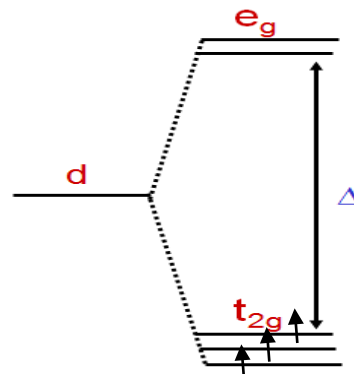
If crystal field splitting Δ is bigger than LS-coupling:

$$\Delta \gg \lambda \vec{L} \cdot \vec{S}$$

i.e. crystal electric fields are bigger than internal magnetic fields, only lowest levels are occupied.

Occupation for more than 1 electron in d orbitals:

- For d^2 - d^9 systems the electron-electron interactions must be taken into account.
- For d^1 - d^3 systems, Hund's rule applies and predicts that the electrons will not pair and occupy the t_{2g} set.

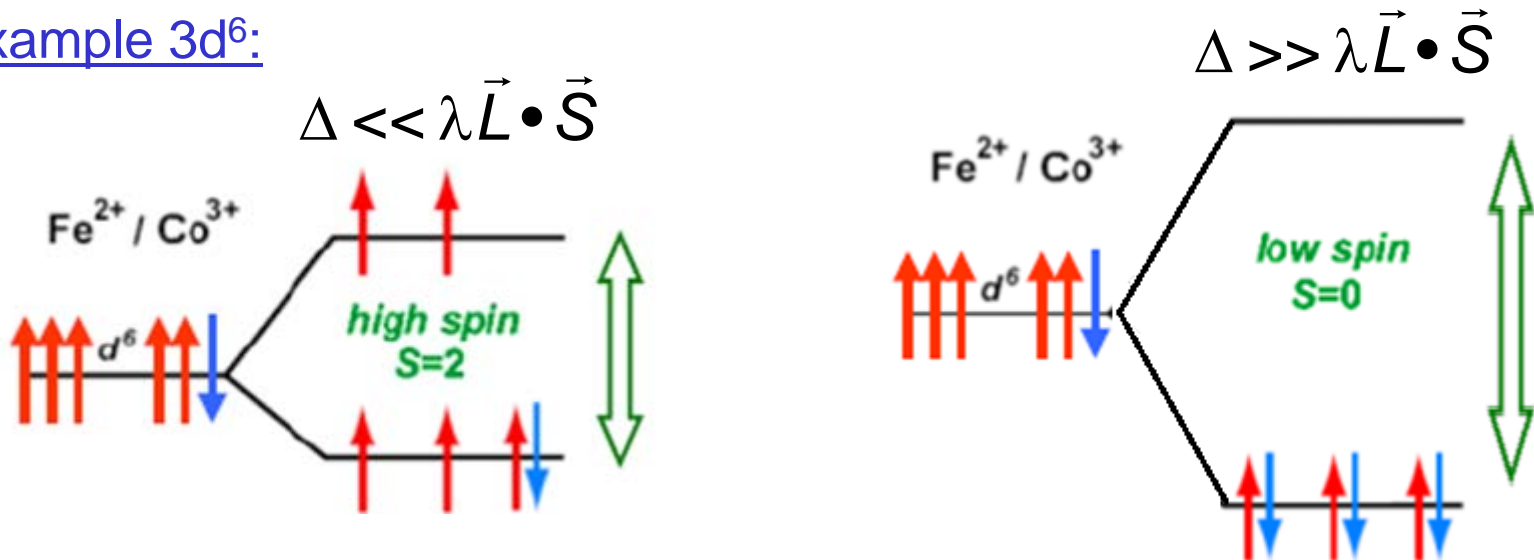




High spin – low spin case

- For d^4 - d^7 systems, there are two possibilities:
 - **low spin case** or **strong field situation**: Electrons occupy t_{2g} set and pair up to 6 electrons, then occupy e_g level.
 - **high spin case** or **weak field situation**; Electrons occupy t_{2g} and e_g levels according to Hund's rule.

Example $3d^6$:



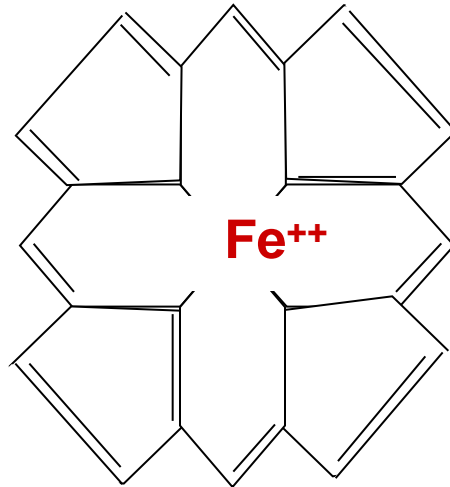
Examples for high-spin low-spin transitions:

1. Verwey transition of magnetite, Jahn-Teller transitions, oxy-deoxy transition



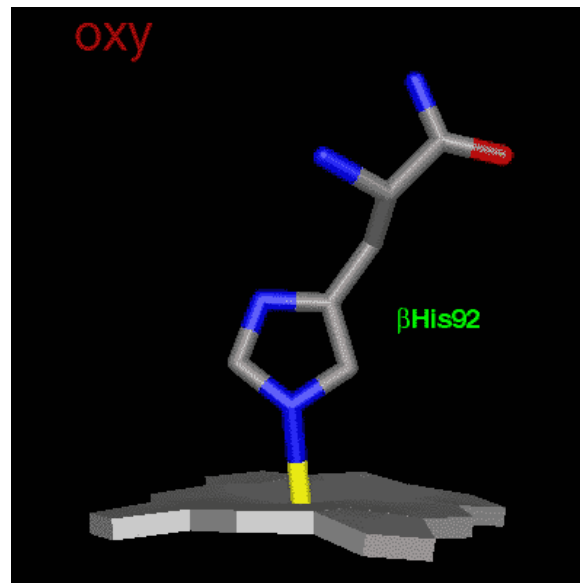
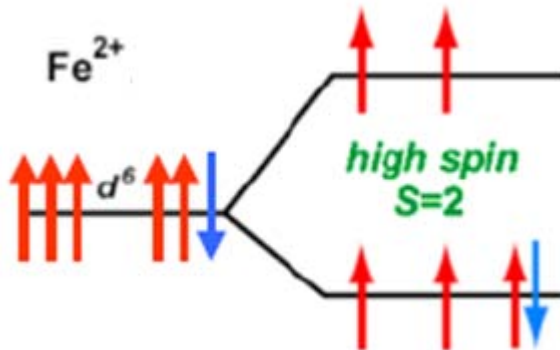
High spin – low spin transition in heme molecule with O₂ - cycling

Heme protein.....

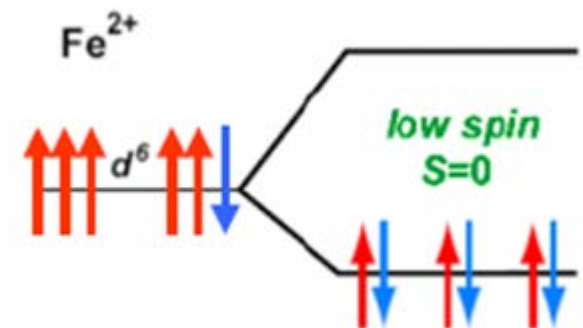


.....is magnetic
3d⁶ state

w/o O₂ – binding
deoxy



with O₂ – binding
oxy





Consequences from a strong crystal field

If crystal field has low symmetry, the degeneracy is lifted and the time average yields zero orbital moment:

$$\longrightarrow \langle L_z \rangle = 0$$

The ground state is characterized by an s-character and $(2S+1)$ -degeneracy.

$$J = S \quad \text{and} \quad L = 0$$

The saturation magnetization is then:

$$M_S = \frac{N}{V} g_S \mu_B S = \frac{N}{V} \mu_B 2S$$

Magnetization measurements yield directly S , the maximum S value in the d-shell is $S=5/2$ with $m = 5\mu_B$ (i.e. Cr^+ ($3d^5 4s^0$) and Mn^{2+} ($3d^5 4s^0$)).



Transition metals: determination of g-value

EPR – FMR resonance frequency:

$$\hbar\omega = g\mu_B B_{res}$$

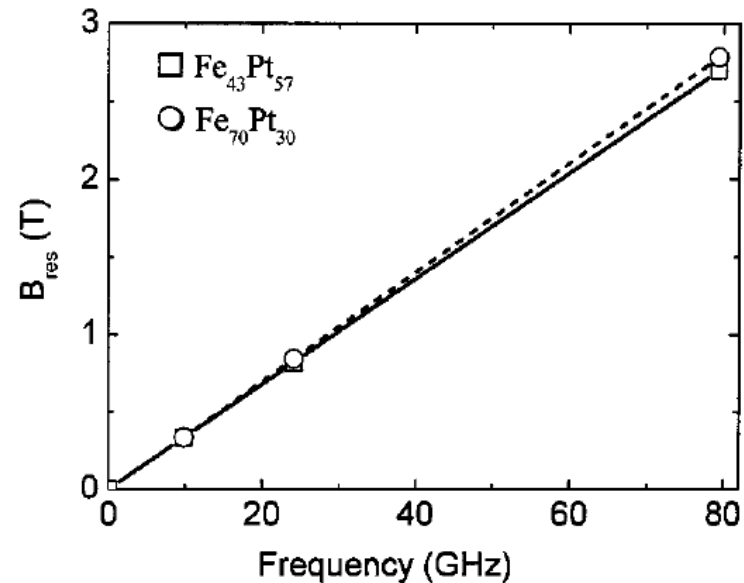
g-value from the slope.

Ratio of magnetic moments:

$$\frac{m_L}{m_S} = \frac{g - 2}{2}$$

Most metal ions show a g-value of 2.1 - 2.2.

Thus, in reality the orbital contribution is on the order of 0.1 – 0.2, i.e. orbital moment is not completely quenched. Remaining orbital moment is responsible for magnetic anisotropy.



M. Ulmeanu et al. PRB 69 (2004)



6. Magnetic moment of rare earth ions

Crystal field splitting in rare earth ions is small in the meV-range:

- The inner 4f - shell is well screened from the outer shells $5s^2p^66s^2$, which take part in the chemical bonding. Therefore, 4f electrons are more localized.
- LS – coupling is strong because of higher Z atoms compared to the 3d atoms. Here the limit holds:

$$\Delta \ll \lambda \vec{L} \cdot \vec{S}$$

$4f^n$
magnetic inner orbitals

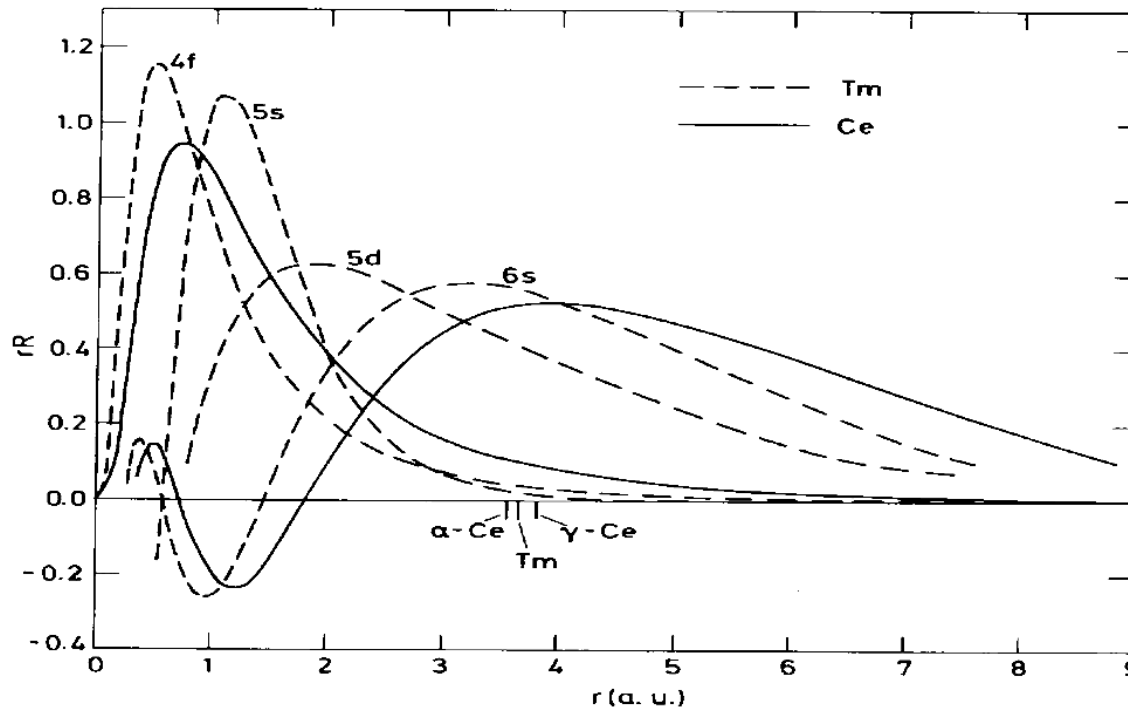
$5s^2 5p^6$
spherically symmetric screening because of filled shells

$5d^1 6s^2$
chemical binding

- The f-levels are filled according to Hund's rule and Russel-Saunders-coupling is a good approximation.



Wave functions of rare earth ions



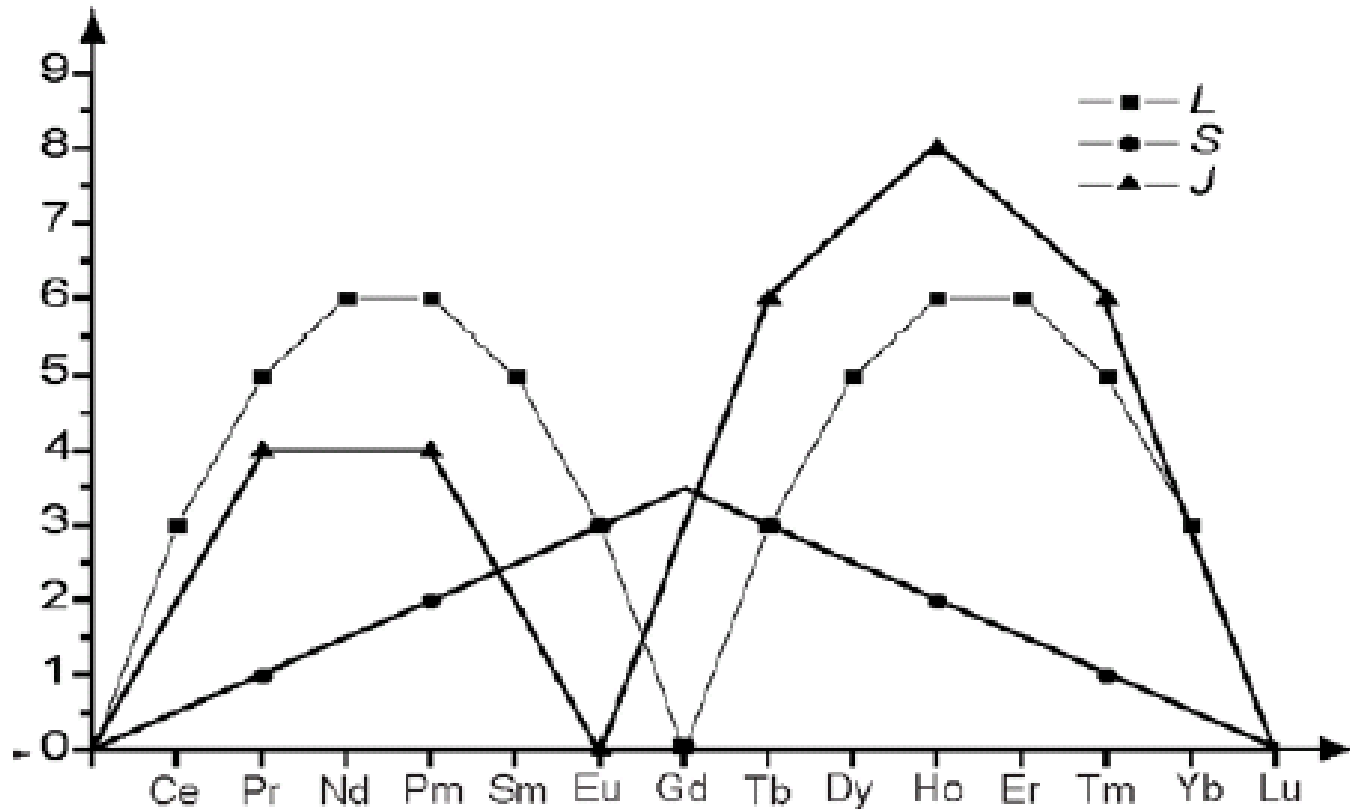


Overview of 4f-rare earth ions

f-Schale (L=3)												
n	$m_L = 3$	2	1	0	-1	-2	-3	S	$L= \sum L_z $	J	Symbol	
1	↓							1/2	3	5/2	} $J= L-S $	$2F_{5/2}$
2	↓	↓						1	5	4		$3H_4$
3	↓	↓	↓					3/2	6	9/2		$4I_{9/2}$
4	↓	↓	↓	↓				2	6	4		$5I_4$
5	↓	↓	↓	↓	↓			5/2	5	5/2		$6H_{5/2}$
6	↓	↓	↓	↓	↓	↓		3	3	0		$7F_0$
7	↓	↓	↓	↓	↓	↓	↓	7/2	0	7/2		$8S_{7/2}$
8	↓↑	↓	↓	↓	↓	↓	↓	3	3	6	} $J=L+S$	$7F_6$
9	↓↑	↓↑	↓	↓	↓	↓	↓	5/2	5	15/2		$6H_{15/2}$
10	↓↑	↓↑	↓↑	↓	↓	↓	↓	2	6	8		$5I_8$
11	↓↑	↓↑	↓↑	↓↑	↓	↓	↓	3/2	6	15/2		$4I_{15/2}$
12	↓↑	↓↑	↓↑	↓↑	↓↑	↓	↓	1	5	6		$3H_6$
13	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓	1/2	3	7/2		$2F_{7/2}$
14	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	0	0	0		$1S_0$



L and S according to Hund's Rule in 4f shell





Example: Ce^{3+} (one electron in the f-shell)

m_L	$4f^1$	}	$S = \frac{1}{2}$	${}^2F_{5/2}$	
-3	—		$L = 3$		
-2	—		$J = L - S = 3 - \frac{1}{2} = \frac{5}{2}$		
-1	—		$g_J = \frac{3}{2} + \frac{3/4 - 12}{2 \times 35/4} = 0.857$		
0	—				
1	—				$p^J = g_J \sqrt{J(J+1)} = 2.53$
2	—				$p^{\text{exp}} = 2.4$
3	— ↑				

➔ For rare earth ions with 3+ ionization, good agreement between calculated and measured p^J -values:

$$p^J = g_J \sqrt{J(J+1)} \cong p^{\text{exp}}$$

Therefore Hund's rule holds

Magnetism follows from the Zeeman splitting of the lowest J-levels.

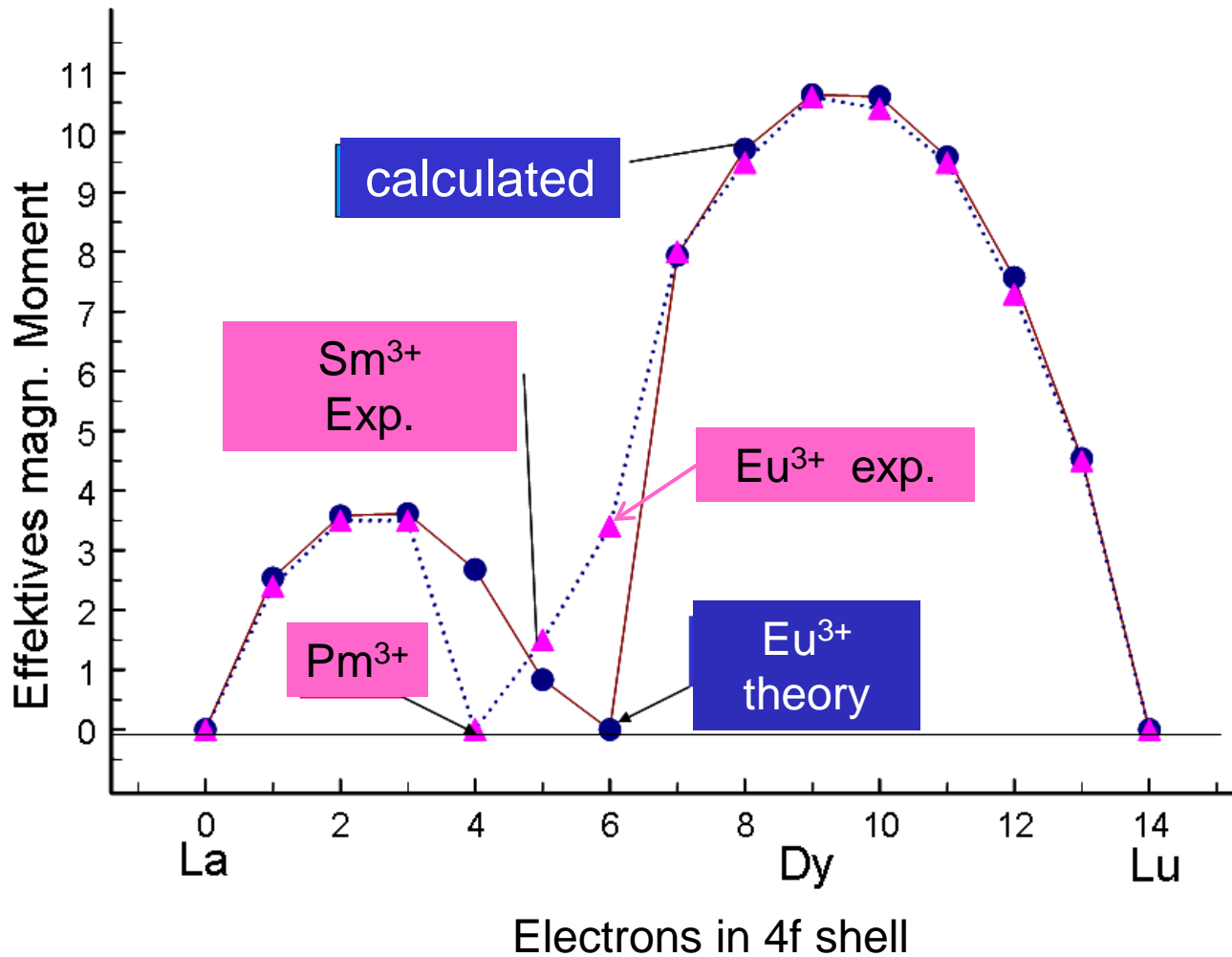


Examples for 4f-rare earth metal ions (near 300 K)

Ion	Konfiguration	Basisniveau	p^J	p^{exp}
Ce ³⁺	4f ¹ 5s ² p ⁶	² F _{5/2}	2.54	2.51
Pr ³⁺	4f ² 5s ² p ⁶	³ H ₄	3.58	3.56
Nd ³⁺	4f ³ 5s ² p ⁶	⁴ I _{9/2}	3.62	3.5
Pm ³⁺	4f ⁴ 5s ² p ⁶	⁵ I ₄	2.68	0
Sm ³⁺	4f ⁵ 5s ² p ⁶	⁶ H _{5/2}	0.85	1.74
Eu ³⁺	4f ⁶ 5s ² p ⁶	⁷ F ₀	0	3.4
Gd ³⁺	4f ⁷ 5s ² p ⁶	⁸ S _{7/2}	7.94	7.98
Tb ³⁺	4f ⁸ 5s ² p ⁶	⁷ F ₆	9.72	9.77
Dy ³⁺	4f ⁹ 5s ² p ⁶	⁶ H _{15/2}	10.63	10.63
Ho ³⁺	4f ¹⁰ 5s ² p ⁶	⁵ I ₈	10.60	10.4
Er ³⁺	4f ¹¹ 5s ² p ⁶	⁴ I _{15/2}	9.59	9.5
Tm ³⁺	4f ¹² 5s ² p ⁶	³ H ₆	7.57	7.61
Yb ³⁺	4f ¹³ 5s ² p ⁶	² F _{7/2}	4.53	4.5
Lu ³⁺	4f ¹⁴ 5s ² p ⁶	¹ S ₀	0.0	0.0



Comparison of calculated and measured effective moments for rare earth ions



In general good agreement between theory and experiment, aside from some characteristic deviations.

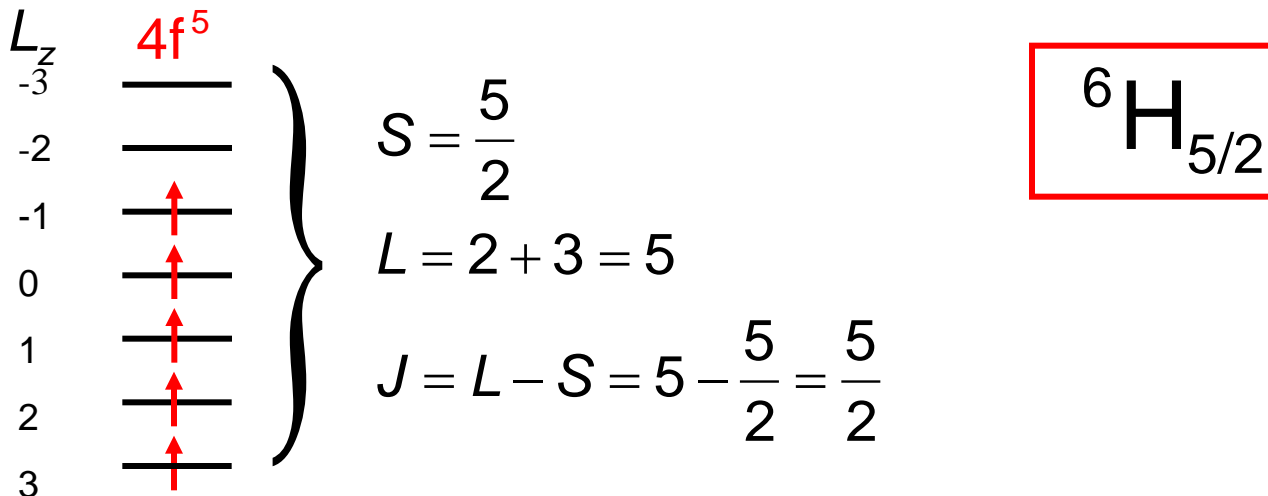


Deviations for Sm^{3+} und Eu^{3+}

	p^J	p^{exp}
Sm^{3+}	0.845	1.74
Eu^{3+}	0	3.4

Reason: small $\vec{L} \cdot \vec{S}$ - coupling for these ions.

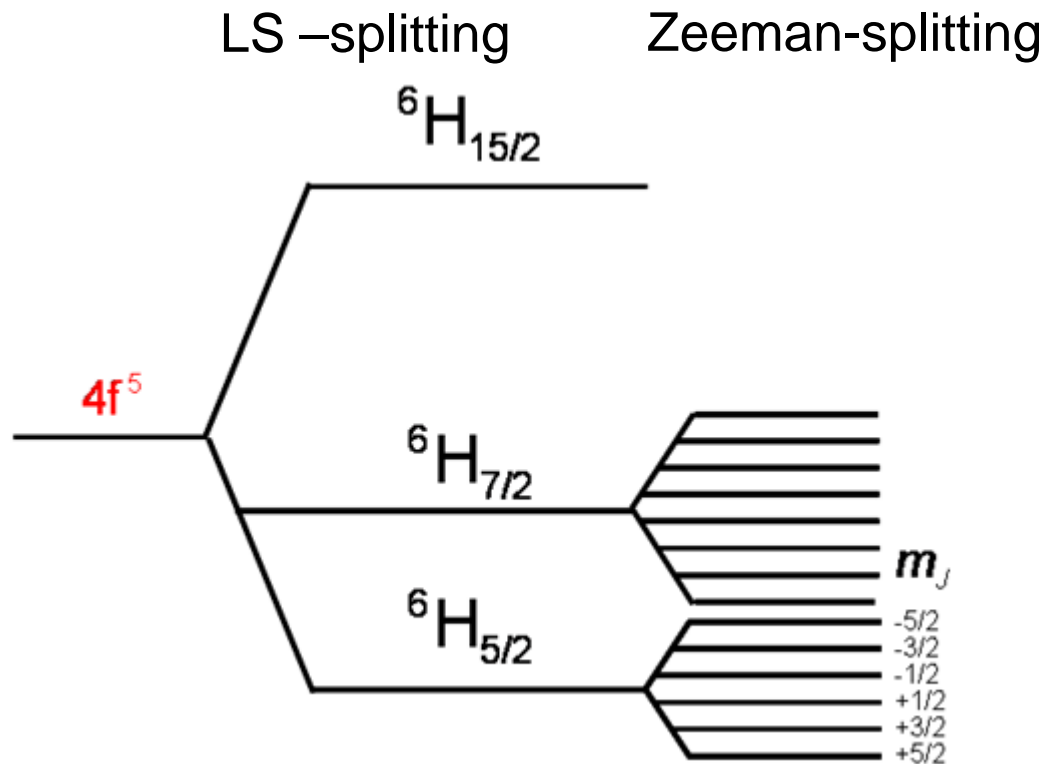
Example: Sm^{3+} (configuration $4f^5$)



The next higher term: $J = L - S + 1 = \frac{5}{2} + 1 = \frac{7}{2}$ or ${}^6\text{H}_{7/2}$



LS splitting for Sm



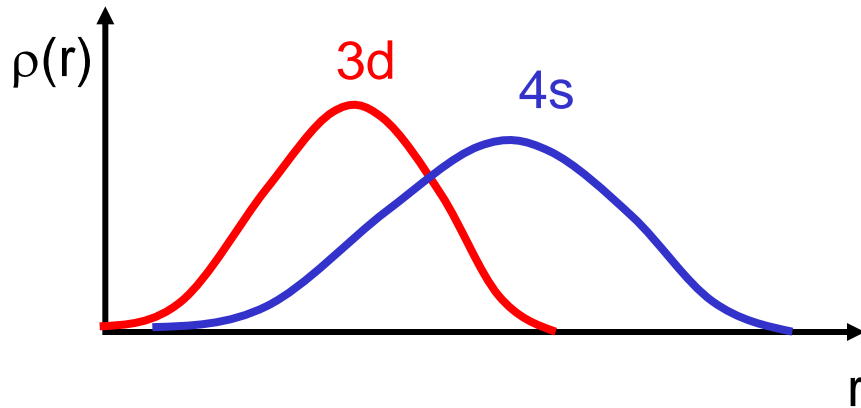
The $\vec{L} \cdot \vec{S}$ splitting is of the order of 300 K, i.e. rather weak. Thus at RT levels of the higher states are already occupied. In a magnetic field, level mixing occurs.

Similar argument also applies for Eu. Because of low LS-coupling, levels mix as a function of field and temperature.



Summary

3d-metal ions

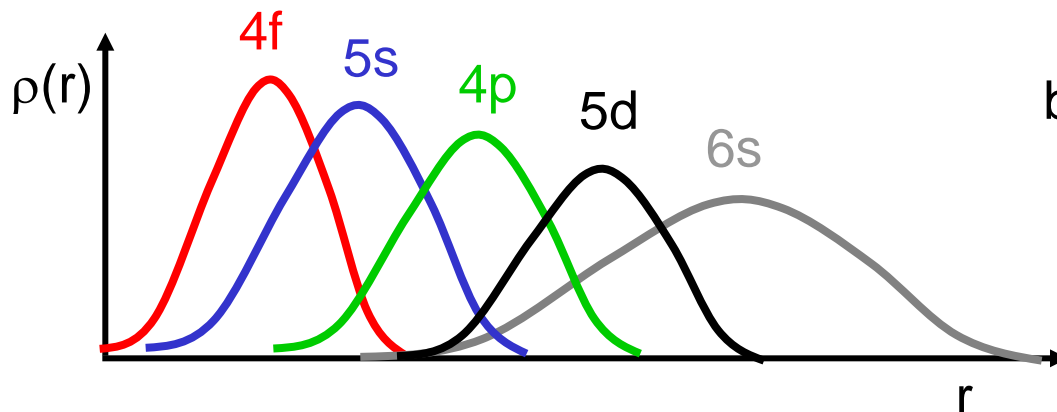


- a) 3d und 4s-electrons hybridize
- b) $\vec{L} \cdot \vec{S}$ coupling is weak

$$\lambda \vec{L} \cdot \vec{S} \ll \Delta = \text{c.f.}$$

- c) orbital moment becomes quenched

4f-rare earth ions



- a) 4f and 6s wave functions well separated
- b) LS – coupling is valid and

$$\lambda \vec{L} \cdot \vec{S} \gg \Delta = \text{c.f.}$$