Crystal (ligand) field theory

Literature

- C.E. Housecroft, A.G. Sharpe: Inorganic chemistry

Crystal (ligand) field theory

- Sphere symmetry
- jj-coupling, LS- coupling

Schrödinger equation

$$\underbrace{-\frac{\hbar^2}{2m}\Delta}_{\textit{kinetic energy}}\Psi(r)+\underbrace{\hat{V}(r)}_{\textit{potential energy}}\Psi(r)=E\Psi(r)$$

$$\Delta=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

Hydrogen atom:

$$\hat{V}=\frac{e^2}{4\pi\varepsilon_o r}$$

Δ in spherical coordinates:

$$\Psi_{n,l,m}=R_{n,l}(r)\cdot Y_{l,m}(\theta,\varphi)$$

$$\Delta\approx\frac{\partial^2}{\partial r^2}+\frac{\partial^2}{\partial\theta^2}+\frac{\partial^2}{\partial\varphi^2}$$

m: electron mass

ε_o: permitivity of vacuum

Ψ: wave functions

e: electron charge

E: energy

ħ: Planck's constant

R: radial function

Y: angular function

$$\hat{H}\Psi_{n,l,m}=E_n\Psi_{n,l,m}\qquad\hat{H}=\hat{T}+\hat{V}$$

$$\hat{L}^2Y_{l,m}=l(l+1)\hbar^2Y_{l,m}$$

$$\hat{L}_zY_{l,m}=m_l\hbar Y_{l,m}$$

n: principal quantum number

l: orbital quantum number

determine the orbital angular momentum

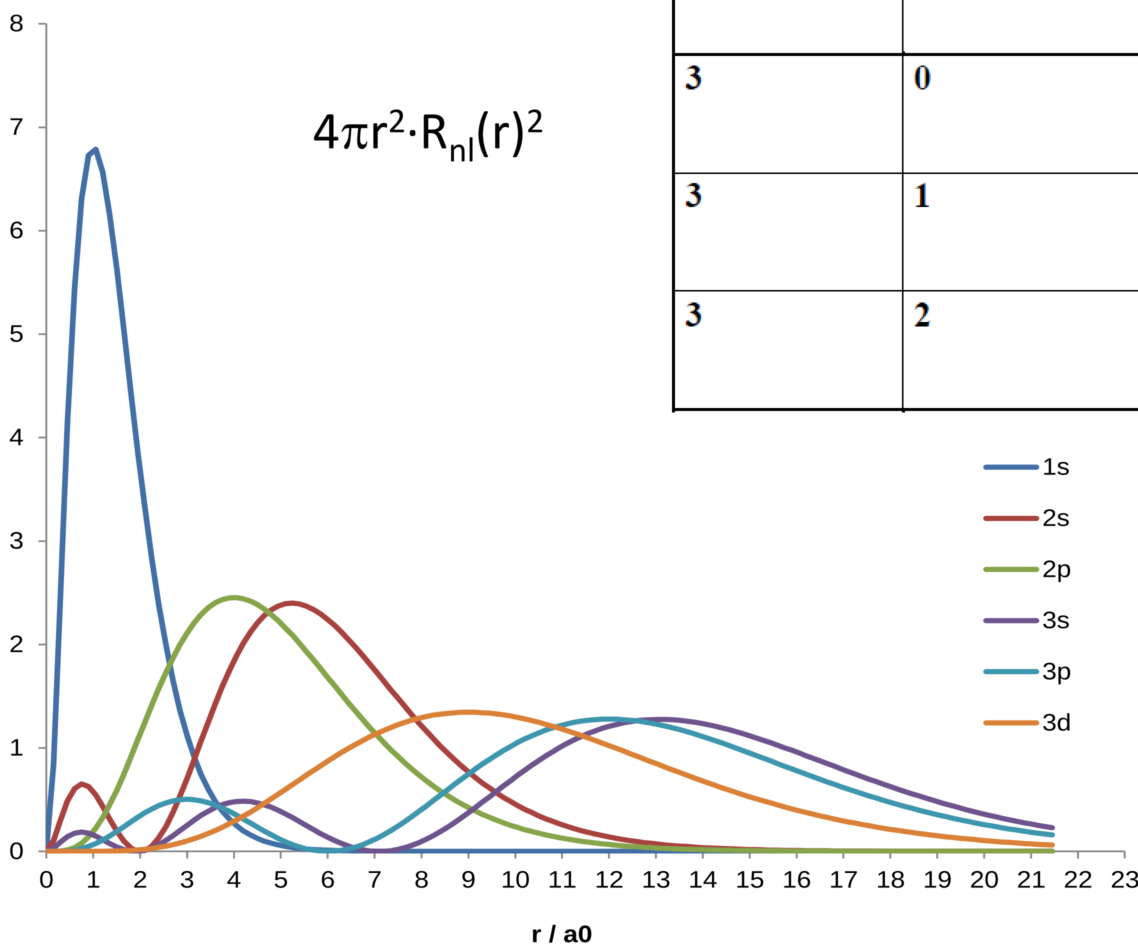
$l = 0 \ldots n-1$

m_l: magnetic quantum number

projection of the angular momentum into z-axis

$m_l = -l \ldots l$

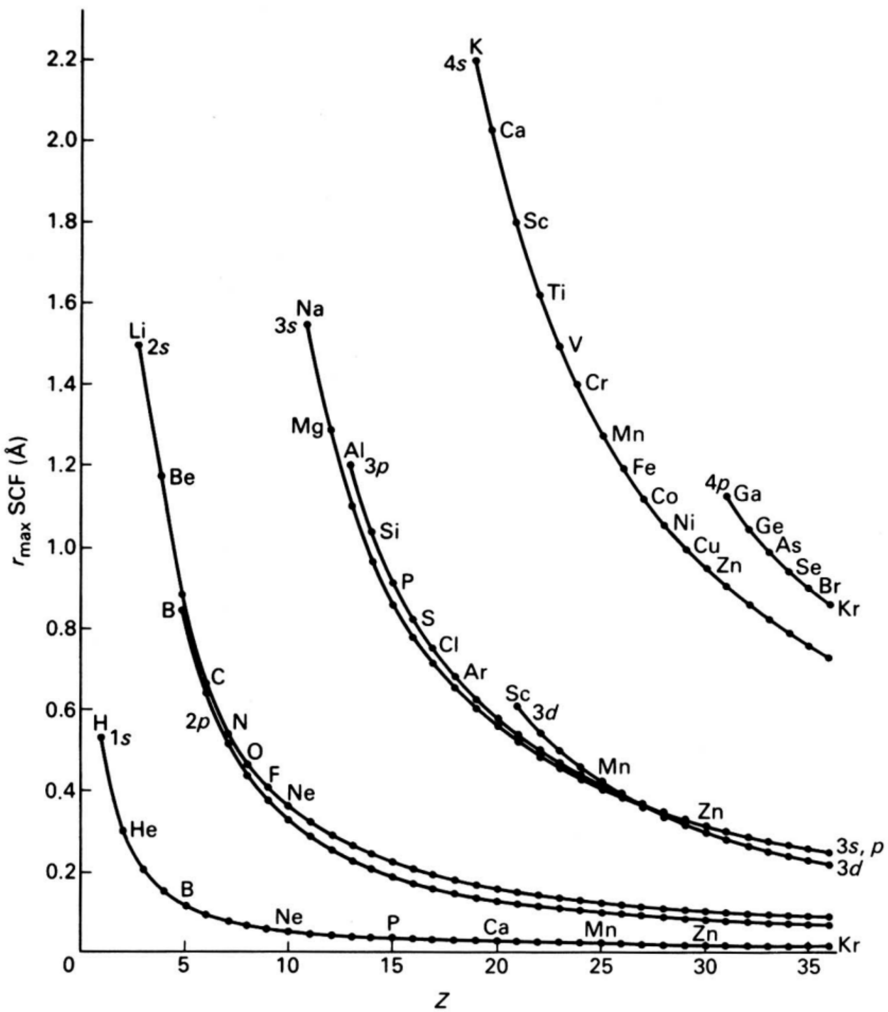
n	l	$R_{nl}(r)$
1	0	$2a_0^{-3/2}\exp\left(-\frac{r}{a_0}\right)$
2	0	$2^{-1/2}a_0^{-3/2}\left(1-\frac{r}{2a_0}\right)\exp\left(-\frac{r}{2a_0}\right)$
2	1	$(24)^{-1/2}a_0^{-5/2}r\exp\left(-\frac{r}{2a_0}\right)$
3	0	$2\cdot 3^{-5/2}a_0^{-3/2}\left(3-\frac{2r}{a_0}+\frac{2r^2}{9a_0^2}\right)\exp\left(-\frac{r}{3a_0}\right)$
3	1	$2^{3/2}\,3^{-7/2}a_0^{-5/2}r\left(2-\frac{r}{3a_0}\right)\exp\left(-\frac{r}{3a_0}\right)$
3	2	$2^{3/2}\,3^{-9/2}\,5^{-1/2}a_0^{-7/2}r^2\exp\left(-\frac{r}{3a_0}\right)$



Bohr's radius a_0 = 0.52918 Å

The distance of the electron (maximum of the orbital 1s density) from nuclei in hydrogen atom

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$



The radius of maximal electron density

Effective nuclear charge

a0* = a0 / Z*

Z* = Z - σ

σ = screening constant, a sum over all electrons

The electrons are merged into groups ()

(1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p)(5d)(5f)...

Slater's rules:

electron on the right does not contribute to σ

Electrons inside the group screen 0.35 (1s only 0.30)

n–1 (s,p) screen 0.85

n–2 and lower screen 1.00

If the electron is in d or f, all electron on the left screen 1.0

An example for Fe (26):

$$
\begin{array}{llllllll}
4s & : 0.35 \times 1 & + & 0.85 \times 14 & + & 1.00 \times 10 & = & 22.25 \Rightarrow Z_{\text{eff}}(4s) = 3.75 \\
3d & : 0.35 \times 5 & & & + & 1.00 \times 18 & = & 19.75 \Rightarrow Z_{\text{eff}}(3d) = 6.25 \\
3s, 3p & : 0.35 \times 7 & + & 0.85 \times 8 & + & 1.00 \times 2 & = & 11.25 \Rightarrow Z_{\text{eff}}(3s, 3p) = 14.75 \\
2s, 2p & : 0.35 \times 7 & + & 0.85 \times 2 & & & = & 4.15 \Rightarrow Z_{\text{eff}}(2s, 2p) = 21.85 \\
1s & : 0.30 \times 1 & & & & & = & 0.30 \Rightarrow Z_{\text{eff}}(1s) = 25.7
\end{array}
$$

Solution of Schrödinger equation (complex function):

$Y_l^{m_l}$

$$Y_0^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}$$

$$Y_1^{-1}(x) = \frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot e^{-i\varphi} \cdot \sin\theta$$

$$Y_1^0(x) = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cdot \cos\theta$$

$$Y_1^1(x) = \frac{-1}{2}\sqrt{\frac{3}{2\pi}} \cdot e^{i\varphi} \cdot \sin\theta$$

$$Y_2^{-2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \cdot e^{-2i\varphi} \cdot \sin^2\theta$$

$$Y_2^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}} \cdot e^{-i\varphi} \cdot \sin\theta \cdot \cos\theta$$

$$Y_2^0(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{5}{\pi}} \cdot (3\cos^2\theta - 1)$$

$$Y_2^1(\theta,\varphi) = \frac{-1}{2}\sqrt{\frac{15}{2\pi}} \cdot e^{i\varphi} \cdot \sin\theta \cdot \cos\theta$$

$$Y_2^2(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \cdot e^{2i\varphi} \cdot \sin^2\theta$$

$$Y_3^{-3\ldots 3}$$

Linear combination: (real function):

$$s = Y_0^0$$

$$p_z = Y_1^0$$

$$p_x = \tfrac{1}{\sqrt{2}}\left(Y_1^1 + Y_1^{-1}\right)$$

$$p_y = \tfrac{-i}{\sqrt{2}}\left(Y_1^1 - Y_1^{-1}\right)$$

$$d_{z^2} = Y_2^0$$

$$d_{x^2-y^2} = \tfrac{1}{\sqrt{2}}\left(Y_2^2 + Y_2^{-2}\right)$$

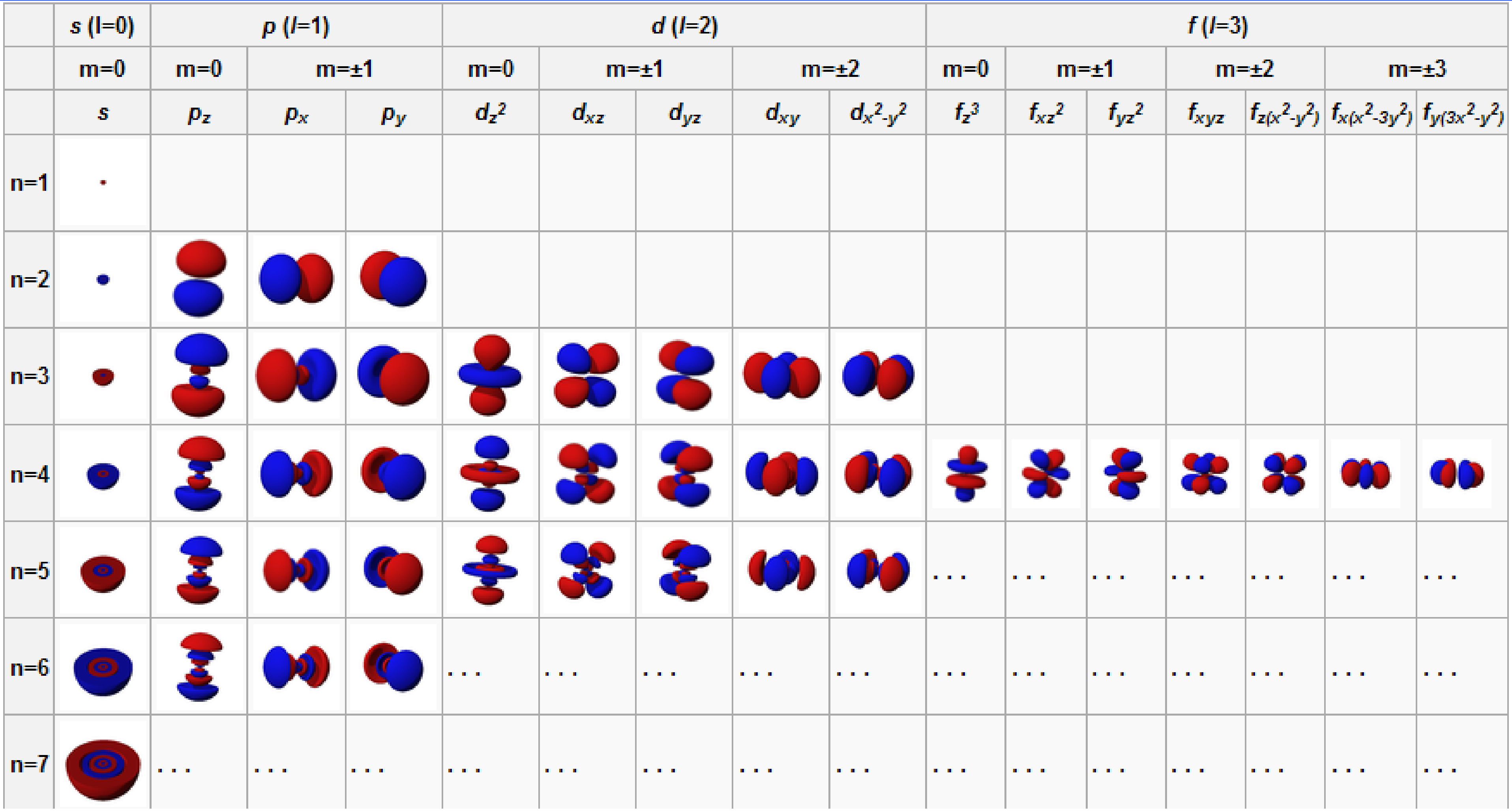
$$d_{xy} = \tfrac{-i}{\sqrt{2}}\left(Y_2^2 - Y_2^{-2}\right)$$

$$d_{xz} = \tfrac{-1}{\sqrt{2}}\left(Y_2^1 - Y_2^{-1}\right)$$

$$d_{yz} = \tfrac{i}{\sqrt{2}}\left(Y_2^1 + Y_2^{-1}\right)$$

$$f = \ldots$$

Atomic orbitals

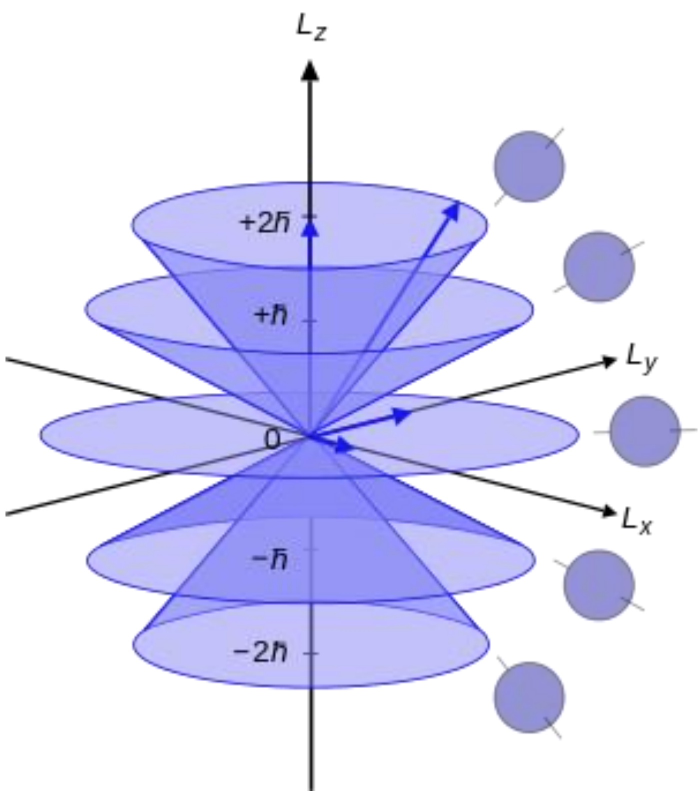


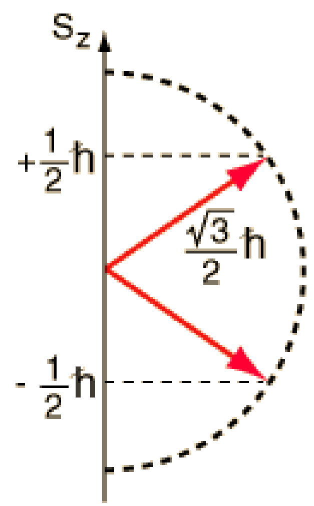
Orbital and spin angular momentun

$$\hat{H}\Psi_{n,l,m} = E_n \Psi_{n,l,m} \qquad \hat{H} = \hat{T} + \hat{V}$$

$$\hat{L}^2 Y_{l,m} = l(l+1)\hbar^2 Y_{l,m} \qquad \hat{s}^2 = \hbar^2 s(s+1) \qquad s = \tfrac{1}{2}$$

$$\hat{L}_z Y_{l,m} = m_l \hbar Y_{l,m} \qquad \hat{s}_z = \hbar m_s = \pm\frac{\hbar}{2}$$





m: electron mass

ε_o: permitivity of vacuum

Ψ: eigenfunctions

e: electron charge

E: energy

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R: radial function

Y: angular function

n: principal quantum number

l: orbital quantum number

determine the orbital angular momentum

$l = 0 \dots n-1$

m_l: magnetic quantum number

projection of the angular momentum into z-axis

$m_l = -l \dots l$

s: spin angular momentum

m_s: projection into z-axis

$m_s = -1/2 \dots 1/2$

Dirac's equation

$$E = c\sqrt{\vec{p}^2 + m_0^2 c^2}$$

Relativistic formula for the total energy of a free particle

$$E = c\sqrt{-\hbar^2\Delta + m_0^2 c^2} = -i\hbar c\vec{\alpha}\nabla + \beta m_0 c^2$$

where $\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ $\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$

Pauli matrixes: $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$|\vec{s}| = \sqrt{s(s+1)}\hbar$$

$$s = \tfrac{1}{2}$$

$$s_z = m_s\hbar$$

$$m_s = -\tfrac{1}{2}, \tfrac{1}{2}$$

s: spin quantum number

determines angular momentum of electron

m_s: projection into z-axis

m_s = -s … s

Spin-orbit coupling

$$\hat{H}_{so} = \lambda \vec{S}\vec{L}$$

λ > 0 : less than ½ occupied orbital,
J=|L-S|, direction of L and S opposite
λ< 0 : more than ½ occupied orbital,
J=L+S, direction of L and S identical

3*d* < 4*d* < 5*d*
$M^{2+} < M^{3+} < \ldots$

Spin orbit interaction is known in atomic physics as relativistic correction of the electron energies ($\vec{s}$, $\vec{p}$, and $\vec{L}$ mean vector operators of spin, momentum and angular momentum)

$$V_{SL} = \frac{\hbar}{4m_0c^2}\vec{s} \cdot \nabla V \times (\vec{p}/m_0)$$

$$V_{SL,sph} = \frac{\hbar}{4m_0c^2}\frac{1}{r}\frac{dV}{dr}\vec{L} \cdot \vec{s}$$

Approximate solution of Dirac's equation:

$$\hat{H}_D = \hat{H}_{Schr} + \hat{V}_m + \hat{V}_D + \hat{V}_{so}$$

V_m : Relativistic mass correction
V_D : Contact interaction (Darwin's term), significant for *s* orbitals only.
V_{so} : Spin-orbit coupling

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} + eV}_{\text{non-relativistic}} + \underbrace{\frac{\hat{p}^4}{8m^2c^2}}_{\text{K.E. correction}} + \underbrace{\frac{\hbar^2}{8m^2c^2}\nabla^2 V}_{\text{Darwin term}} + \underbrace{\frac{\hbar}{4m^2c^2}\vec{\sigma}\bullet(\vec{\nabla}V \times \hat{\mathbf{p}})}_{\text{SOI}}$$

Gyromagnetic ratio γ is a ration of magnetic momentum μ and angular momentum l

$$\gamma = \frac{\vec{\mu}}{\vec{l}}$$

m: electron mass
e: electron charge
ħ: Planck's constant
l: orbital angular momentum
s: spin angular momentum
μ_B: Bohr's magneton
r: radius of electron circuit
v: velocity of electron
τ: time of electron circulation
I: current
μ: magnetic moment

$$\gamma_l = -1\frac{\mu_B}{\hbar} = -\frac{e}{2m}$$

Gyromagnetic ratio for orbital momentum

$$\gamma_s = -2\frac{\mu_B}{\hbar} = -\frac{e}{m}$$

Gyromagnetic ratio for spin momentum

$$\mu_B = \frac{e\hbar}{2m}$$

Derivation for orbital angular momentum:

$$\tau = 2\pi r / v$$

$$I = -e/\tau = -ev/2\pi r$$

$$\vec{\mu} = \vec{I}S = (-e\vec{v}/2\pi\vec{r})(\pi r^2)$$

$$\vec{\mu} = -\frac{e}{2}\vec{v}\times\vec{r}$$

$$\vec{l} = m\,\vec{r}\times\vec{v}$$

$$\vec{\mu} = -\frac{e}{2m_e}\vec{l}$$

One-electron scheme
(energy only depends on the principal quantum number n)

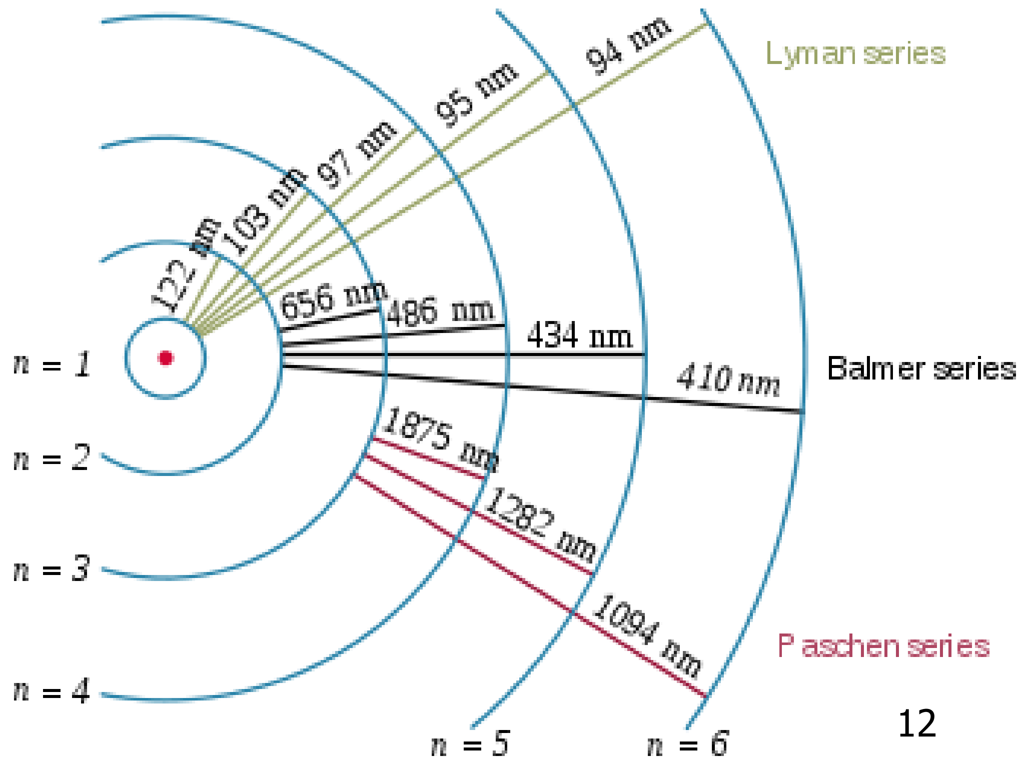
3s —— 3p —— 3d ——

2s —— 2p ——

1s ——

Hydrogen atom – 1 electron:
Wave length of the transitions between energy levels is determined by Rydberg's formula:

$$\frac{1}{\lambda_{\mathrm{vac}}} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$



Energy of orbitals in sphere symmetry

One-electron scheme (energy only depends on the principal quantum number n)

3s —— 3p —— 3d ——

2s —— 2p ——

1s ——

J: total angular momentum

J = |L+S| … |L-S|

M_J: -J, ... , J

j = |l+s| … |l-s|

m_j = -j, ... , j

Many-electrons scheme   J=|L+S| … |L-S| j=|l+s| … |l-s|

Coulombic interaction is predominant

3d ——

3p ——

3s ——

2p ——

2s ——

1s ——

LS coupling **J** ~ **L** + **S** = Σl + Σs

Valence electrons, spectroskopic symbols

spin-orbit interaction is predominant

$3d_{5/2}$

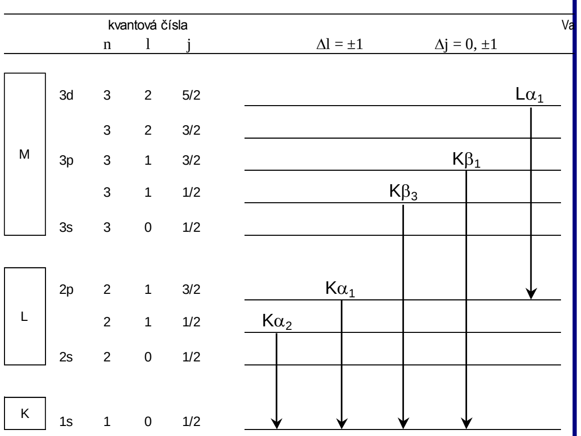
$3p_{3/2}$ $3d_{3/2}$

$3s_{1/2}$ $3p_{1/2}$

$2p_{3/2}$

$2s_{1/2}$ $2p_{1/2}$

$1s_{1/2}$



j-j coupling **J** ~ Σ**j** = Σ(**s**+**l**)

Core electrons

one electron

Orbital momentum

$l = 0, 1, 2, 3, \dots$

$m_l = 0$

Spin momentum

$s = {}^1/_2$

$m_s = \pm {}^1/_2$

LS coupling
so<Coulomb

Orbital momentum

$L = \sum m_l$ (occupied orbitals)

$M_L = -L, \dots, L$

Spin momentum

$S = \sum m_s$ (occupied orbitals)

$M_S = -S, \dots, S$

electron state of atom

Total momentum

$J = |L - S|, \dots, L + S$

$M_J = -J, \dots, J$

$^{2S+1}L_J$

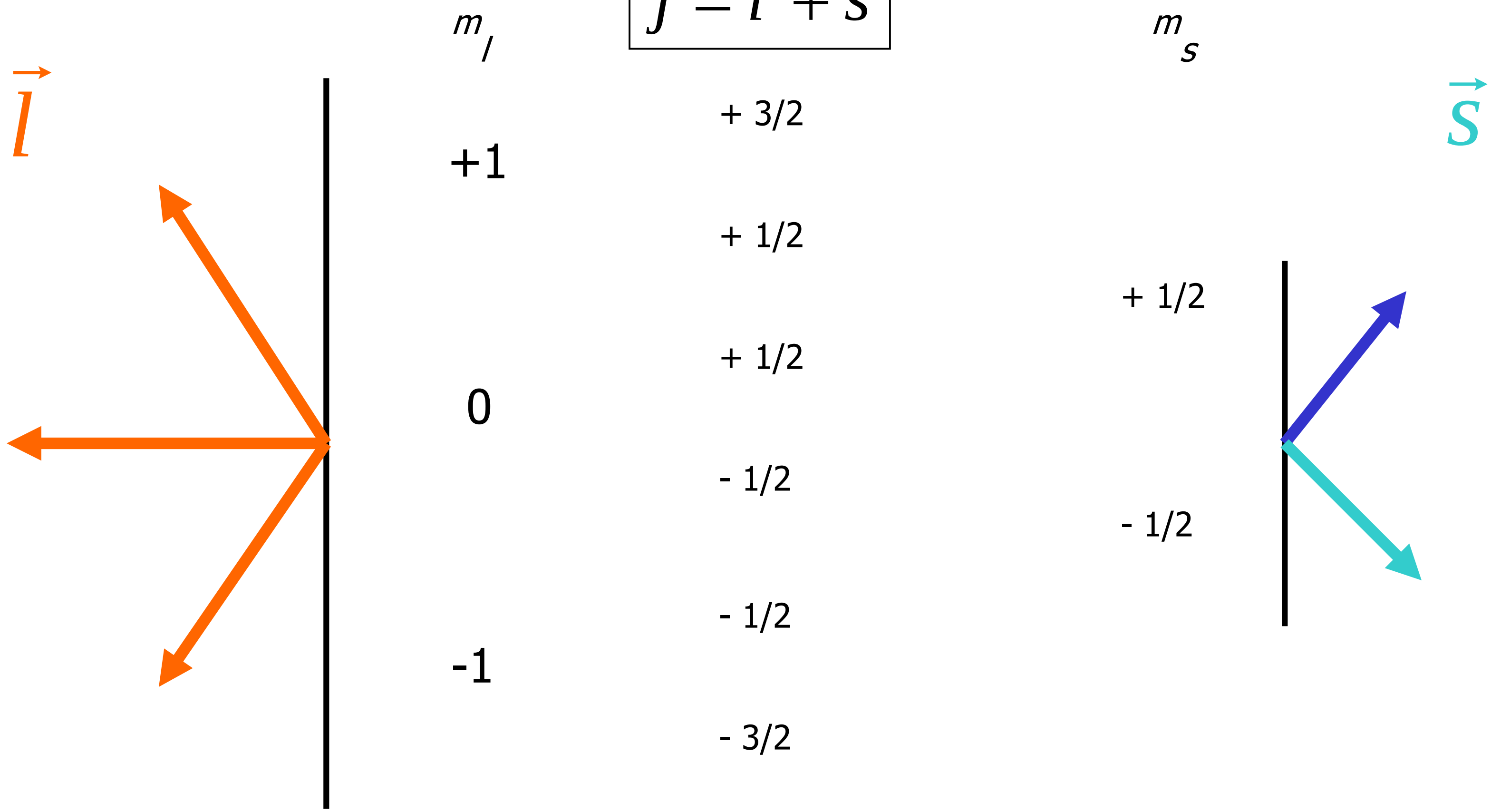
jj coupling
so>Coulomb

Total momentum

$j = |l - s|, \dots, l + s$

$m_j = -j, \dots, j$

$$\vec{j} = \vec{l} + \vec{s}$$



m_j = -3/2, -1/2, +1/2, +3/2 ⟷ j = 3/2 $p_{3/2}$

m_j = -1/2, +1/2 ⟷ j = 1/2 $p_{1/2}$

spin-orbit interaction is predominant

$3d_{5/2}$

$3p_{3/2}$ $3d_{3/2}$

$3s_{1/2}$ $3p_{1/2}$

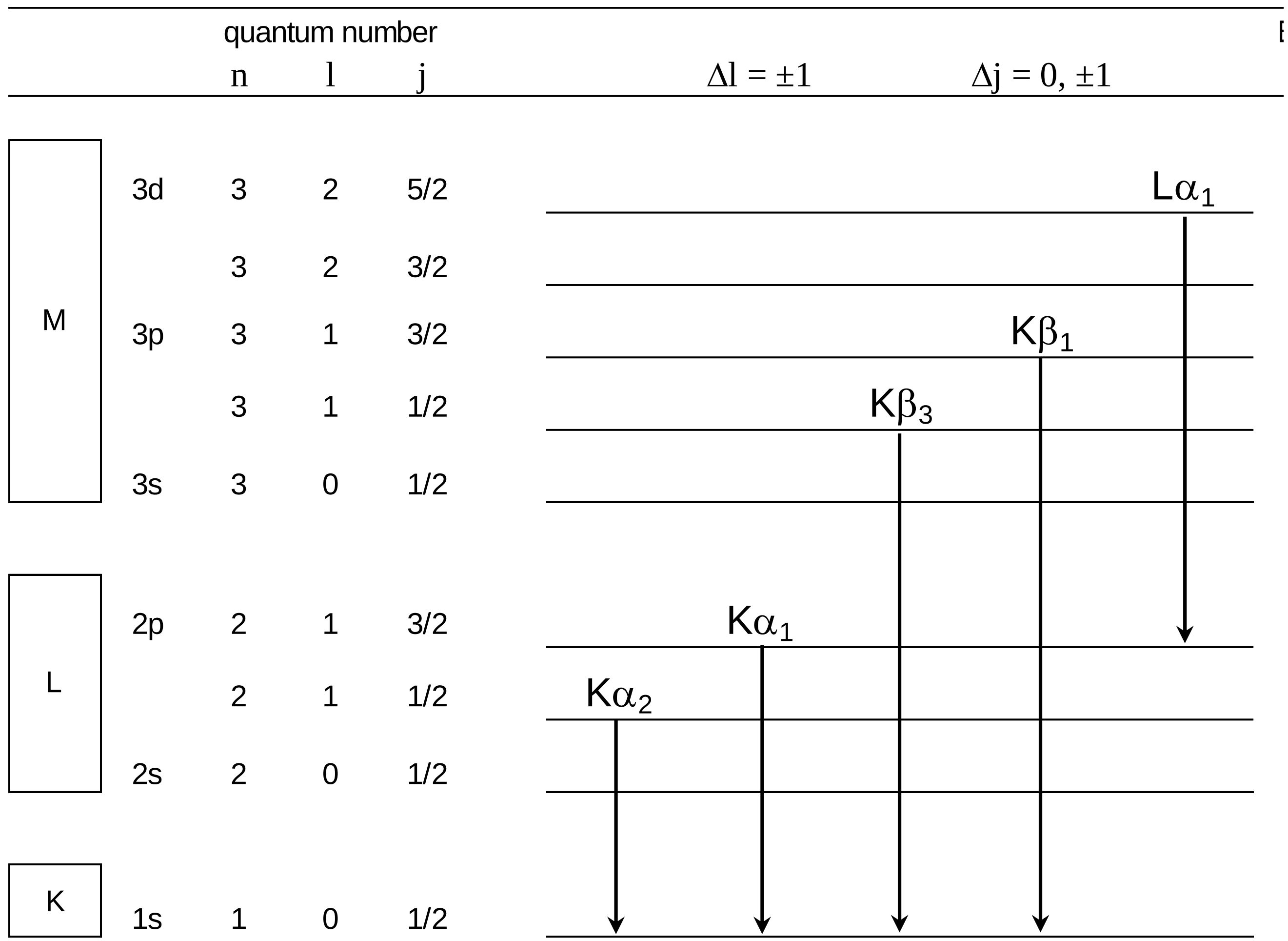
$2p_{3/2}$

$2s_{1/2}$ $2p_{1/2}$

$1s_{1/2}$

j-j coupling $\mathbf{J} \sim \Sigma \mathbf{j} = \Sigma(\mathbf{s}+\mathbf{l})$

Core electrons



one electron

orbital momentum

$$\left|\vec{\mathbf{l}}\right| = \sqrt{l(l+1)}\hbar \qquad l_z = m_l\hbar$$

spin momentum

$$\left|\vec{\mathbf{s}}\right| = \sqrt{s(s+1)}\hbar \qquad s_z = m_s\hbar$$

the whole atom

orbital momentum

$$\left|\vec{\mathbf{L}}\right| = \sqrt{L(L+1)}\hbar \qquad L_z = M_L\hbar$$

$$M_L = \sum m_l$$

spin momentum

$$\left|\vec{\mathbf{S}}\right| = \sqrt{S(S+1)}\hbar \qquad S_z = M_S\hbar$$

$$M_S = \sum m_s$$

electronic state of the atom

$$^{2S+1}L$$

multiplicity = (2S+1)(2L+1)

L: S, P, D, F, G, H, I, …

Russel-Saunders scheme:

(LS-coupling)
spin-orbit coupling

$$\vec{\mathbf{L}} = \sum_i \vec{\mathbf{l}}_i \qquad \vec{\mathbf{S}} = \sum_i \vec{\mathbf{s}}_i$$

$$\left|\vec{\mathbf{J}}\right| = \sqrt{J(J+1)}\hbar \qquad J_z = M_J \hbar \qquad \vec{\mathbf{J}} = \vec{\mathbf{L}} + \vec{\mathbf{S}}$$

$J = L+S, L+S-1, \ldots, |L-S|$

$L+S$: $x>y$; $|L-S|$: $x<y$ — **ground state**

$2S+1$ values for $S<L$
$2L+1$ values for $S>L$

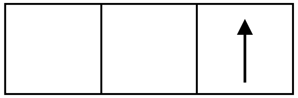
$M_J = -J, \ldots, 0, \ldots, J$ → $2J+1$ values

x – number of electrons
y – number of orbitals

state of the atom $\quad {}^{2S+1}L_J \quad$ multiplicity = (2J+1)

p^1

m_l: -1 0 1



$l = 1$ L = 1 P

s = ½ S = ½ 2S+1=2

J = 1+½, 1+½-1 (= |1-½|)

$$^2P_{3/2},\ ^2P_{1/2}$$

Multiplicity of the state ^2P:

$(2L+1)\times(2S+1) = 3\times2 = 6$

$\Sigma\ (2J+1) = (2\times3/2+1)+(2\times1/2+1) = 4+2 = 6$

Spectroscopic symbols – ground state

occupation of orbitals starts from maximal m_l.

n : number of electrons

n_m : number of electrons in state m (m_l , m_s).

$$L = \sum_{m_l}^{-L\ldots L} m_l \times n_{m_l}$$

$$S = \sum_{m_s}^{-\frac{1}{2},\frac{1}{2}} m_s \times n_{m_s}$$

$^{2S+1}L_J$

m_l:	-2	-1	0	1	2	n	L	$\mathbf{L}$	S	$\mathbf{2S+1}$	J	$\mathbf{J}$
						0	L=0	S	S=0	1	|L-S|	J=0
					↑	1	L=2	D	S=1/2	2	|L-S|	J=3/2
				↑	↑	2	L=3	F	S=1	3	|L-S|	J=2
			↑	↑	↑	3	L=3	F	S=3/2	4	|L-S|	J=3/2
		↑	↑	↑	↑	4	L=2	D	S=2	5	|L-S|	J=0
	↑	↑	↑	↑	↑	5	L=0	S	S=5/2	6	L+S	J=5/2
	↑	↑	↑	↑	↑↓	6	L=2	D	S=2	5	L+S	J=4
	↑	↑	↑	↑↓	↑↓	7	L=3	F	S=3/2	4	L+S	J=9/2
	↑	↑	↑↓	↑↓	↑↓	8	L=3	F	S=1	3	L+S	J=4
	↑	↑↓	↑↓	↑↓	↑↓	9	L=2	D	S=1/2	2	L+S	J=5/2
	↑↓	↑↓	↑↓	↑↓	↑↓	10	L=0	S	S=0	1	L+S	J=0

d^n	GS
d^1	$^2D_{3/2}$
d^2	$^3F_2$
d^3	$^4F_{3/2}$
d^4	$^5D_0$
d^5	$^6S_{5/2}$
d^6	$^5D_4$
d^7	$^4F_{9/2}$
d^8	$^3F_4$
d^9	$^2D_{5/2}$
d^0,d^{10}	$^1S_0$

d^n	GS
d^1	$^2D_{3/2}$
d^2	$^3F_2$
d^3	$^4F_{3/2}$
d^4	$^5D_0$
d^5	$^6S_{5/2}$
d^6	$^5D_4$
d^7	$^4F_{9/2}$
d^8	$^3F_4$
d^9	$^2D_{5/2}$
d^{10}	$^1S_0$

f^n	GS
f^1	$^2F_{5/2}$
f^2	$^3H_4$
f^3	$^4I_{9/2}$
f^4	$^5I_4$
f^5	$^6H_{5/2}$
f^6	$^7F_0$
f^7	$^8S_{7/2}$

f^n	GS
f^8	$^7F_6$
f^9	$^6H_{15/2}$
f^{10}	$^5I_8$
f^{11}	$^4I_{15/2}$
f^{12}	$^3H_6$
f^{13}	$^2F_{7/2}$
f^{14}	$^1S_0$

microstate: – specific electron configuration in partially filled shell (subshell).
– occupation of individual orbitals by electrons with spin up or down

number of microstates:

$$N = \frac{(2o)!}{e!(2o-e)!}$$

o – number of orbitals
e – number of electrons

orbitals: $\boldsymbol{m_l}$ electrons: $\boldsymbol{m_s}$ = ½, -½ (↑, ↓)

Ex.: atom C $2p^2$ N = 6!/(2!)(4!) = 15

-1	0	1
	↑	↑

Micro- and macrostates of carbon atom ($2p^2$)

-1	0	1	M_L	M_S
	↑	↑	1	1
↑		↑	0	1
↑	↑		-1	1
	↓	↓	1	-1
↓		↓	0	-1
↓	↓		-1	-1
	↑	↓	1	0
↑		↓	0	0
↑	↓		-1	0
	↓	↑	1	0
↓		↑	0	0
↓	↑		-1	0
		↑↓	2	0
	↑↓		0	0
↑↓			-2	0

Find max. M_L, then max. M_S for this M_L.
Decrement states ($-M_L$ až M_L) x ($-M_S$ až M_S) in the table.
Repeat until the table is completely zerofilled.

$M_L \setminus M_S$	-1	0	1
-2	0	1	0
-1	1	2	1
0	1	3	1
1	1	2	1
2	0	1	0

$M_S = 0$
$M_L = 0$
↓
$S = 0$ $L = 0$
→ $^1S_0$

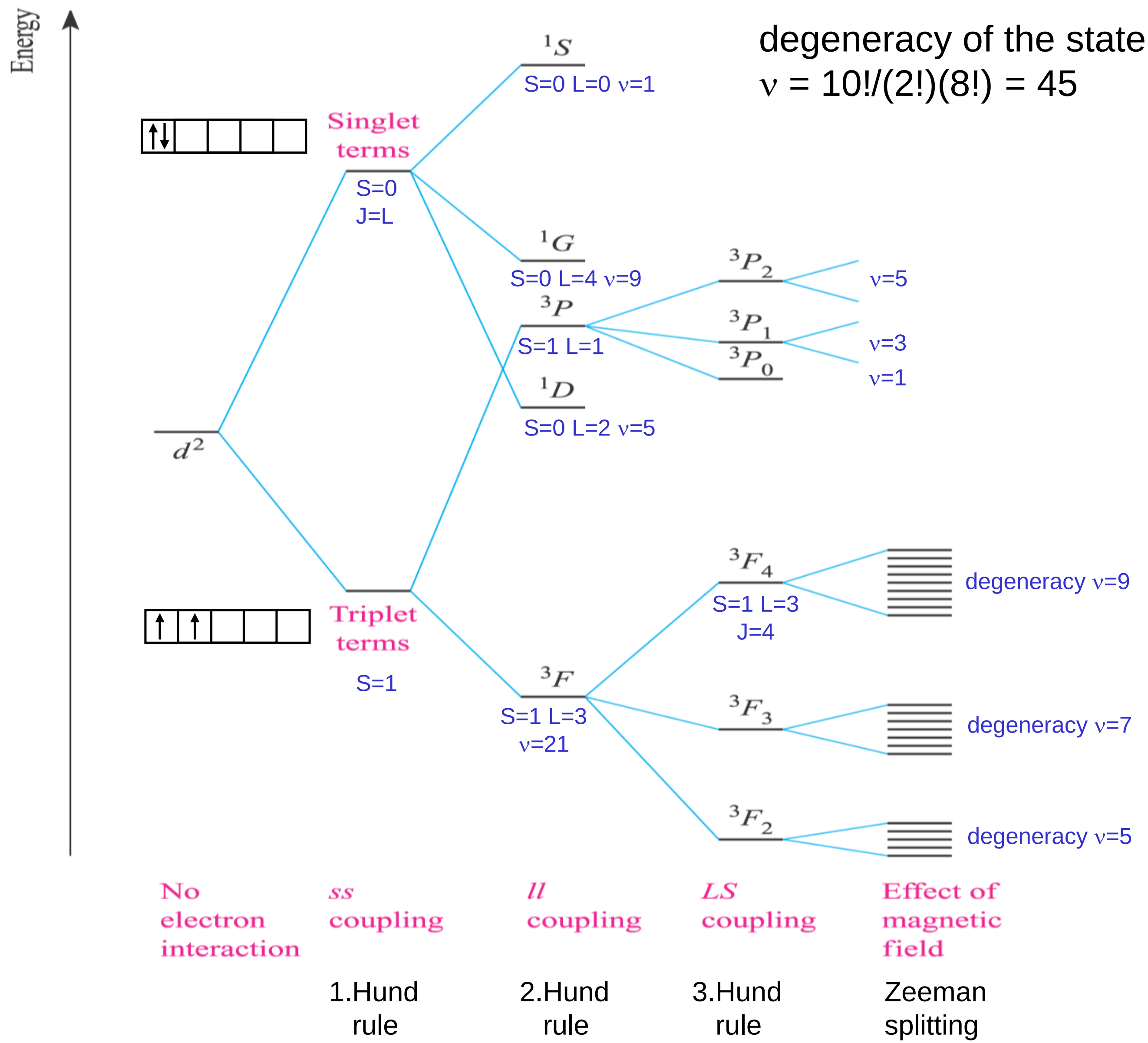
$M_S = -1,0,1$
$M_L = -1,0,1$
↓
$S = 1$ $L = 1$
↓
ground state $^3P_{2,1,0}$

1. max. $2S+1$
2. max. L
3. min./max. J

$M_S = 0$
$M_L = -2,-1,0,1,2$
↓
$S = 0$ $L = 2$
↓
$^1D_2$

Splitting of states for electron configuration d^2 – sphere symmetry

degeneracy of the state d^2:
$\nu = 10!/(2!)(8!) = 45$



Crystal (ligand) field theory

- ligands - ion (point) charges
- electrostatic repulsion with valence electrons of the central atom
- lowering symmetry of the Hamiltonian – new eigenvalues (energy) and eigenvectors (wavefunctions)
- splitting of the energy levels of the atomic orbitals of the central atom

Schoenflies symbols

Schoenflies and international symbols of point groups

System	Schoenflies symbol	International symbol	p
triclinic	C_1	1	1
	C_i	-1	2
monoclinic	C_2	2	2
	C_{1h}	m	2
	C_{2h}	2/m	4
orthorhombic	D_2	222	4
	C_{2v}	mm2	4
	D_{2h}	2/m 2/m 2/m = mmm	8
tetragonal	C_4	4	4
	S_4	-4	4
	C_{4h}	4/m	8
	D_4	422	8
	C_{4v}	4mm	8
	D_{2d}	-42m	8
	D_{4h}	4/m 2/m 2/m = 4/mmm	16
trigonal	C_3	3	3
	C_{3i}	-3	6
	D_3	32	6
	C_{3v}	3m	6
	D_{3d}	-3 2/m = -3m	12
hexagonal	C_6	6	6
	C_{3h}	-6	6
	C_{6h}	6/m	12
	D_6	622	12
	C_{6v}	6mm	12
	D_{3h}	-62m	12
	D_{6h}	6/m 2/m 2/m = 6/mmm	24
cubic	T	23	12
	T_h	2/m -3 = m-3	24
	O	432	24
	T_d	-43m	24
	O_h	4/m -3 2/m = m-3m	48

Symbols of irreducible reprezentations

Depends on the specific group (applies to the two "plane" columns)

by symmetry:	Principal rotation axis (C_n)	Center of inversion (i)	plane $\parallel$ to princip. axis (σ_v)	plane $\perp$ to princip. axis (σ_h)
symmetric	A	g	1	'
antisymmetric	B	u	2	''

C_2:
$p_x \to -p_x$
$p_y \to -p_y$
$\Rightarrow$ B

i:
$d_{xy} \to d_{xy}$
(similarly all d)
$\Rightarrow$ g

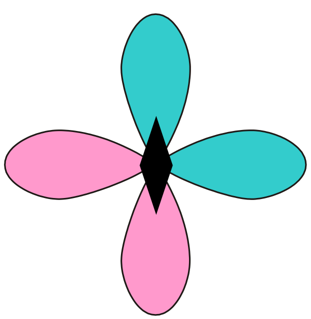
C_4:
$p_x \to p_y$
$p_y \to -p_x$
$\Rightarrow$ E

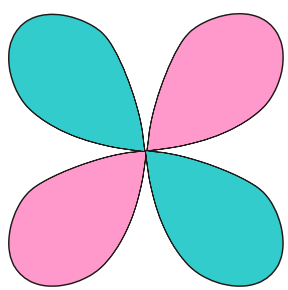
by degeneracy:

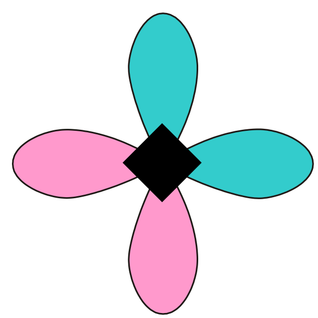
1: A,B

2: E

3: T

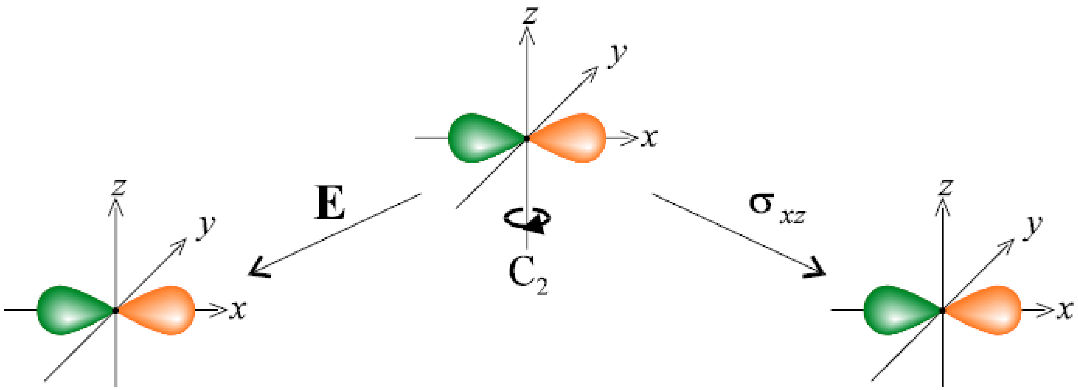




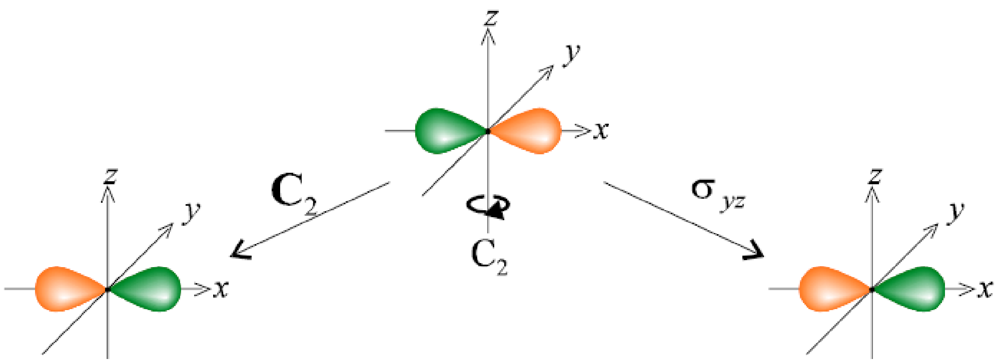


group C_{2v}

$$\mathbf{E}p_x = 1 \times p_x \quad \text{a} \quad \sigma_{xz} p_x = 1 \times p_x, \quad \text{tj.}\ \chi(\mathbf{E}) = 1 \quad \text{a} \quad \chi(\sigma_{xz}) = 1.$$



$$\mathbf{C}_2 p_x = -1 \times p_x \quad \text{a} \quad \sigma_{yz} p_x = -1 \times p_x, \quad \text{tj.}\ \chi(\mathbf{C}_2) = -1 \quad \text{a} \quad \chi(\sigma_{yz}) = -1.$$

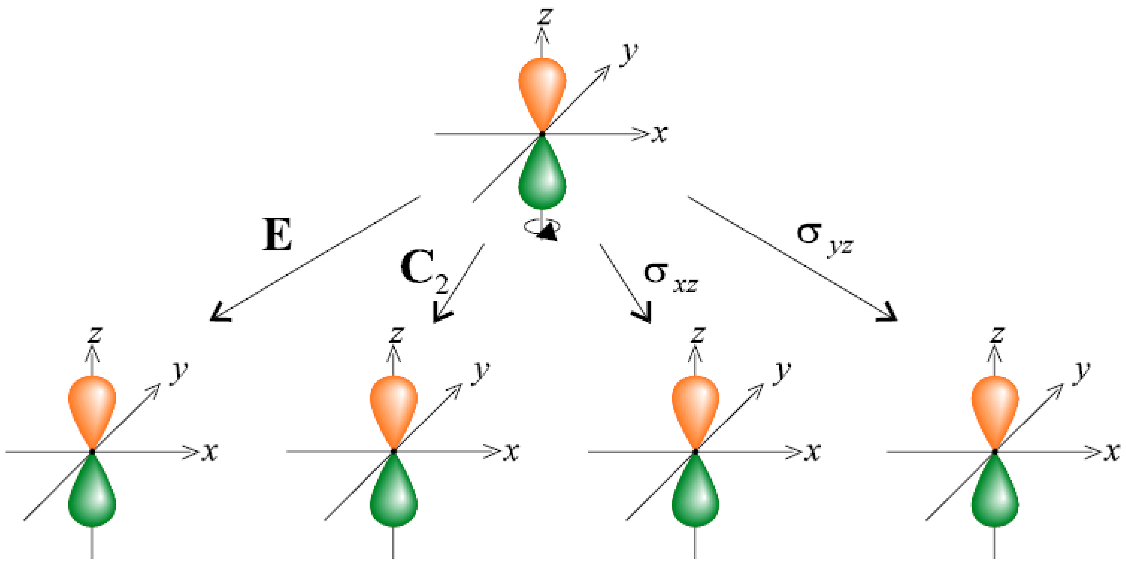


Characters of symmetry operations of the C_{2v} group in the p_x basis

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
B_1	1	–1	1	–1

Labelling of irreducible representations

group C_{2v}



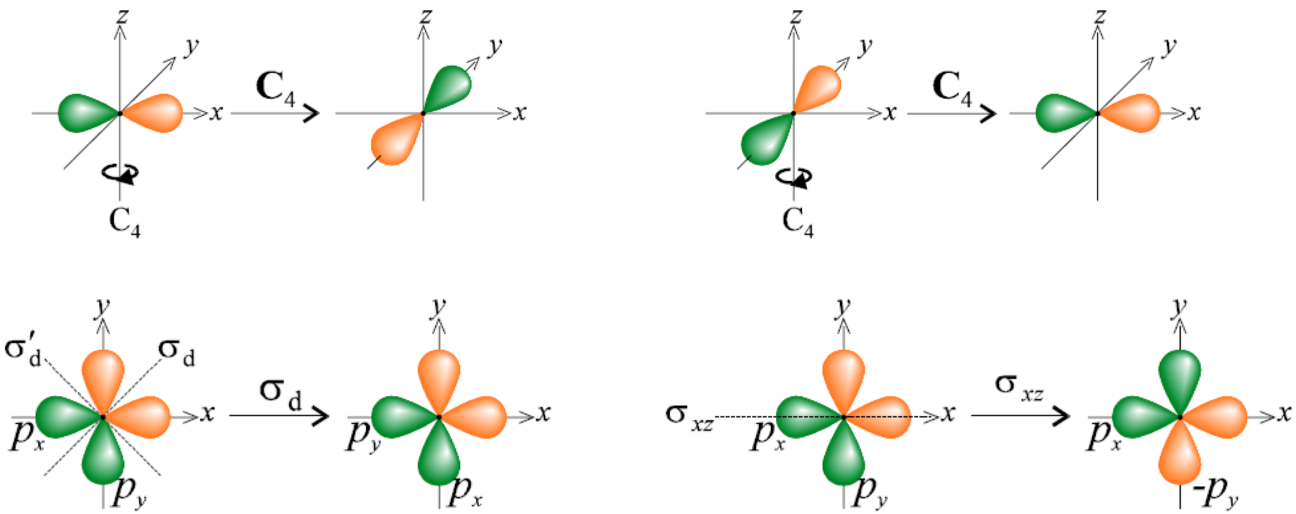
Irreducible representations of the C_{2v} group in the p_z basis

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
A_1	1	1	1	1

group C_{4v}

By applying the symmetry operation C_4 (i.e. rotation by 90° around z-axis) the orbital p_x transforms into orbital $-p_y$, and p_y into p_x.

For degenerate orbitals, the character of the representation equals the sum of the characters corresponding to the individual orbitals that remain in the original place after the transformation or only change their sign.



Degenerate irreducible representations of the C_{4v} group in the (p_x,p_y) basis

C_{4v}	$\mathbf{E}$	$\mathbf{C}_4$	$\mathbf{C}_4^3$	$\mathbf{C}_4^2 = \mathbf{C}_2$	σ_{xz}	σ_{yz}	σ_{yz}	σ'_d
E	2	0	0	–2	0	0	0	0
	K_1	K_2		K_3	K_4		K_5	

Characters of irreducible representations

C_{2v} (2mm)	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

For degenerate orbitals, the character of the representation equals the sum of the characters corresponding to the individual orbitals that remain in the original place after the transformation or only change their sign.

C_{2h}	E	C_2	σ_h	i	h=4	
A_g	1	1	1	1	R_z	xy, x^2, y^2, z^2
A_u	1	1	−1	−1	z	
B_g	1	−1	−1	1	R_x, R_y	xz, yz
B_u	1	−1	1	−1	x, y	

The sum of the second powers of the degeneracies of the individual representations is equal to the order of the group ($h=\Sigma \nu^2$ tj. $4=1^2+1^2+1^2+1^2$)
The number of representations is equal to the number of group classes.

	C_n	i	σ_v	σ_h
symmetric	A	g	1	‵
antisymmetric	B	u	2	‶

Characters of irreducible representations

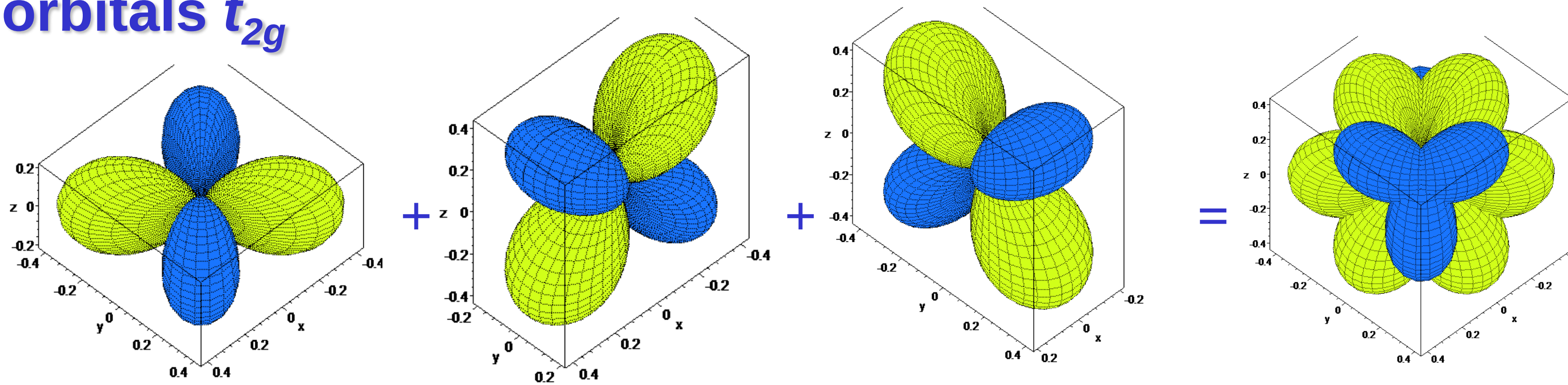
T_d ($\bar{4}3m$)	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	$h=24$	
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

The sum of the second powers of the degeneracies of the individual representations is equal to the order of the group ($h=\Sigma\nu^2$ tj. $4=1^2+1^2+1^2+1^2$). The number of representations is equal to the number of group classes.

O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h=48$	
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

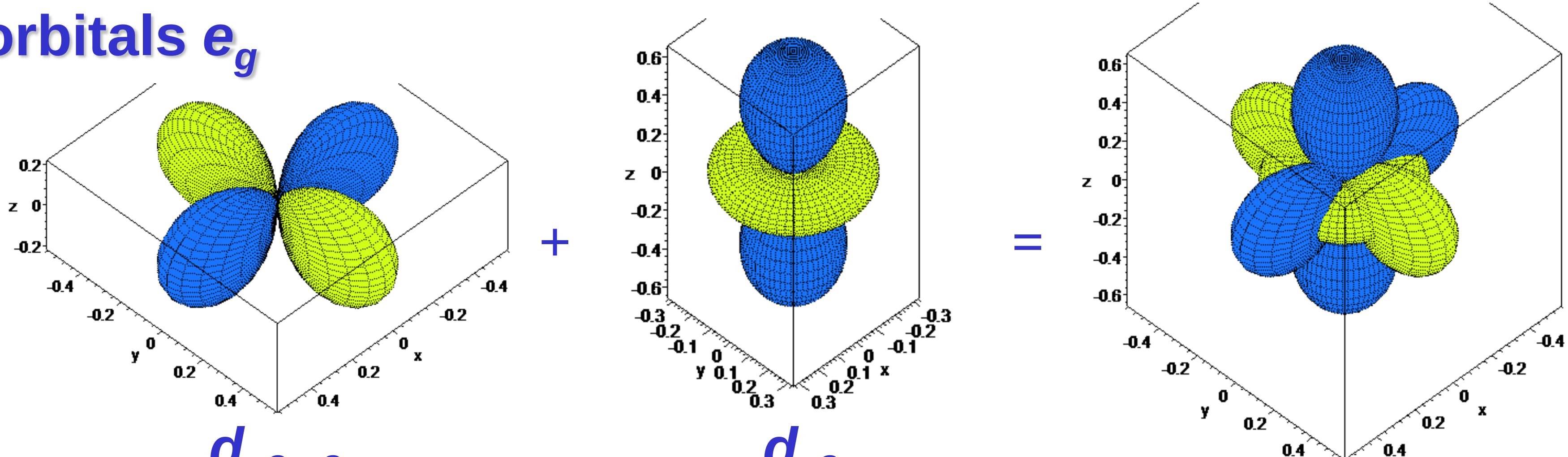
	C_n	i		σ_h
symmetric	A	g	1	'
antisymmetric	B	u	2	''

orbitals t_{2g}



d_{xy} d_{yz} d_{xz}

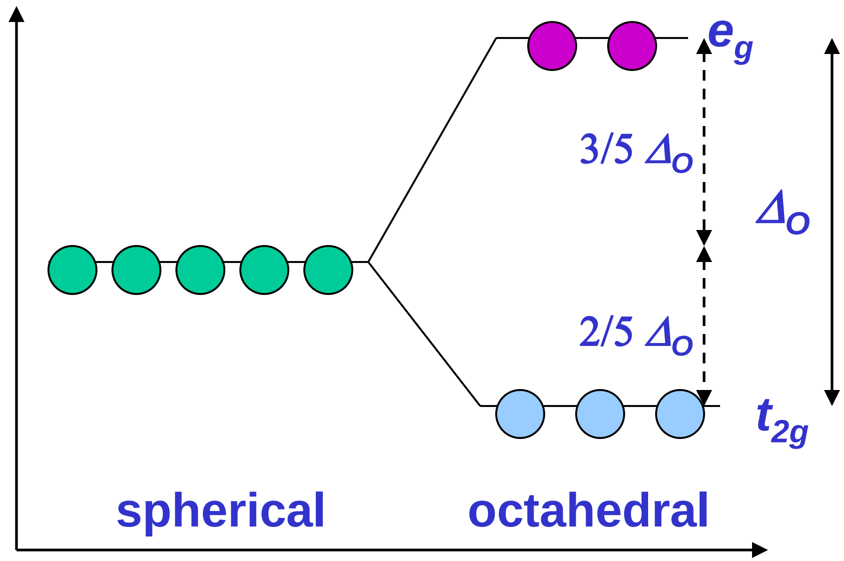
orbitals e_g

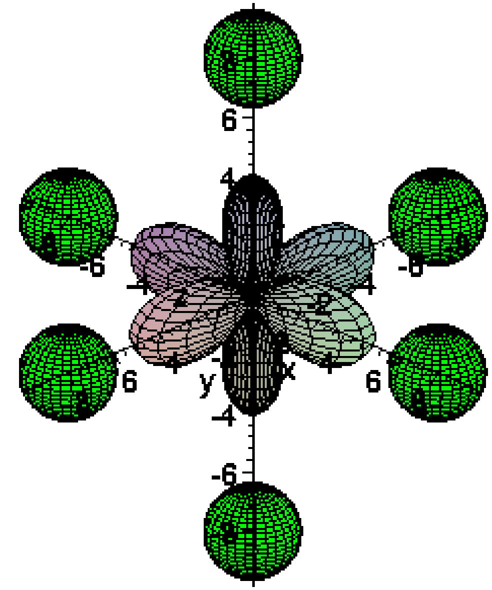


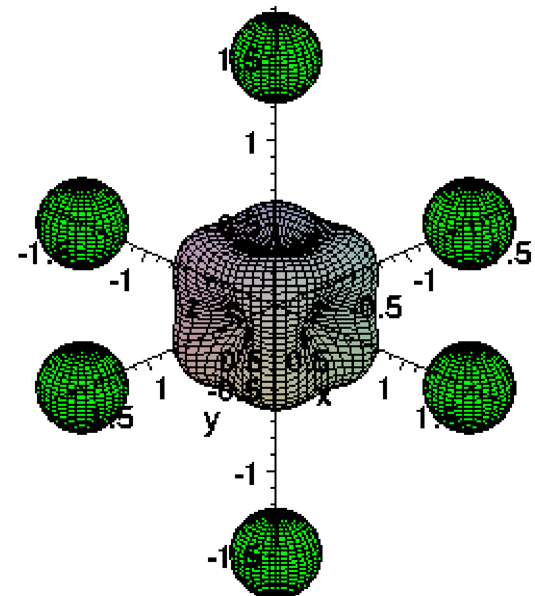
d_{x2-y2} d_{z2}

$(x^2-y^2)/r^2$ $[(z^2-x^2) + (z^2-y^2)]/r^2$

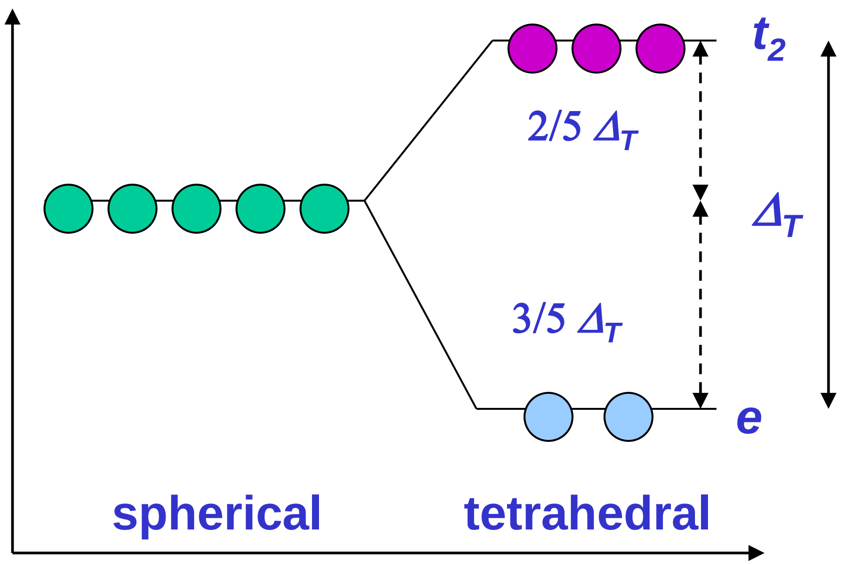
Orbitals d in octahedral field

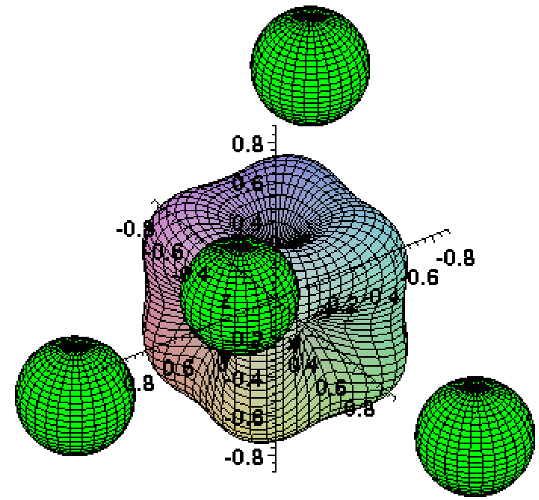


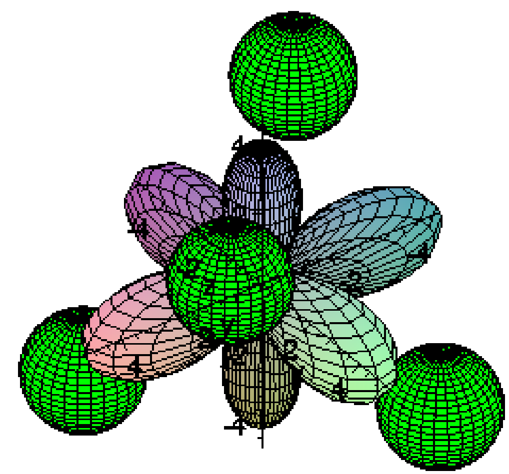




Orbitals d in tetrahedral field



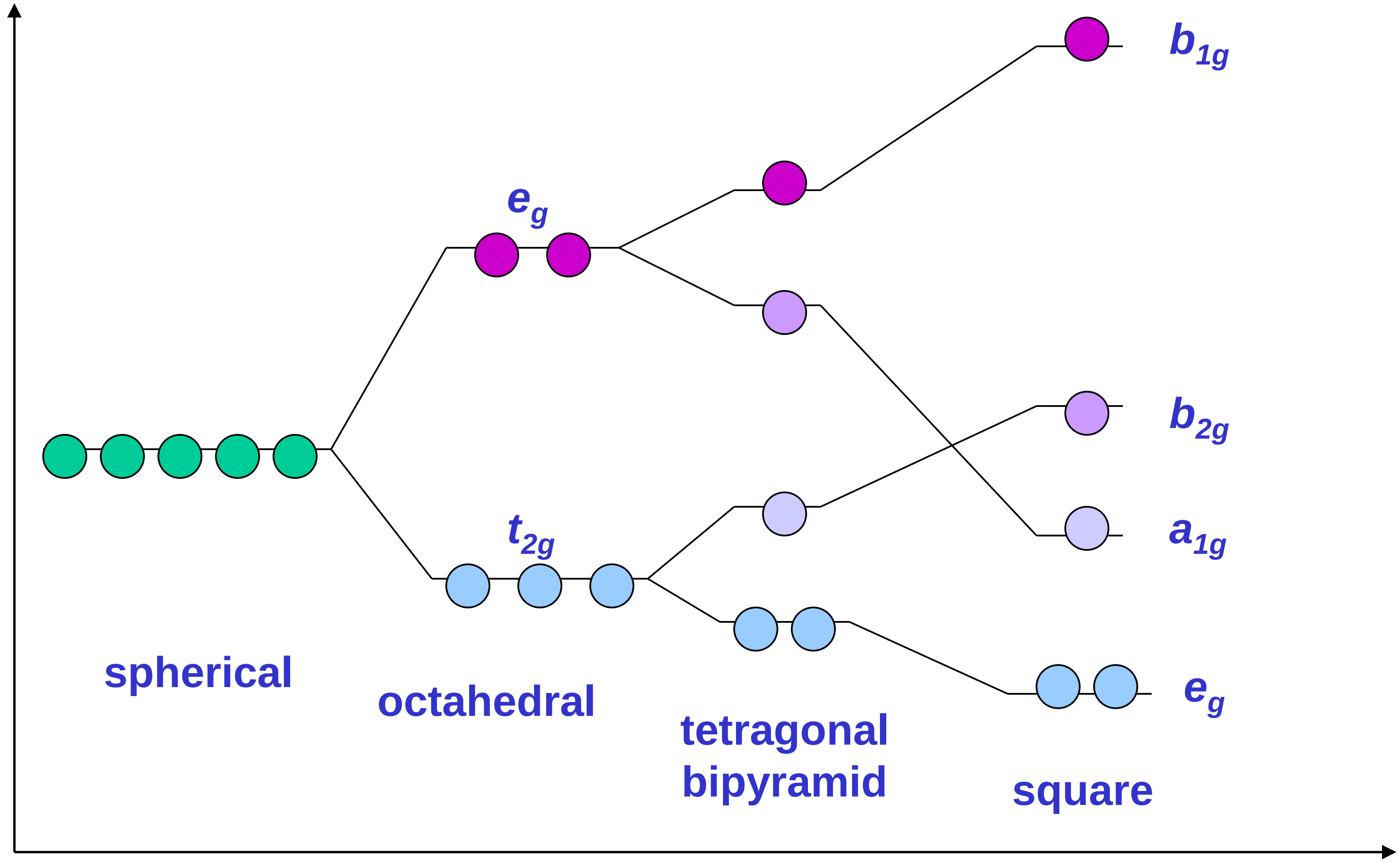




$\Delta_T = 4/9\ \Delta_O$

$\Delta_C = 8/9\ \Delta_O$

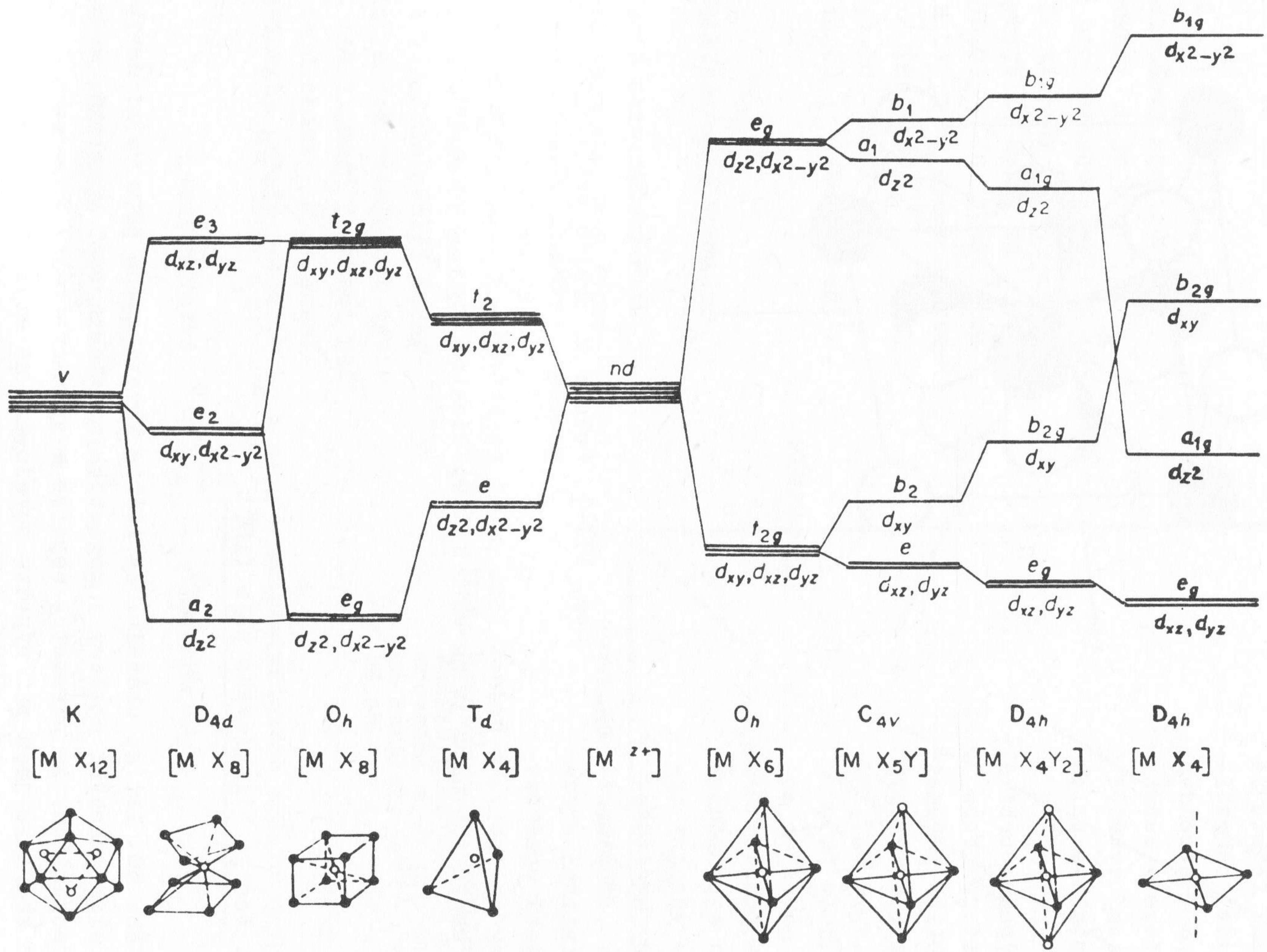
Orbitals d in tetragonal field



Bases of irreducible representations

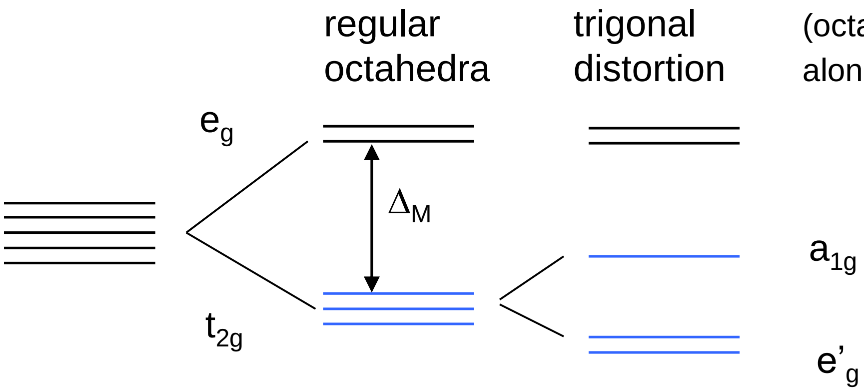
<table>
<tr><th>ψ_i G</th><th>R_3</th><th>O_h</th><th>T_d</th><th>D_{4h}</th><th>C_{4v}</th><th>C_{2v}</th><th>D_{3v}</th></tr>
<tr><td>s</td><td>s_g</td><td>A_{1g}</td><td>A_1</td><td>A_{1g}</td><td>A_1</td><td>A_1</td><td>A_{1g}</td></tr>
<tr><td>p_x</td><td rowspan="3">p_u</td><td rowspan="3">T_{1u}</td><td rowspan="3">T_1</td><td rowspan="2">E_u</td><td rowspan="2">E</td><td>B_1</td><td rowspan="2">E_u</td></tr>
<tr><td>p_y</td><td>B_2</td></tr>
<tr><td>p_z</td><td>A_{2u}</td><td>A_1</td><td>A_1</td><td>A_{2u}</td></tr>
<tr><td>d_{z2}</td><td rowspan="5">d_g</td><td rowspan="2">E_g</td><td rowspan="2">E</td><td>A_{1g}</td><td>A_1</td><td>A_1</td><td rowspan="2">E_g</td></tr>
<tr><td>d_{x2-y2}</td><td>B_{1g}</td><td>B_1</td><td>A_1</td></tr>
<tr><td>d_{xy}</td><td rowspan="3">T_{2g}</td><td rowspan="3">T_2</td><td>B_{2g}</td><td>B_2</td><td>A_2</td><td>A_{1g}</td></tr>
<tr><td>d_{xz}</td><td rowspan="2">E_g</td><td rowspan="2">E</td><td>B_1</td><td rowspan="2">E_g</td></tr>
<tr><td>d_{yz}</td><td>B_2</td></tr>
</table>

Crystal field in various symmetries

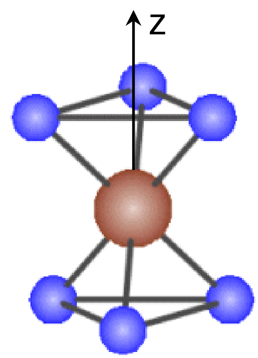


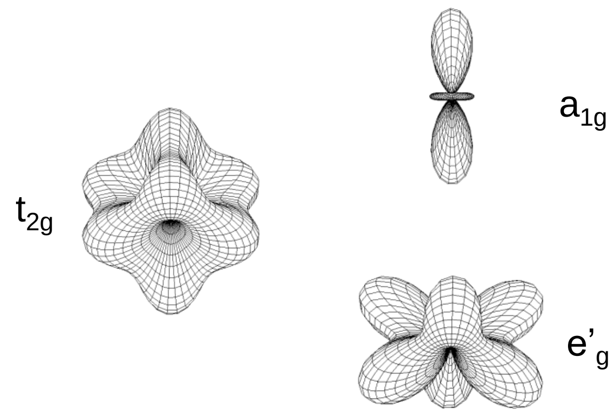
Trigonally distorted octahedra

Trigonally distorted octahedral: t_{2g} orbitals splits further to a_{1g} and e'_g.

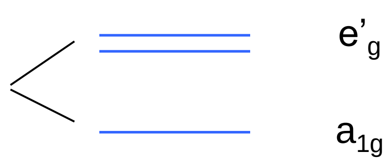


(octahedra **compressed** along trigonal axis z)



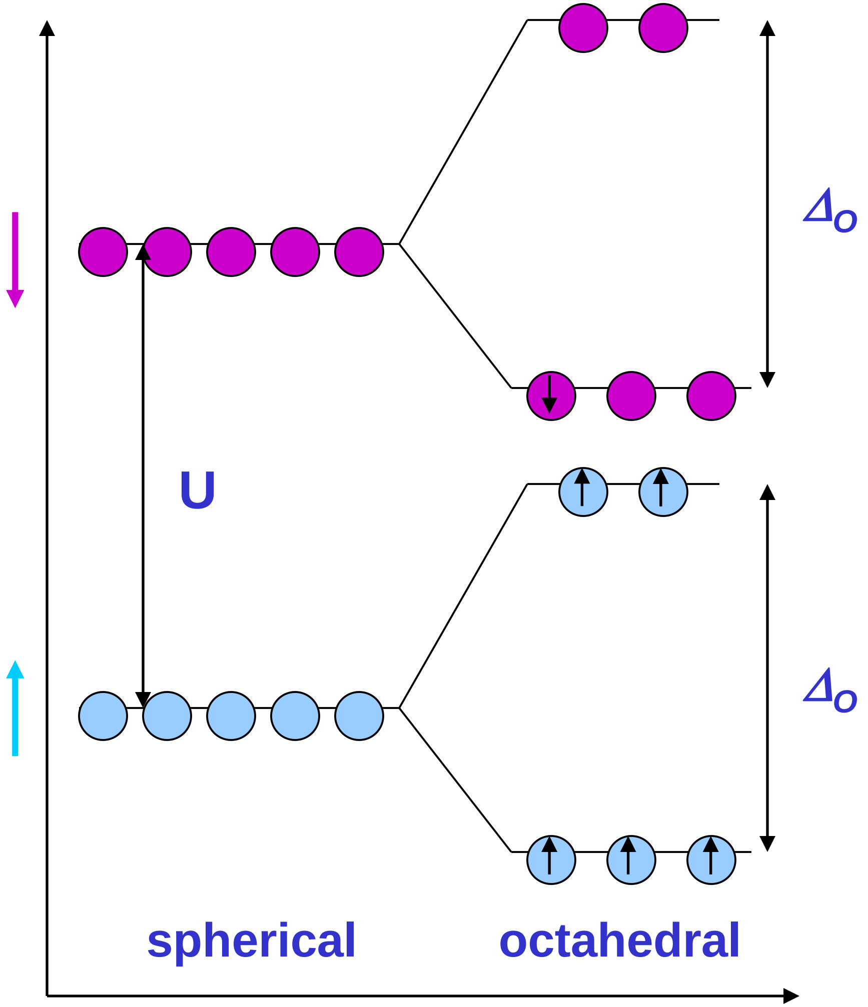


(octahedra **elongated** along trigonal axis z)

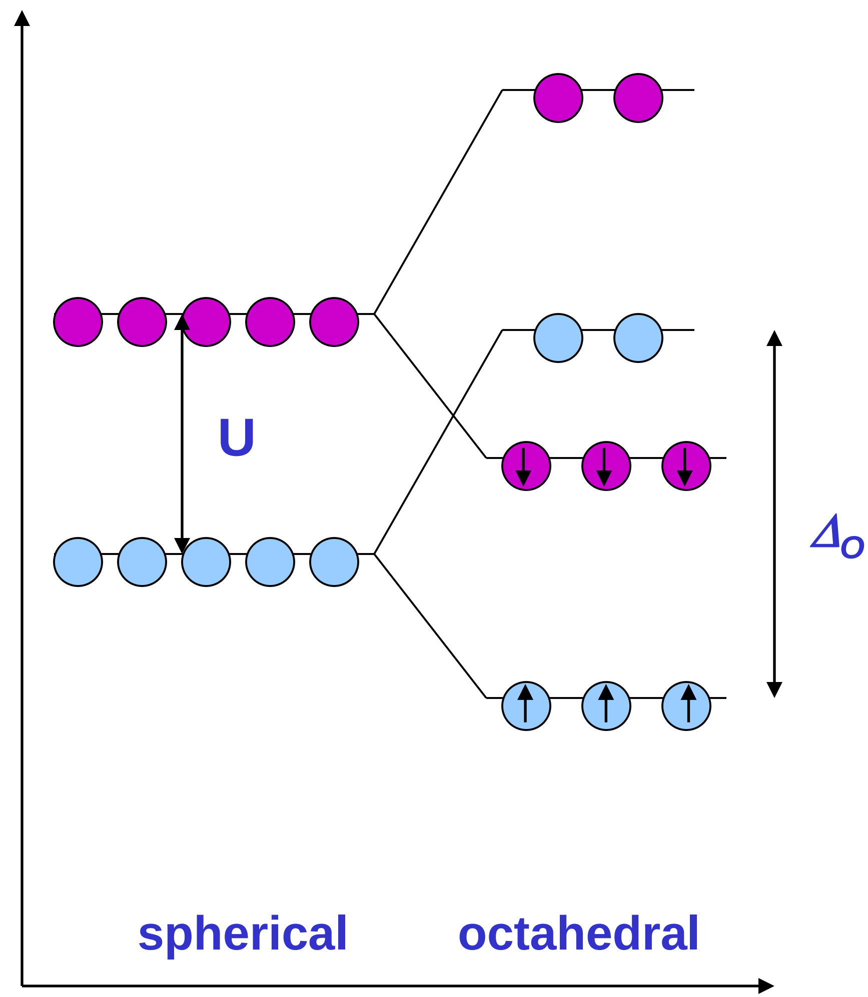


Weak and strong crystal field

Weak field – high spin complexes



Strong field – low spin complexes

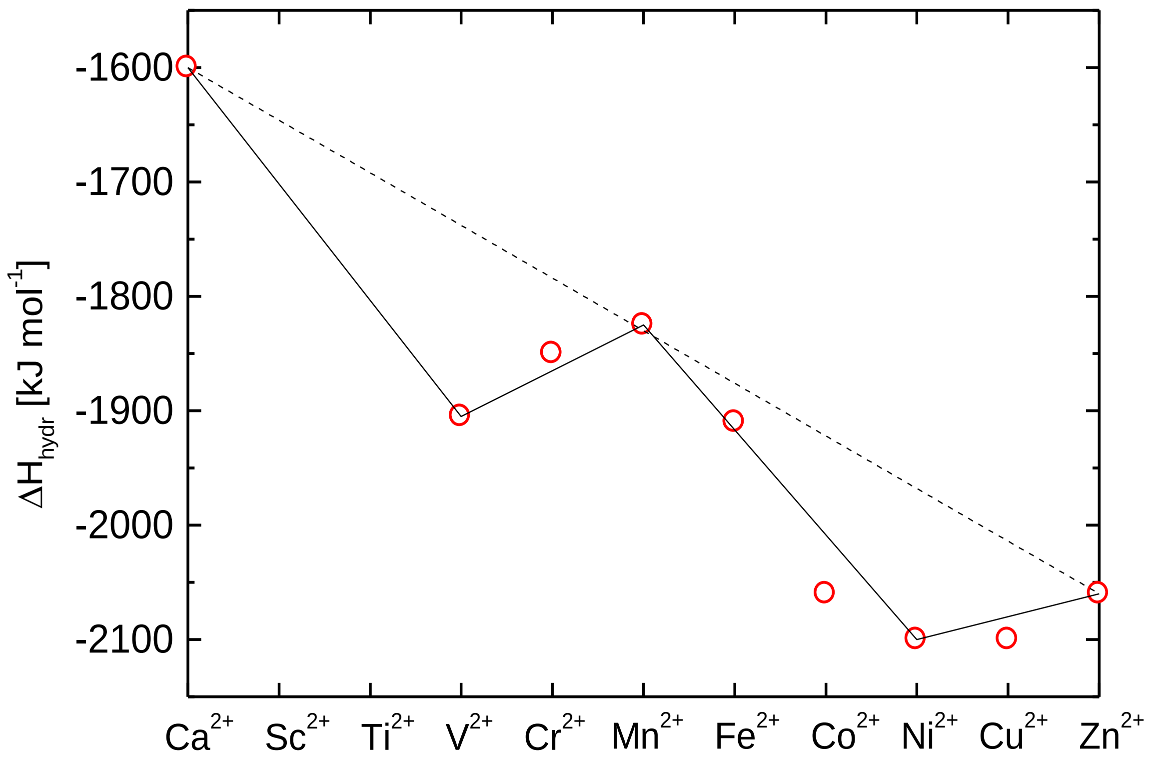


Electron configurations in the weak and strong crystal field

d^n	octahedral				tetrahedral			
n	weak		strong		weak		strong	
	t_{2g}	e_g	t_{2g}	e_g	e	t_2	e	t_2
1	1	0	1	0	1	0	1	0
2	2	0	2	0	2	0	2	0
3	3	0	3	0	2	1	3	0
4	3	1	4	0	2	2	4	0
5	3	2	5	0	2	3	4	1
6	4	2	6	0	3	3	4	2
7	5	2	6	1	4	3	4	3
8	6	2	6	2	4	4	4	4
9	6	3	6	3	4	5	4	5
10	6	4	6	4	4	6	4	6

O_h CFSE = $n_{t2g} \times (-0.4\,\Delta_o) + n_{eg} \times 0.6\,\Delta_o$

T_d CFSE = $n_e \times (-0.6\,\Delta_o) + n_{t2} \times 0.4\,\Delta_o$



Different ligands have different ability to split the *d* levels

- **depends mainly on the degree of covalent interaction with the central atom**
- **increase of the ligand strength due to the π–backbonding (σ donors + π acceptors)**

<u>spektrochemical series</u> – ordering of ligands according their strength

I^- , Br^- , Cl^- , SCN^- , F^- , $S_2O_3^-$, CO_3^{2-} , OH^- , NO_3^- , SO_4^{2-} , H_2O , $C_2O_4^{2-}$, NO_2^- , NH_3 , C_5H_5N , en , NH_2OH^- , H^- , CH_3^- $C_5H_5^-$, CO , CN^-

$$\Delta_o = f_{ligand} \times g_{ion}$$

f_{ligand}

I^-	0.72	NCS^-	1.02
Br^-	0.72	C_5H_5N	1.23
SCN^-	0.73	NH_3	1.25
Cl^-	0.78	en	1.28
NO_3^-	0.82	dien	1.30
F^-	0.90	NO_2^-	1.40
OH^-	0.94	CN^-	~1.7
$C_2O_4^{2-}$	0.98	CO	~1.7
H_2O	1.00		

$\Delta_o = f_{ligand} \times g_{ion}$

3d < 4d < 5d

$M^{2+} < M^{3+} < M^{4+}$

g_{ion} [cm^{-1}] (for $[M(H_2O)_6]$)

V^{2+}	11800	Cr^{2+}	14000	Mn^{2+}	7500
Fe^{2+}	10000	Co^{2+}	9200	Ni^{2+}	8600
Cu^{2+}	13000			Ru^{2+}	19800
Ti^{3+}	20300	V^{3+}	18000	Cr^{3+}	17400
Mn^{3+}	21000	Fe^{3+}	14000	Co^{3+}	20760
Ru^{3+}	28600	Rh^{3+}	17200	Ir^{3+}	32000
Mn^{4+}	23000	Tc^{4+}	30000	Pt^{4+}	36000

Dependence on the central atom

$$\Delta = \frac{5}{3}\frac{Ze^2 r^4}{R^5}$$

Z : ligand charge

R : distance between the central atom (M) and ligand

r : distance of electron in *d* orbital from the nucleus of M

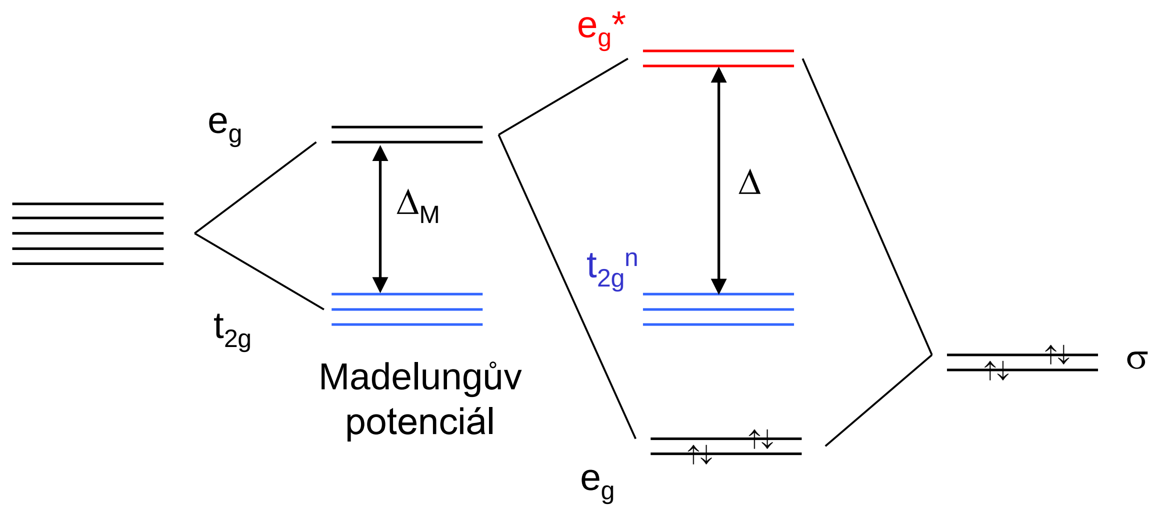
Δ(3d) : Δ(4d) : Δ(5d) = 1 : 1.45 : 1.7

$\Delta(M^{2+}) : \Delta(M^{3+}) : \Delta(M^{4+})$ = 1 : 1.6 : 1.9

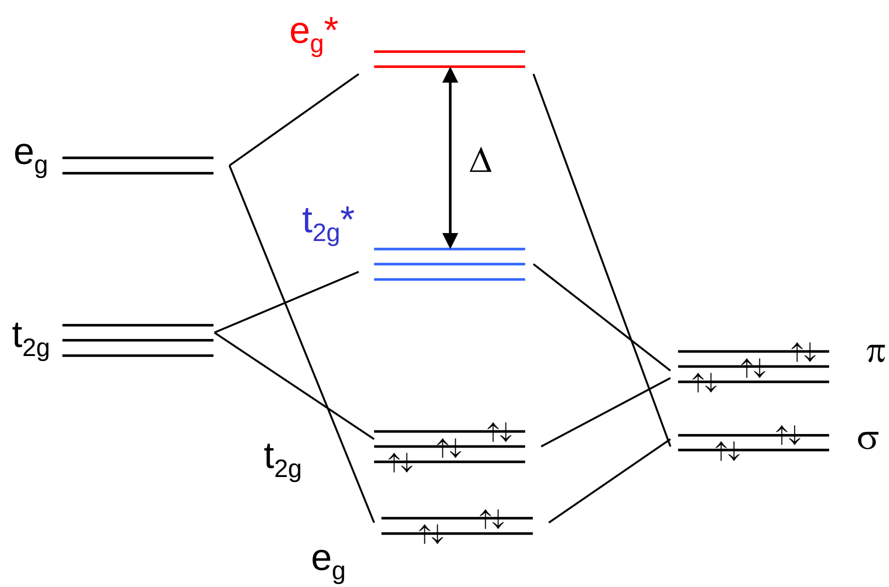
σ-donor, π-donor a π-acceptor

Scheme for d^0

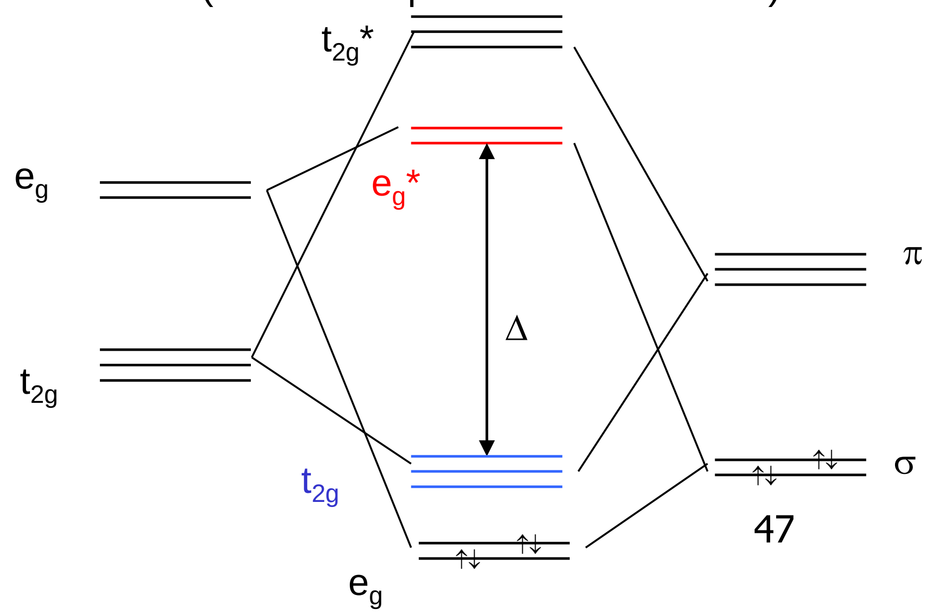
σ- donor
(middle of the spectrochemical series)



σ- donor, π - donor
(beginning of the spectrochemical series)

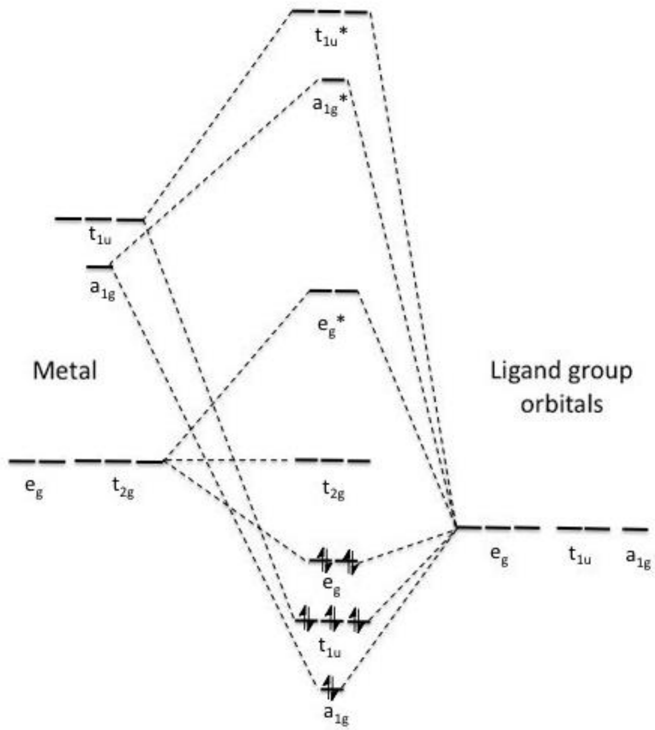


σ- donor, π - acceptor
(end of the spectrochemical series)

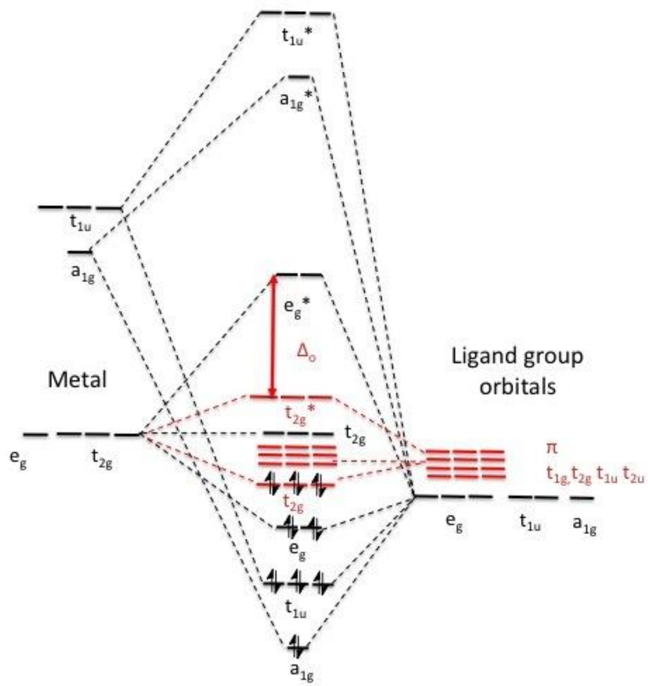


σ-donor, π-donor a π-akceptor

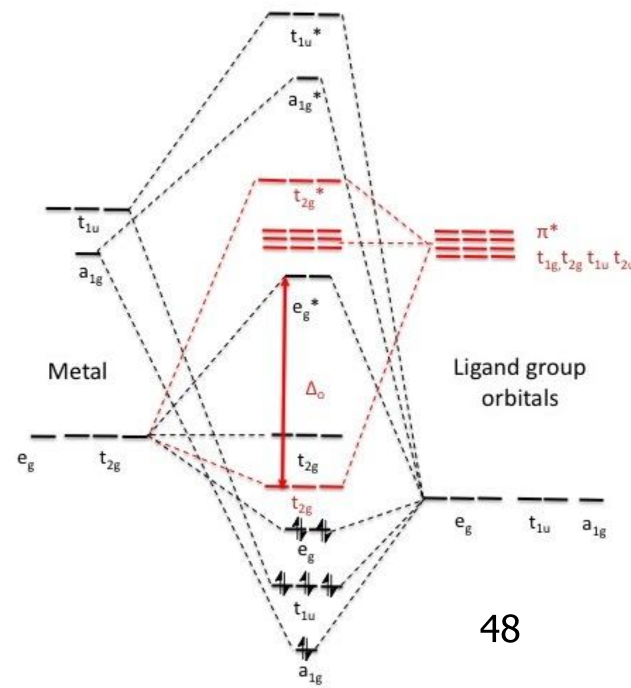
σ- donor



σ- donor, π - donor

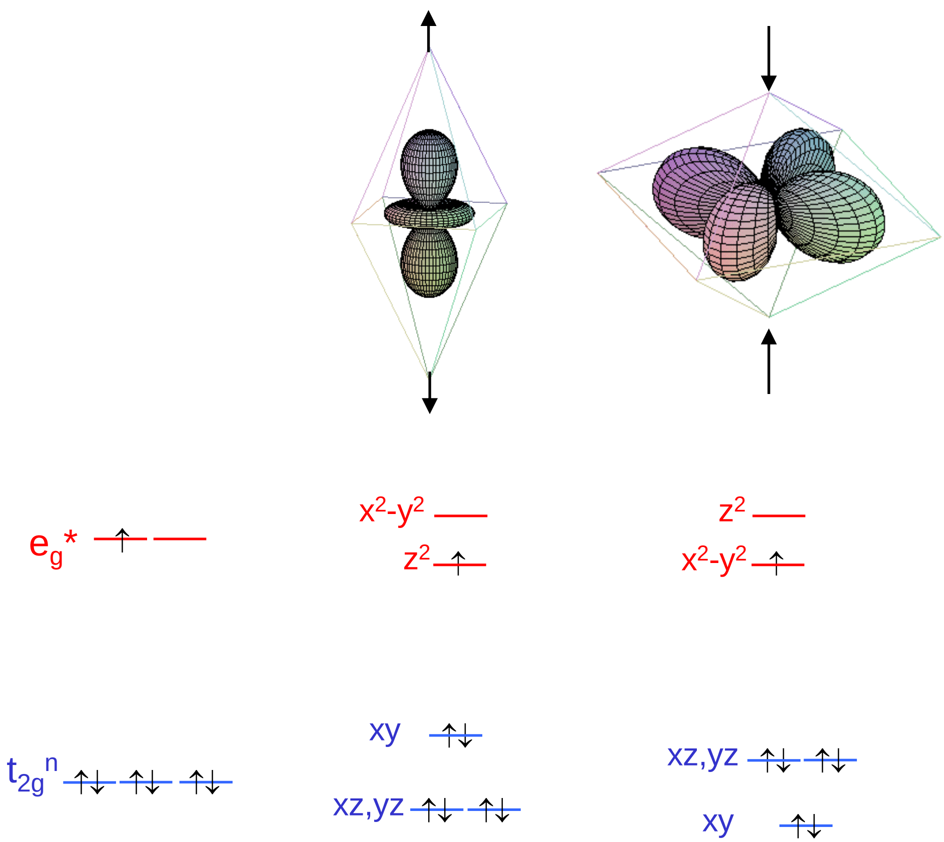


σ- donor, π - acceptor



Jahn-Teller effect

Systems with spin-and-orbitally-degenerated states tend to spontaneously distort the vicinity of the central atom and thereby remove this degeneration



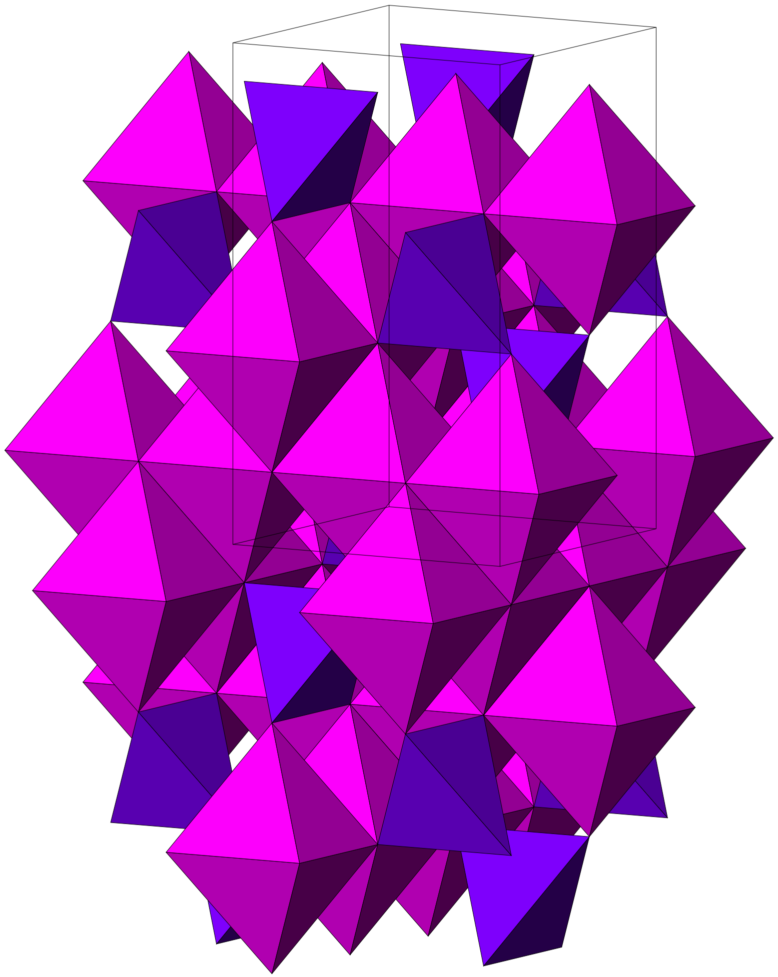
The active electron configurations for octahedra are $t_{2g}^3e_g^1$, $t_{2g}^6e_g^1$ a $t_{2g}^6e_g^3$.

Octahedra is elongated in the direction of the occupied orbital, because the occupation of the anti-bonding molecular orbital is increased

Cooperative Jahn-Teller effect

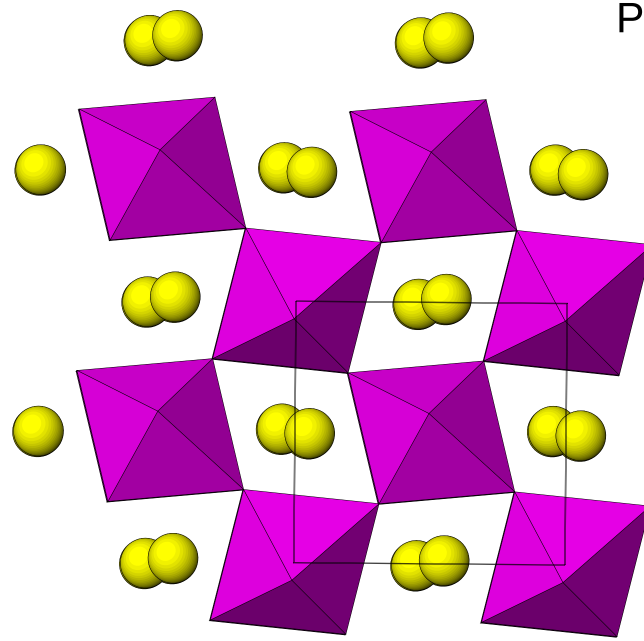
Mn_3O_4

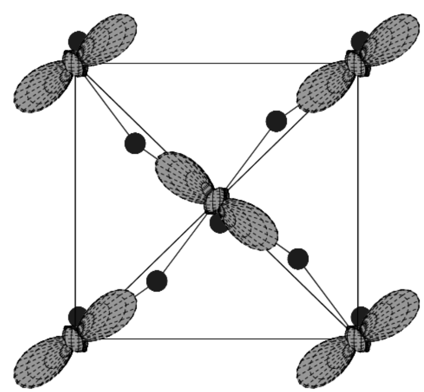
$I4_1/amd$



$LaMnO_3$

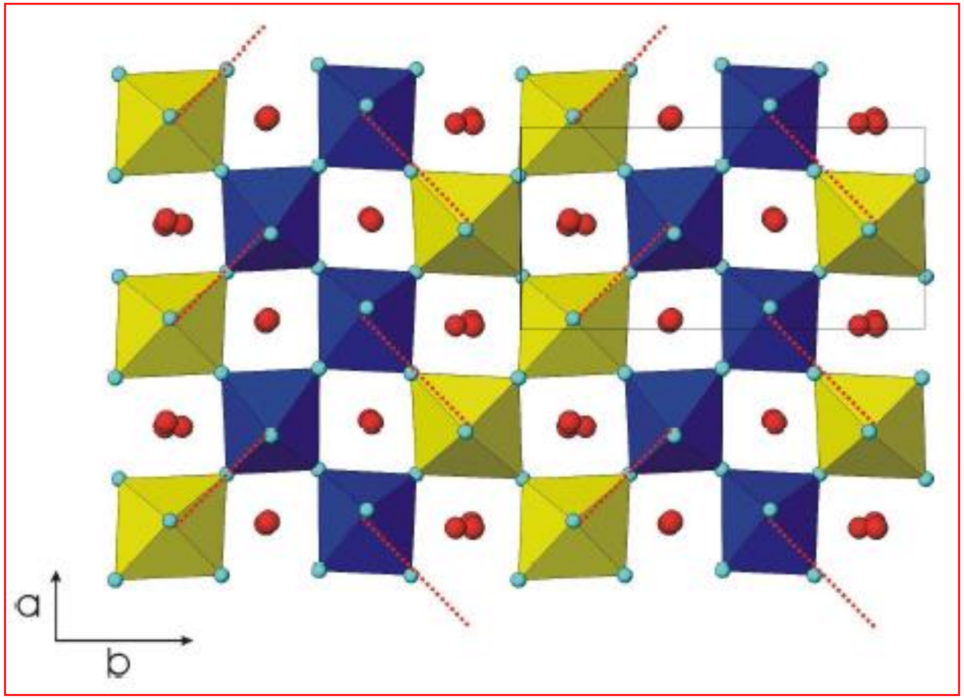
Pbnm

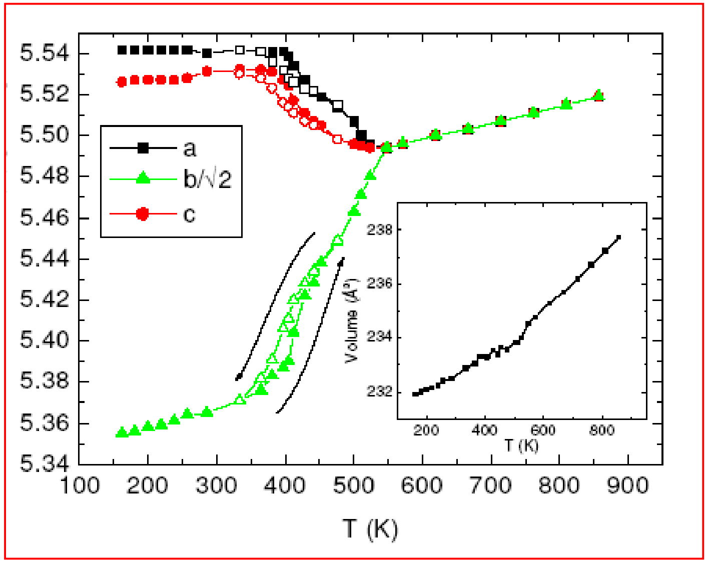




$$t_{2g}^{3}e_{g}^{1} = d_{xz}^{1}d_{yz}^{1}d_{xy}^{1}d_{z^2}^{1}$$

$Bi_{0.5}Sr_{0.5}MnO_3$





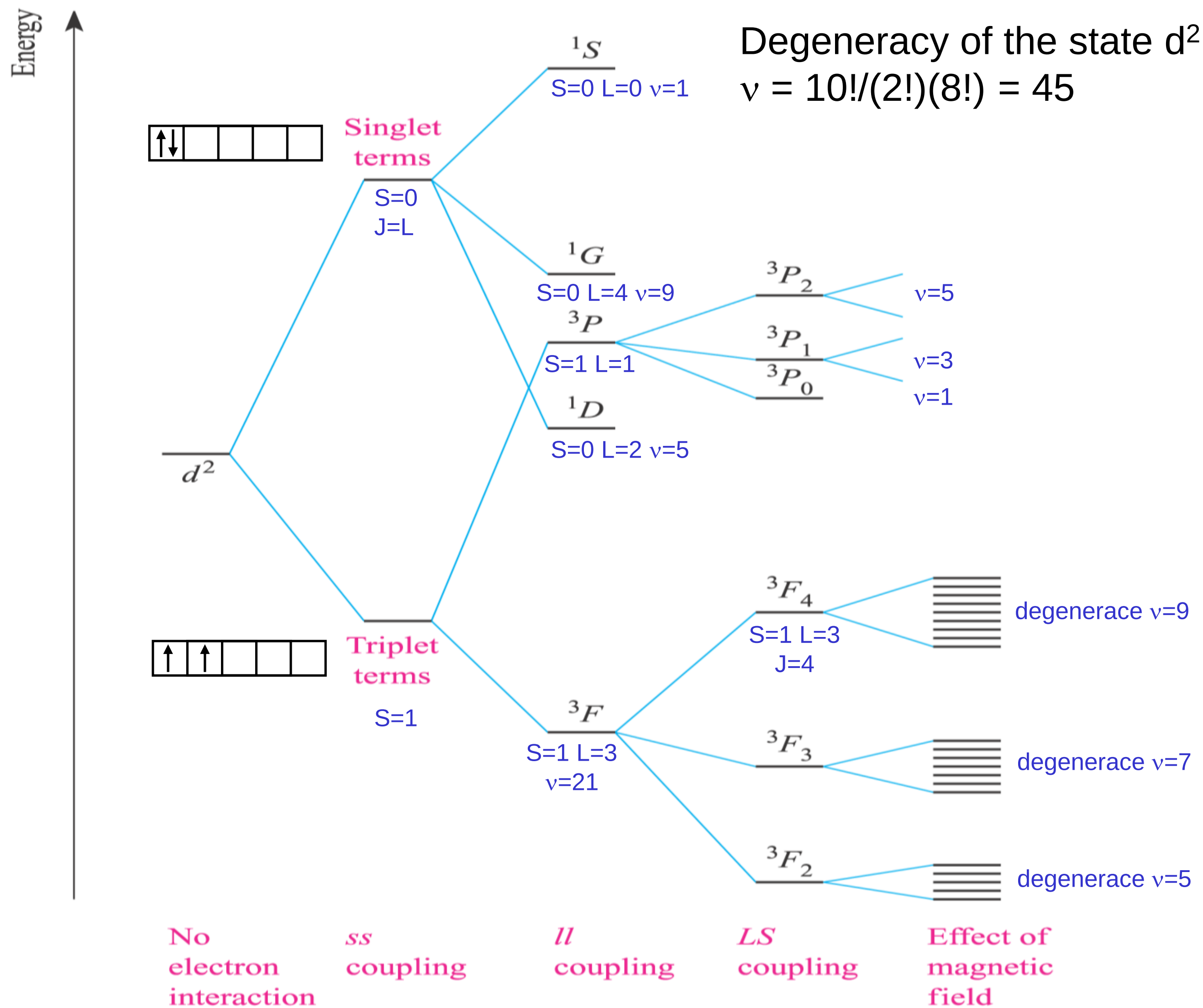
T_{CO} = 530 K

Crystal (ligand) field theory

- Orgel's diagrams
- Tanabe-Sugano diagrams

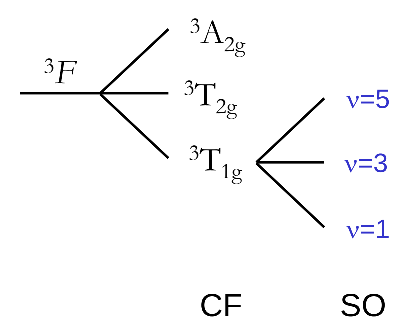
Splitting of states for electron configuration d^2 – spherical symmetry

Degeneracy of the state d^2:
$\nu = 10!/(2!)(8!) = 45$



1.Hund rule | 2.Hund rule | 3.Hund rule | Zeeman splitting

Octahedral crystal field > spin-orbit interaction



3*d*: $H_{CF} > H_{SO}$
4*f*: $H_{SO} > H_{CF}$

Spectroscopic symbols – ground state

occupation of orbitals starts from maximal m_l.

n : number of electrons

n_m : number of electrons in state m (m_l , m_s).

$$L = \sum_{m_l}^{-L \ldots L} m_l \times n_{m_l}$$

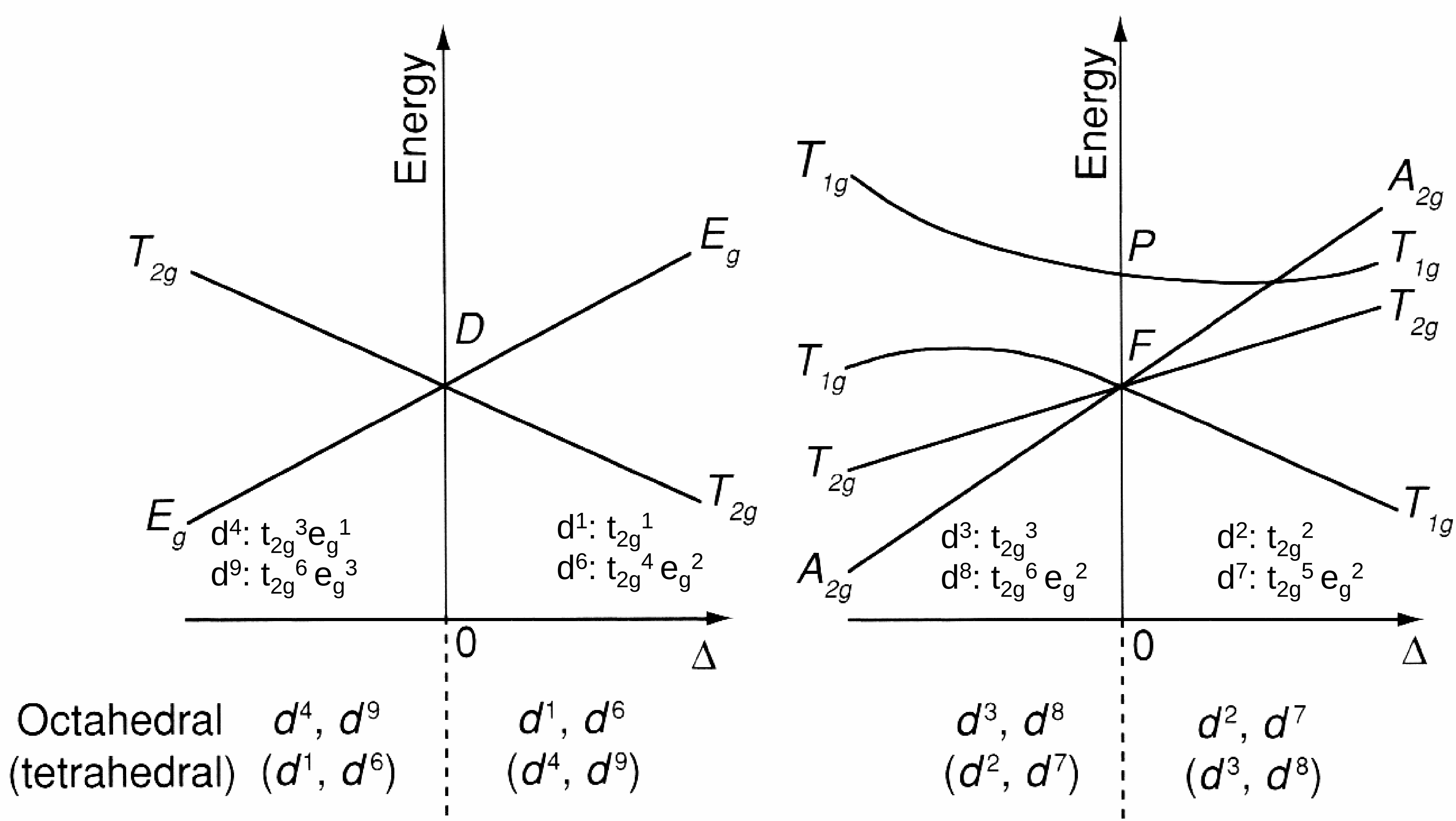
$$S = \sum_{m_s}^{-1/2, 1/2} m_s \times n_{m_s}$$

$^{2S+1}L_J$

m_l:	-2	-1	0	1	2	n	L	**L**	S	**2S+1**	J	**J**
						0	L=0	S	S=0	1	|L-S|	J=0
					↑	1	L=2	D	S=1/2	2	|L-S|	J=3/2
				↑	↑	2	L=3	F	S=1	3	|L-S|	J=2
			↑	↑	↑	3	L=3	F	S=3/2	4	|L-S|	J=3/2
		↑	↑	↑	↑	4	L=2	D	S=2	5	|L-S|	J=0
	↑	↑	↑	↑	↑	5	L=0	S	S=5/2	6	L+S	J=5/2
	↑	↑	↑	↑	↑↓	6	L=2	D	S=2	5	L+S	J=4
	↑	↑	↑	↑↓	↑↓	7	L=3	F	S=3/2	4	L+S	J=9/2
	↑	↑	↑↓	↑↓	↑↓	8	L=3	F	S=1	3	L+S	J=4
	↑	↑↓	↑↓	↑↓	↑↓	9	L=2	D	S=1/2	2	L+S	J=5/2
	↑↓	↑↓	↑↓	↑↓	↑↓	10	L=0	S	S=0	1	L+S	J=0

d^n	GS
d^1	$^2D_{3/2}$
d^2	$^3F_2$
d^3	$^4F_{3/2}$
d^4	$^5D_0$
d^5	$^6S_{5/2}$
d^6	$^5D_4$
d^7	$^4F_{9/2}$
d^8	$^3F_4$
d^9	$^2D_{5/2}$
d^0,d^{10}	$^1S_0$

Orgel's diagrams – d orbitals, octahedra, weak crystal field



- Weak crystal field, i.e. ground state is high spin
- Tetrahedral states does not have subscript $_g$ (tetrahedra does not have inversion symmetry)
- $d^{n+5} = t_{2g}^{x+3} e_g^{y+2}$

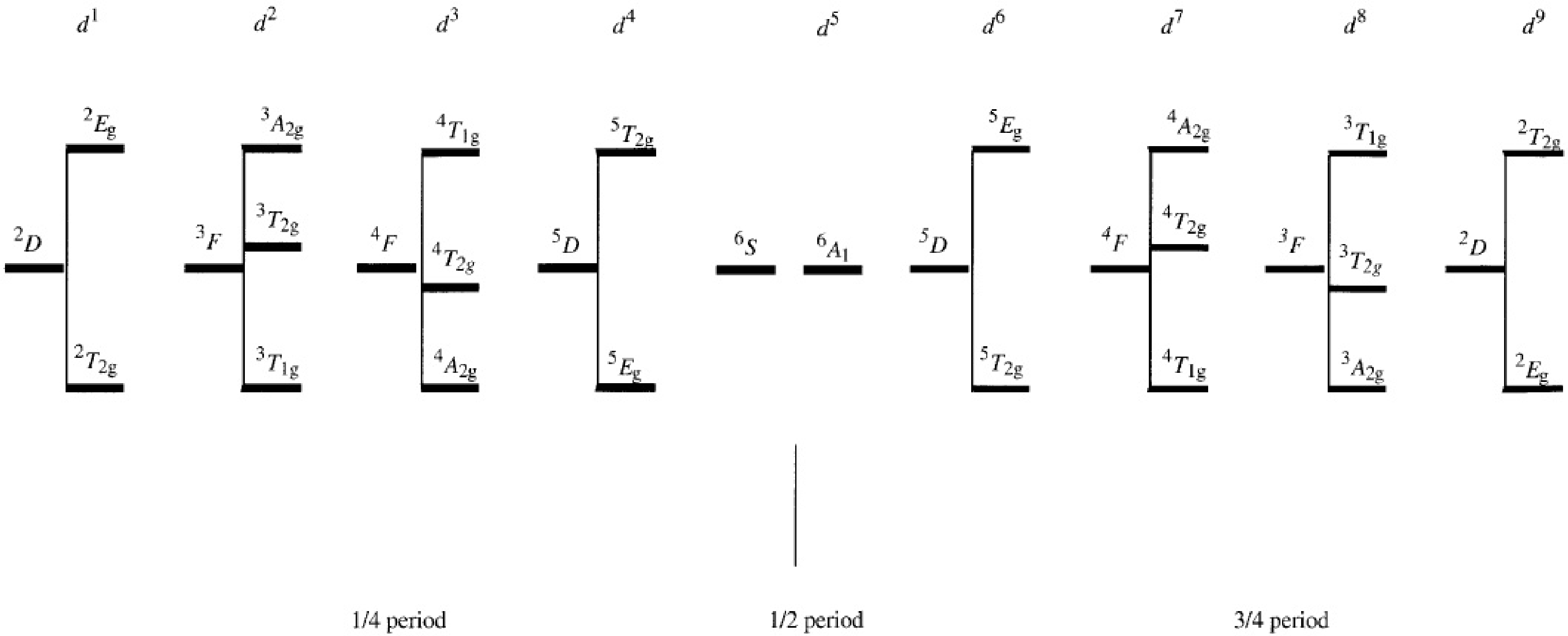
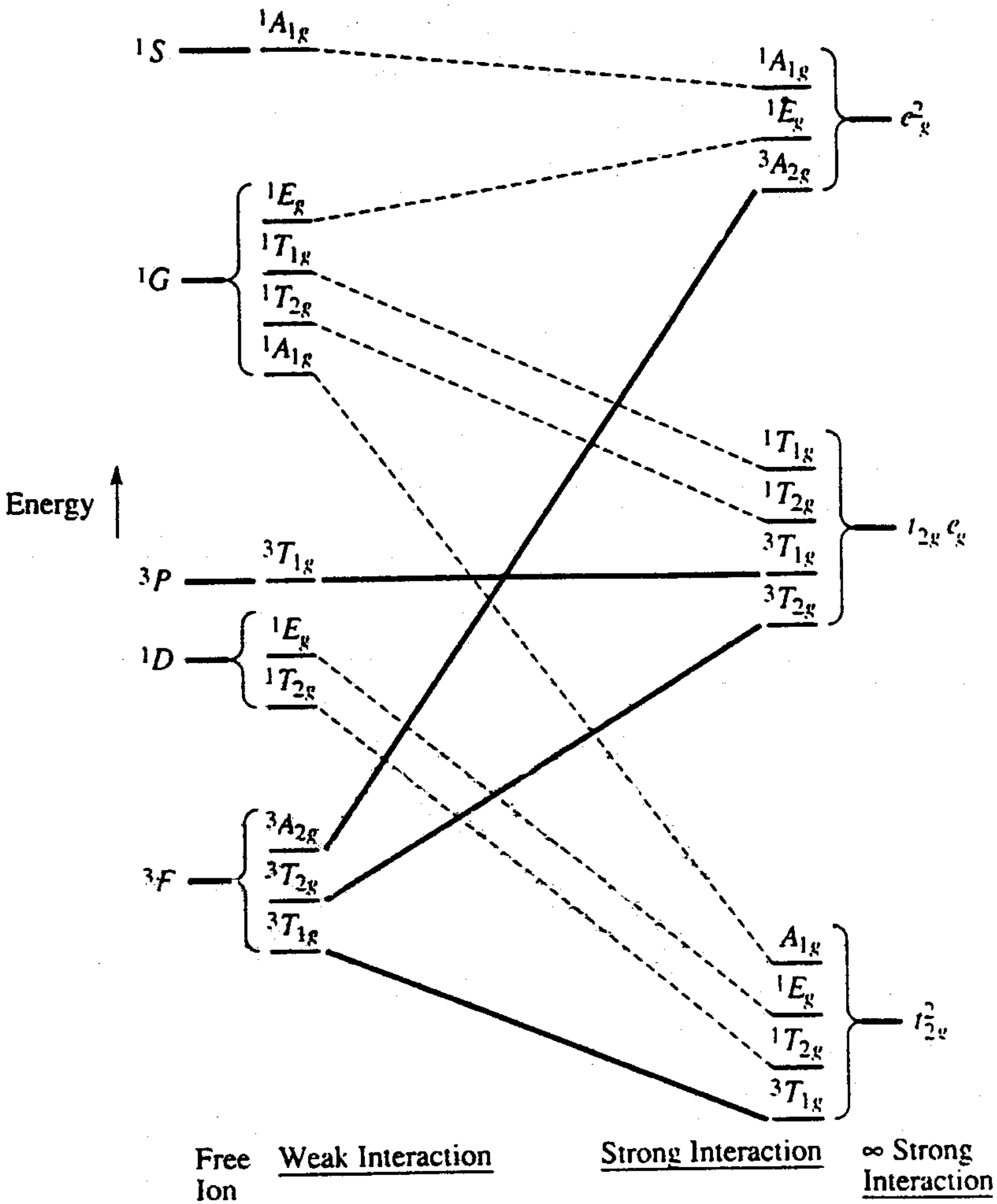
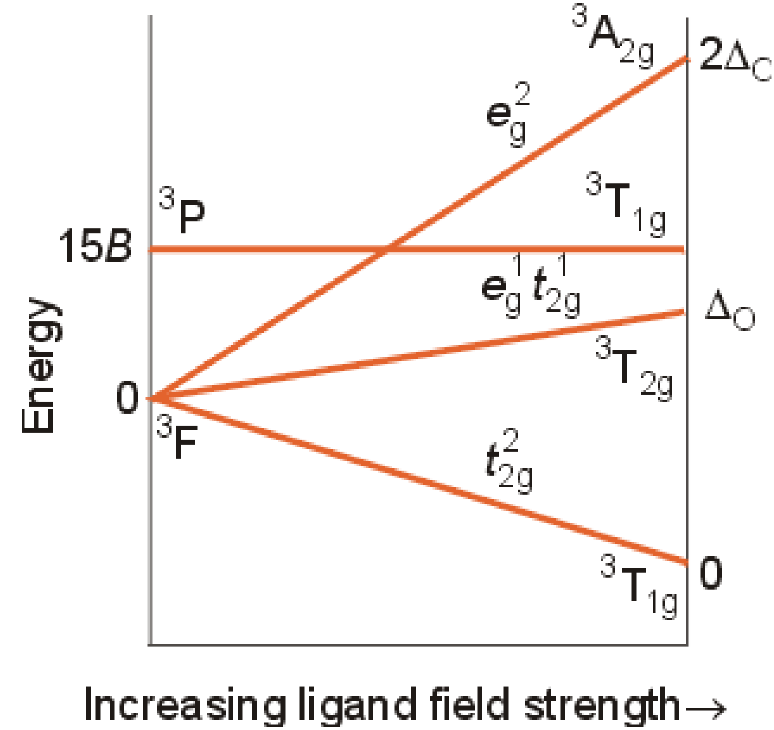


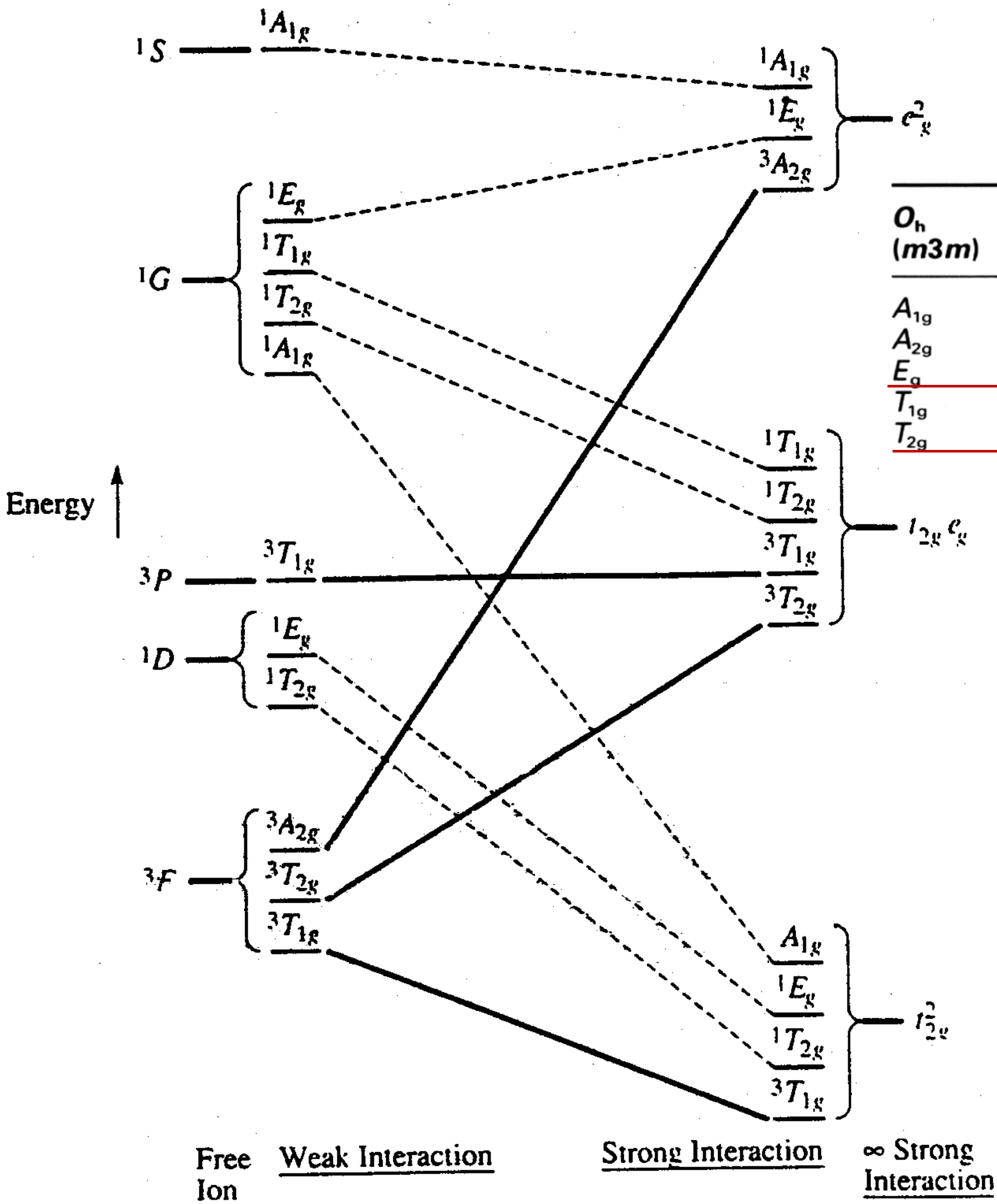
Figure 3-20. The symmetrical pattern of ground term splittings in octahedral symmetry.

Correlation diagram d² – octahedral symmetry





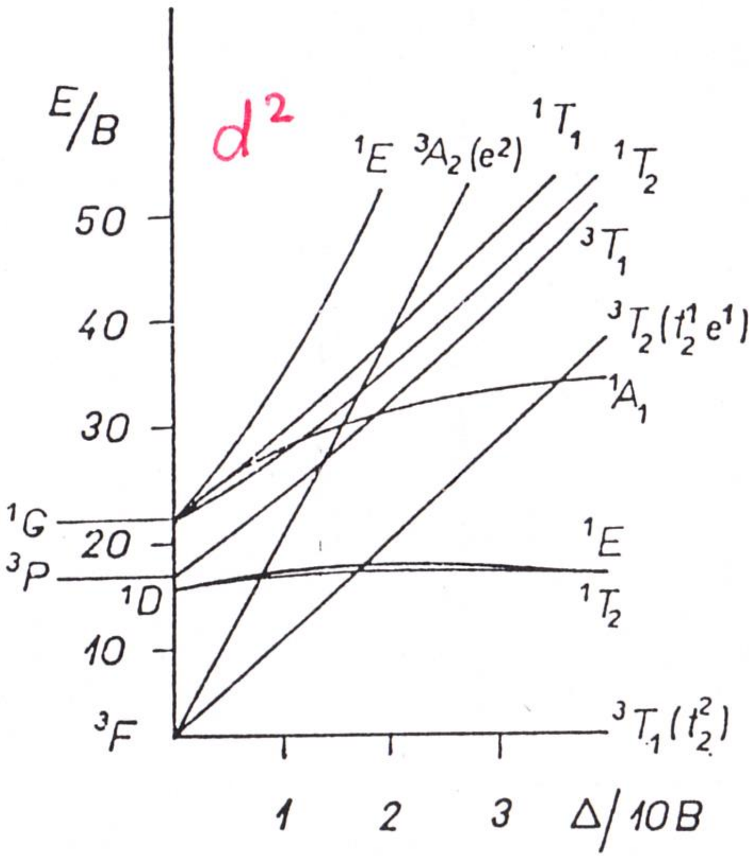
Correlation diagram d^2 – octahedral symmetry



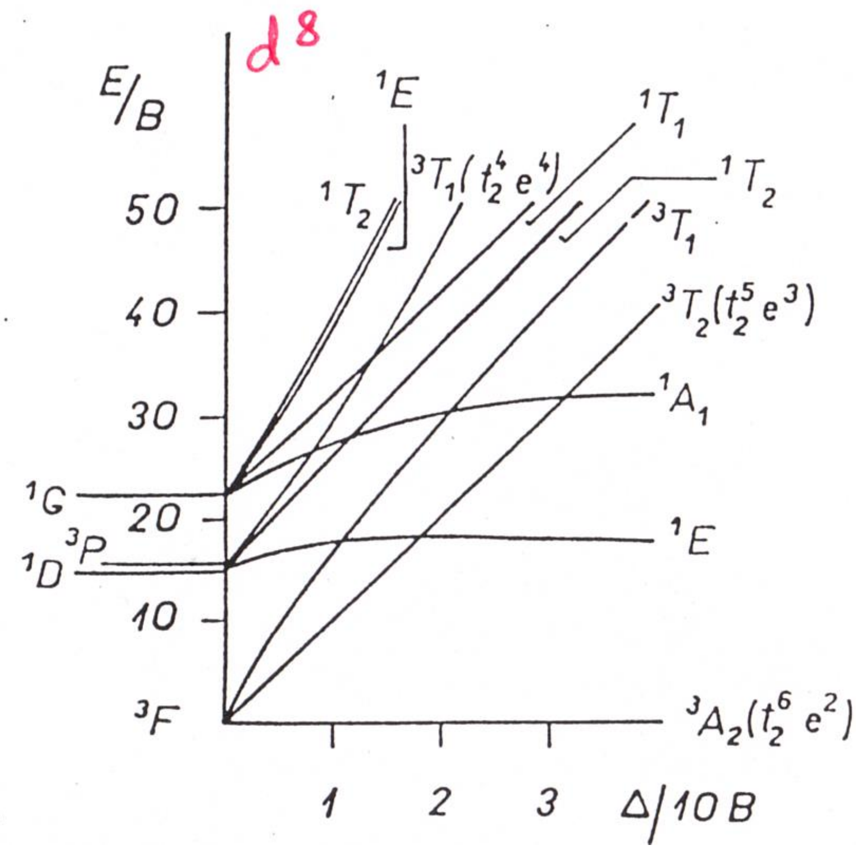
O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1
E_g	2	−1	0	0	2	2	0	−1	2	0
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1

O_h	A_{1g}	A_{2g}	E_g	T_{1g}	T_{2g}
A_{1g}	A_{1g}	A_{2g}	E_g	T_{1g}	T_{2g}
A_{2g}	A_{2g}	A_{1g}	E_g	T_{2g}	T_{1g}
E_g	E_g	E_g	$A_{1g}+A_{2g}+E_g$	$T_{1g}+T_{2g}$	$T_{1g}+T_{2g}$
T_{1g}	T_{1g}	T_{2g}	$T_{1g}+T_{2g}$	$A_{1g}+E_g+T_{1g}+T_{2g}$	$A_{2g}+E_g+T_{1g}+T_{2g}$
T_{2g}	T_{2g}	T_{1g}	$T_{1g}+T_{2g}$	$A_{2g}+E_g+T_{1g}+T_{2g}$	$A_{1g}+E_g+T_{1g}+T_{2g}$

Octahedral field

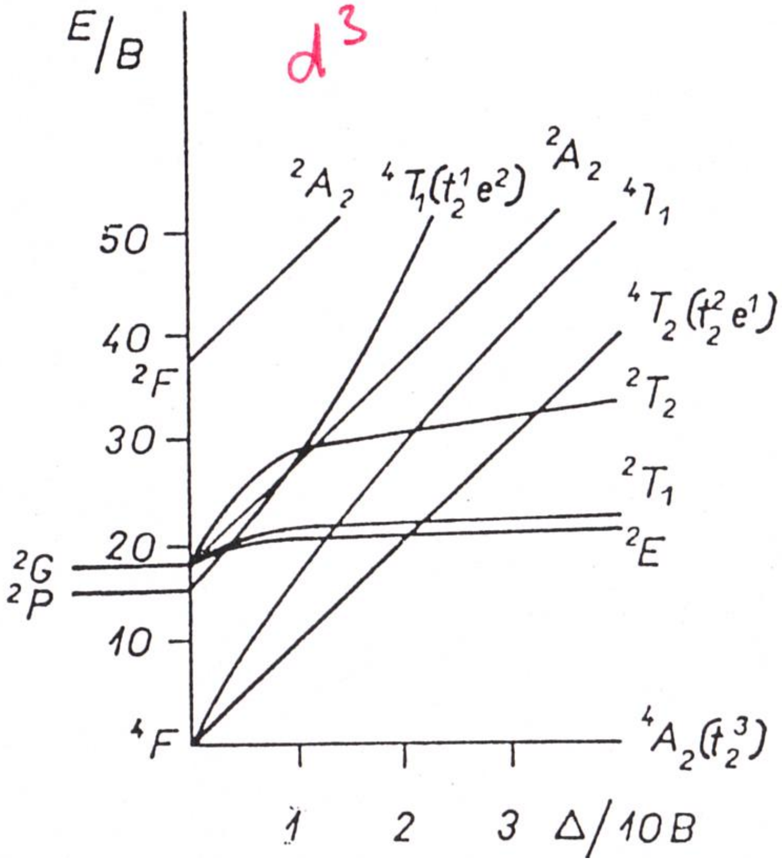


d^2

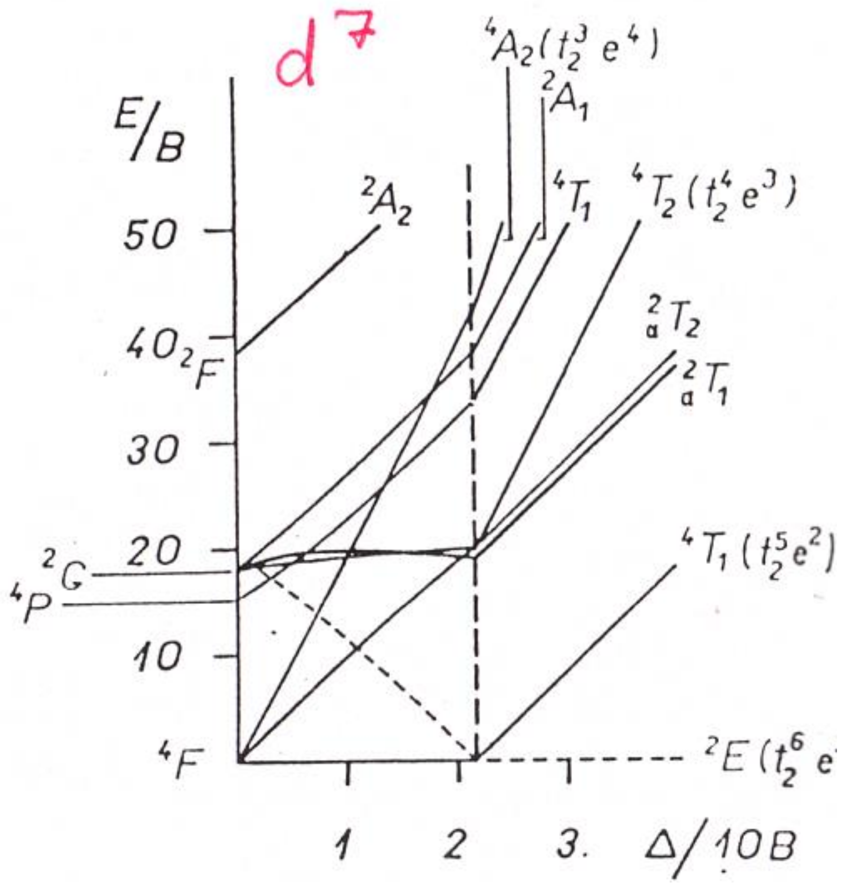


d^8

Octahedral field

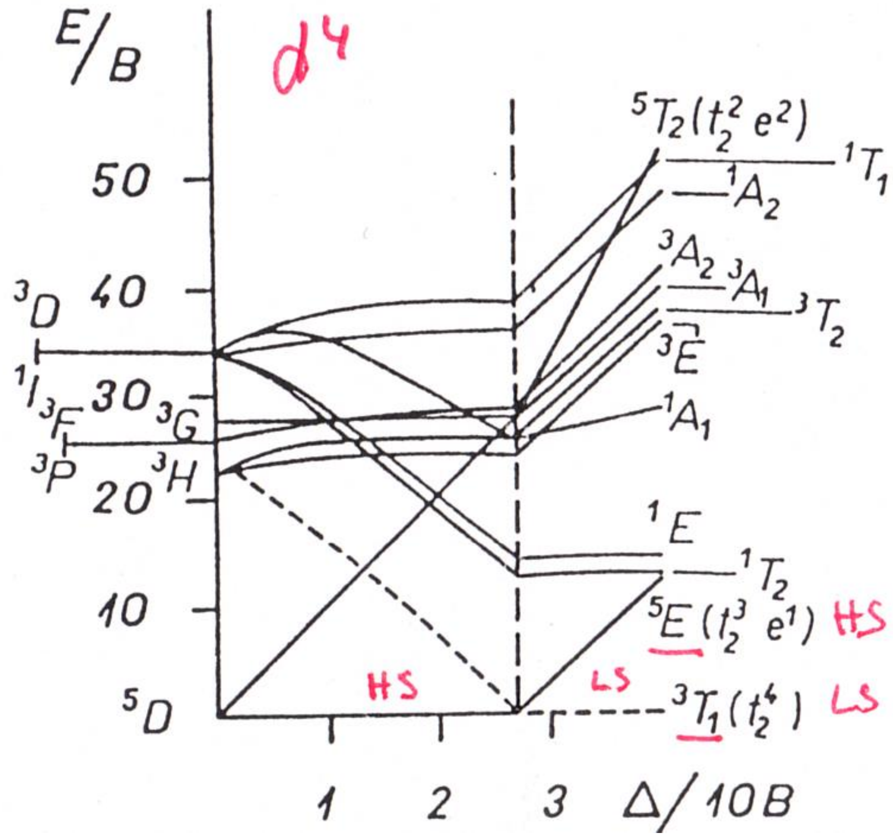


d^3

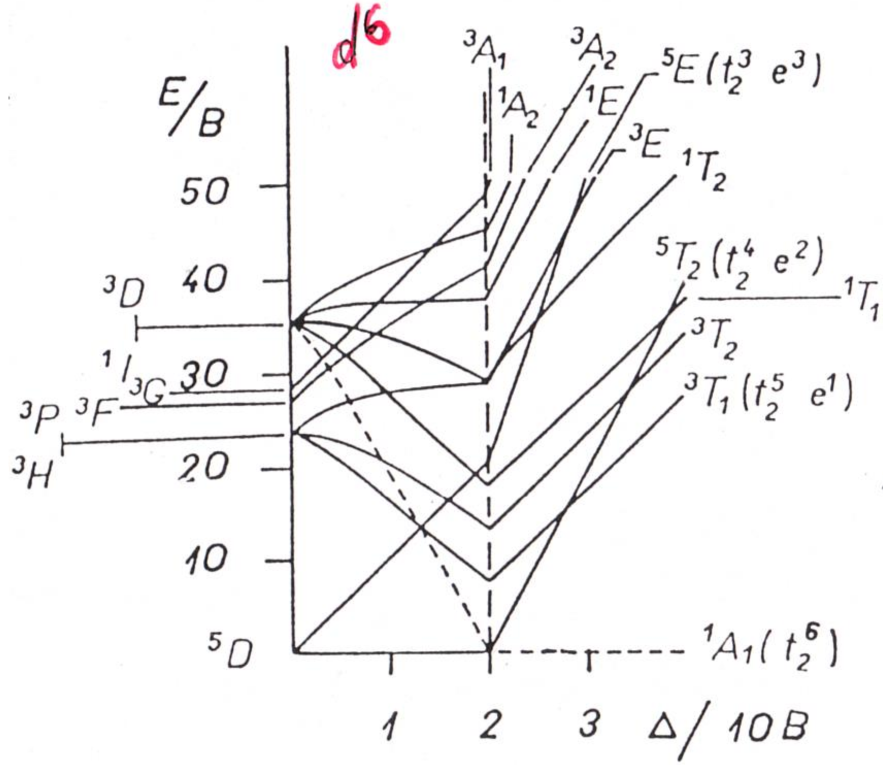


d^7

Octahedral field

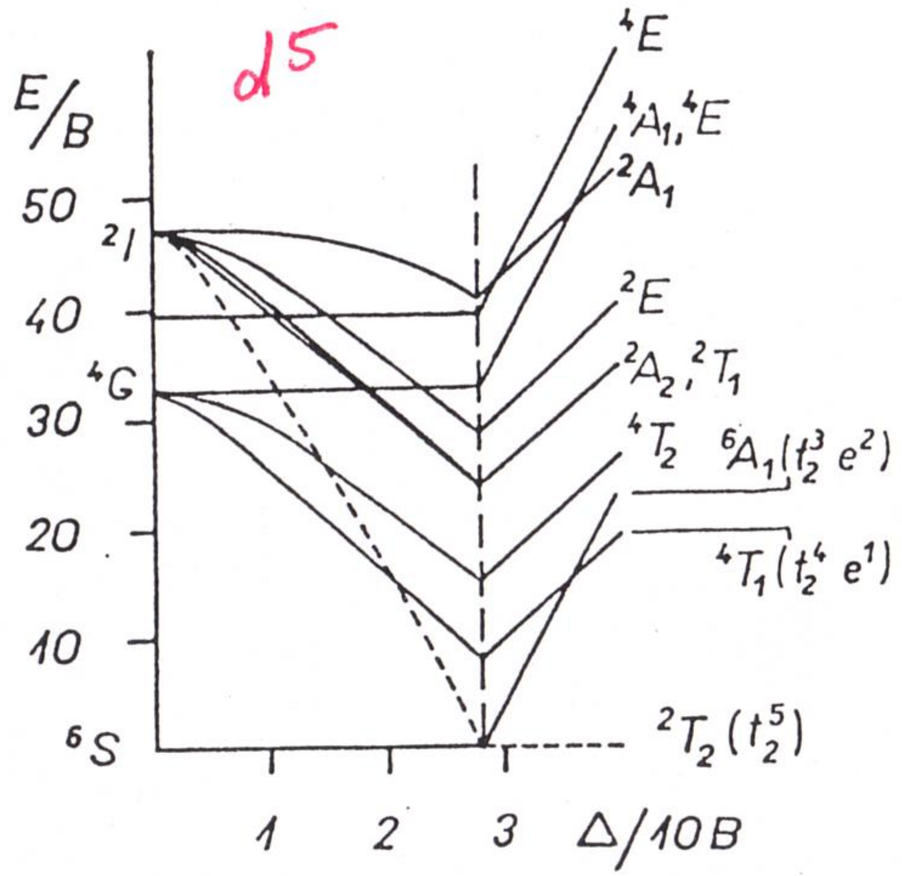


d4



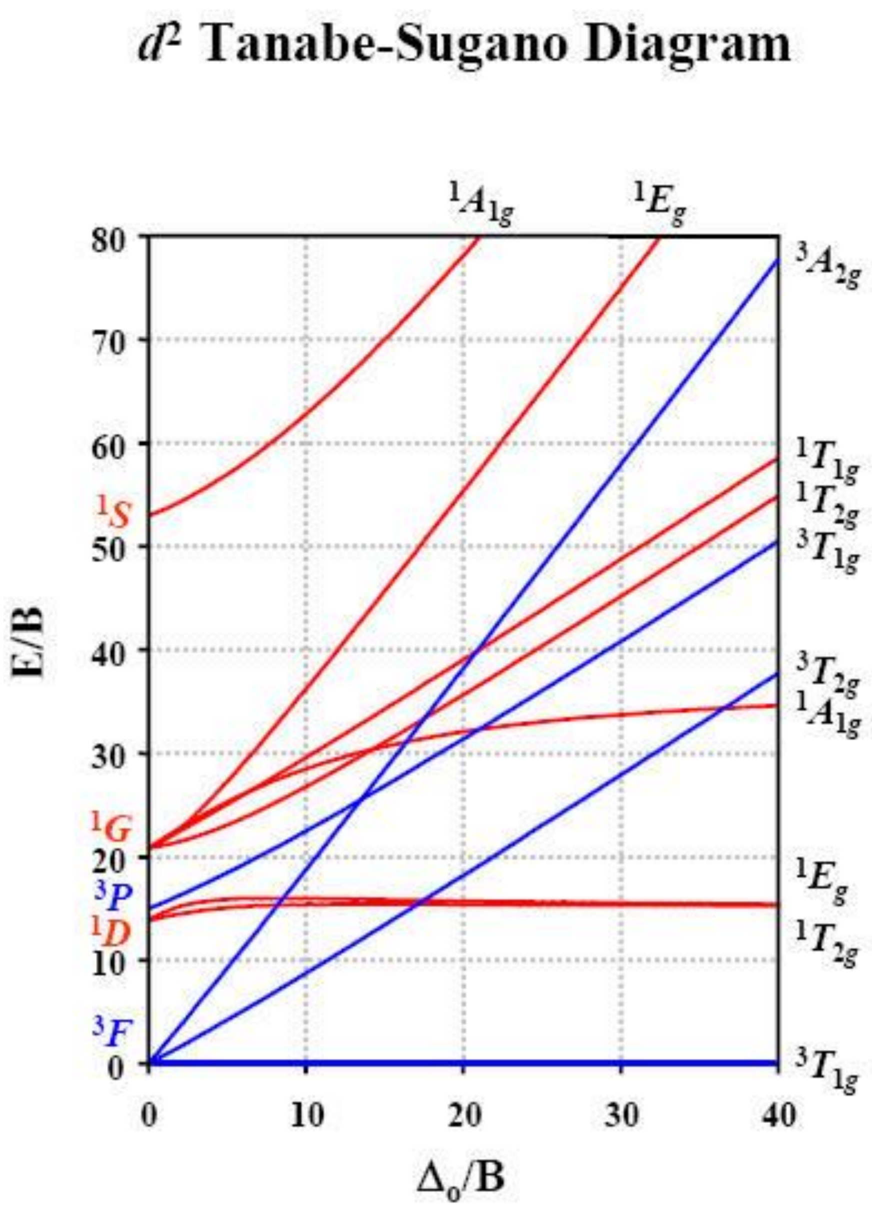
d6

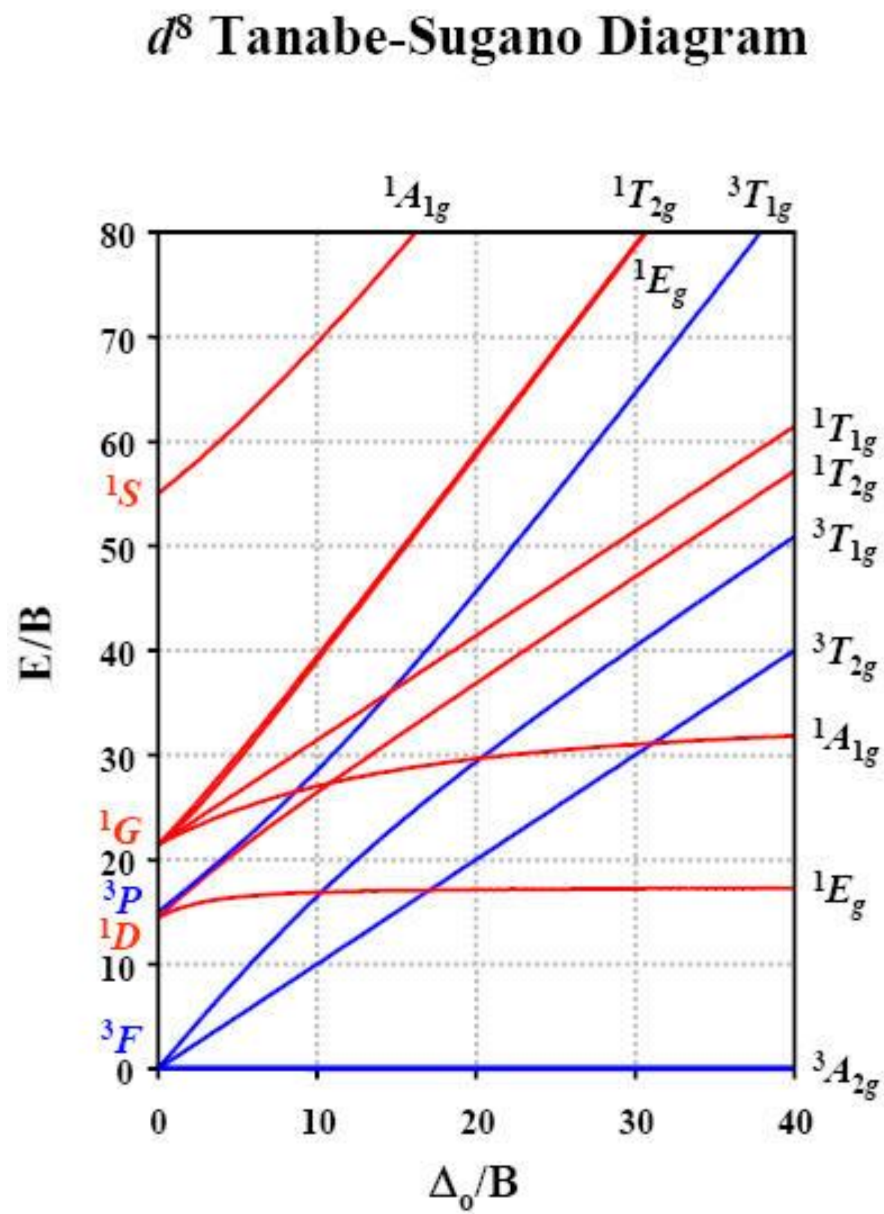
Octahedral field



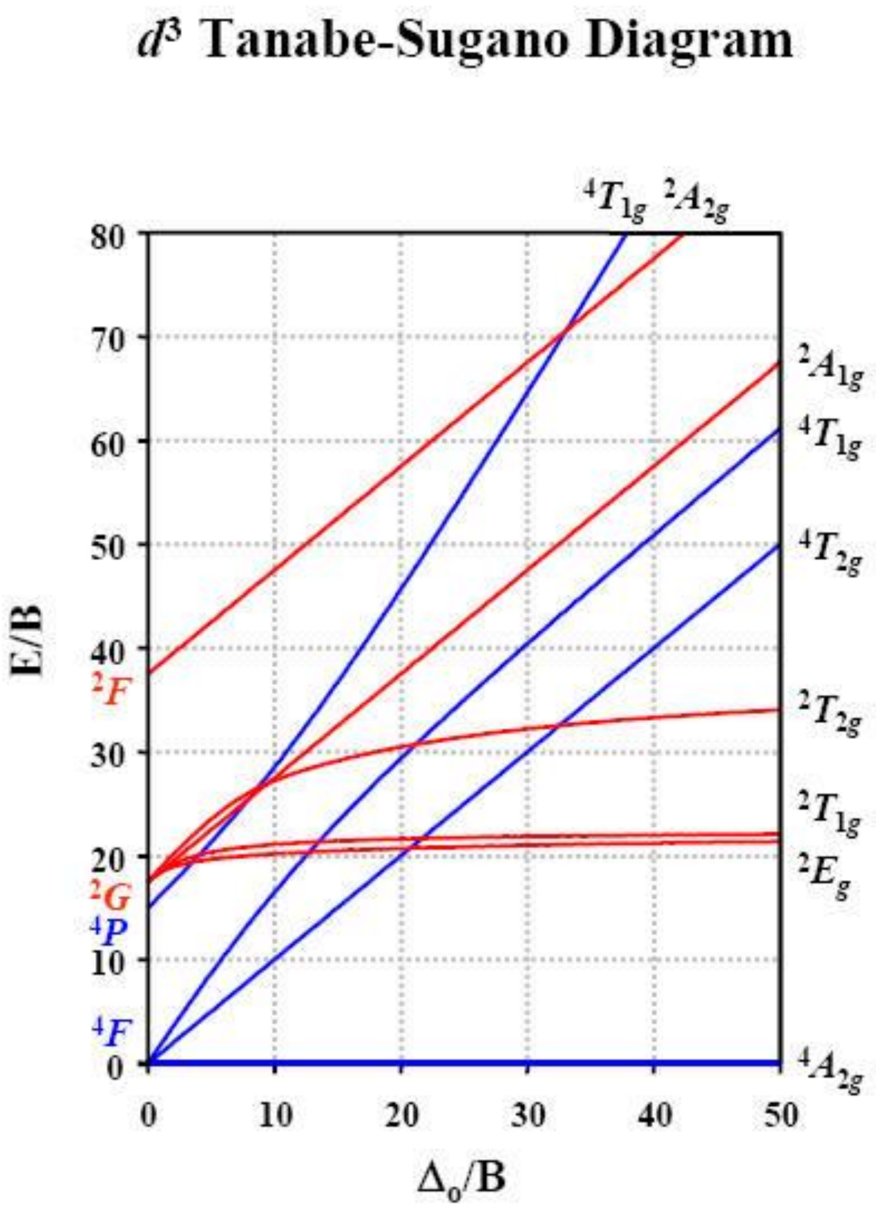
d⁵

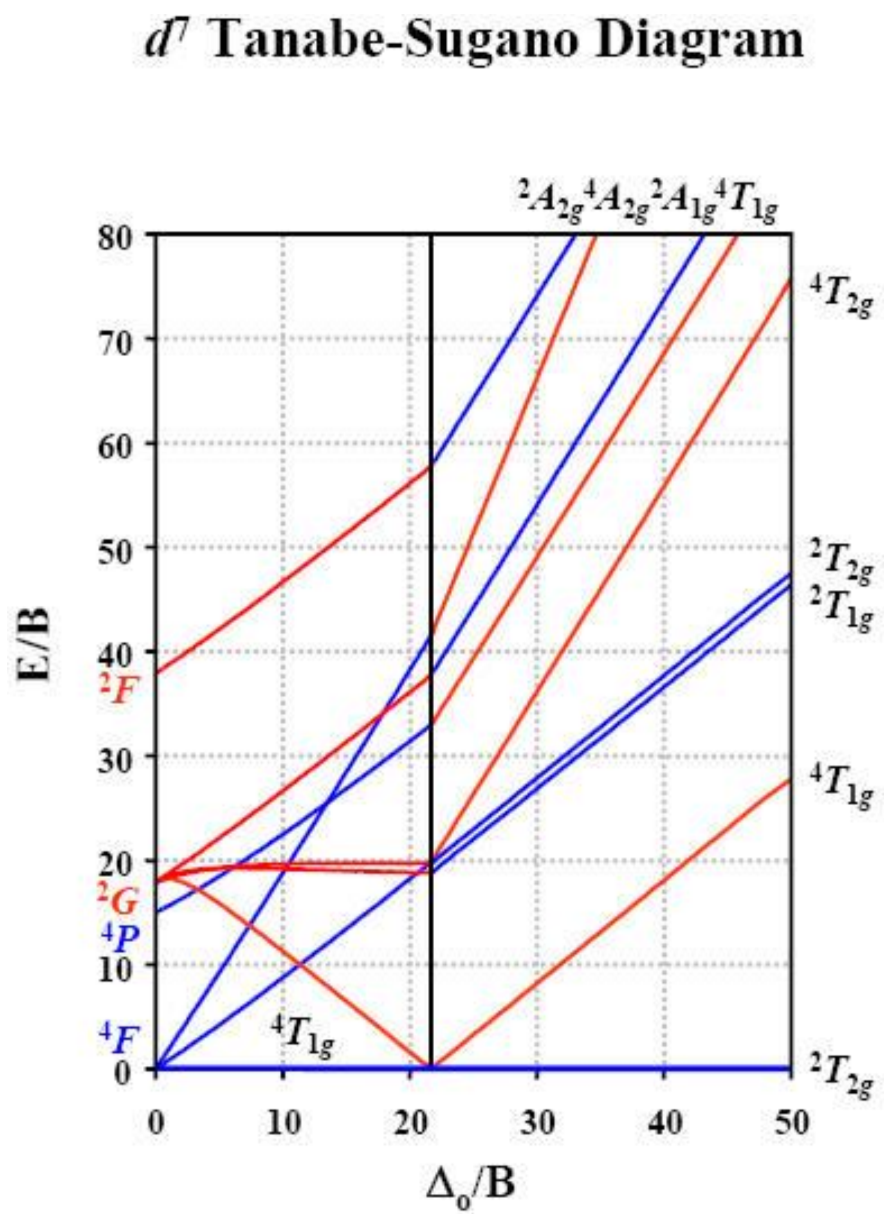
Tanabe-Sugano diagrams – octahedral field – d^2,d^8



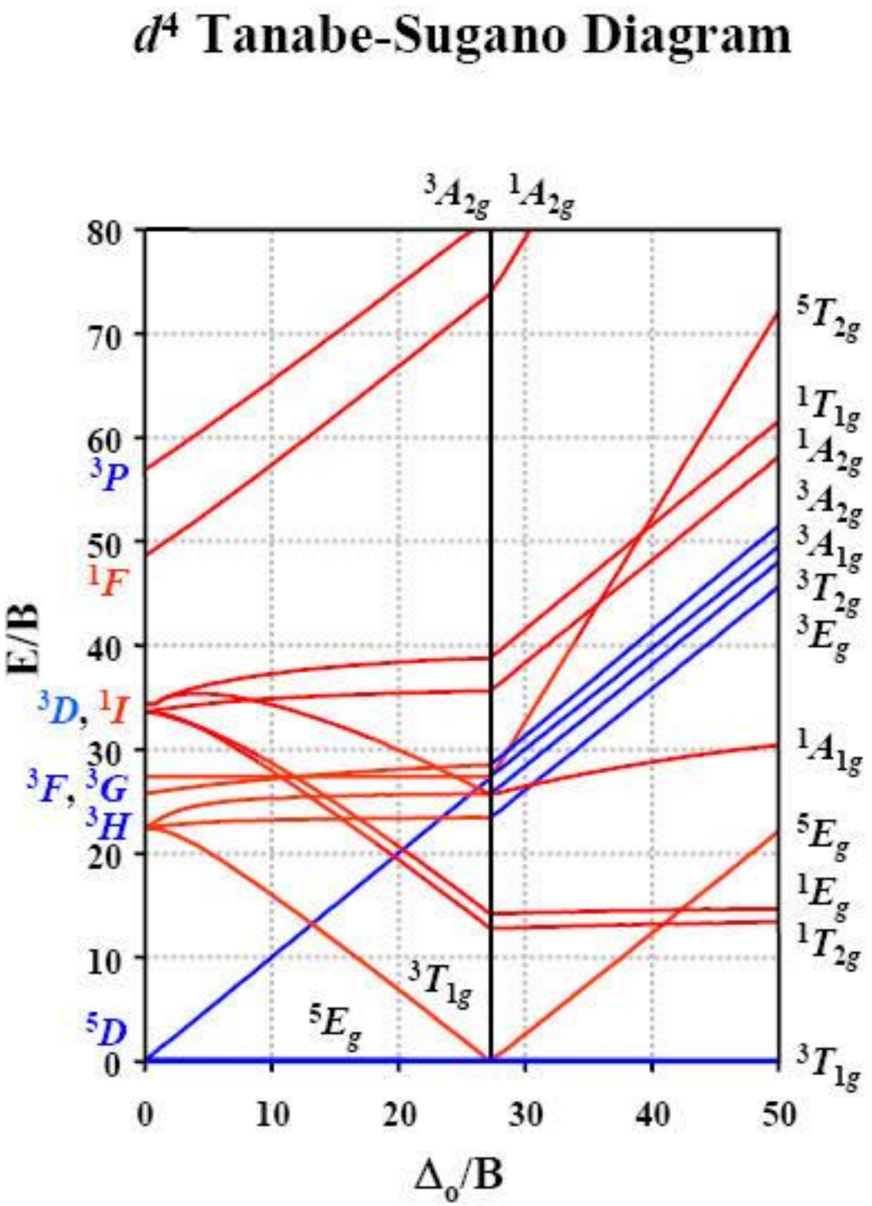


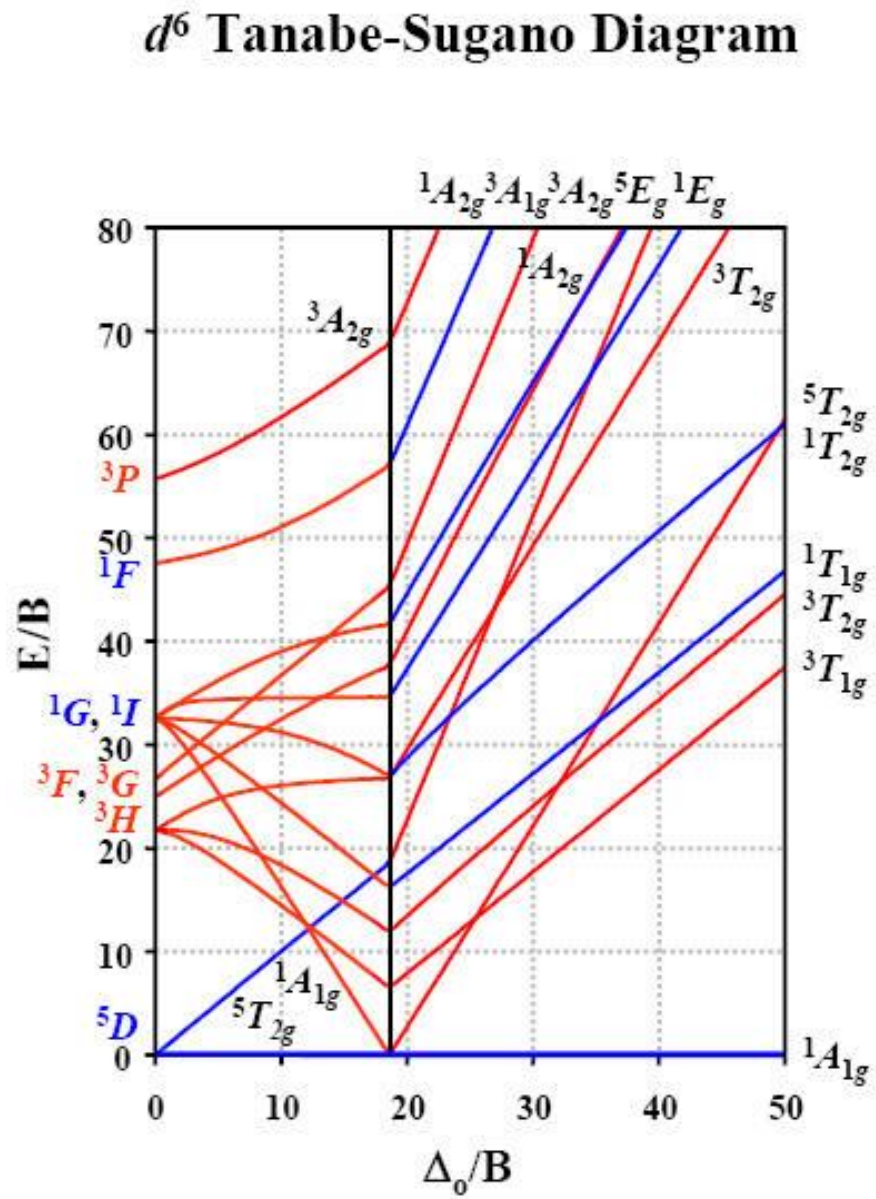
Tanabe-Sugano diagrams – octahedral field – d^3,d^7

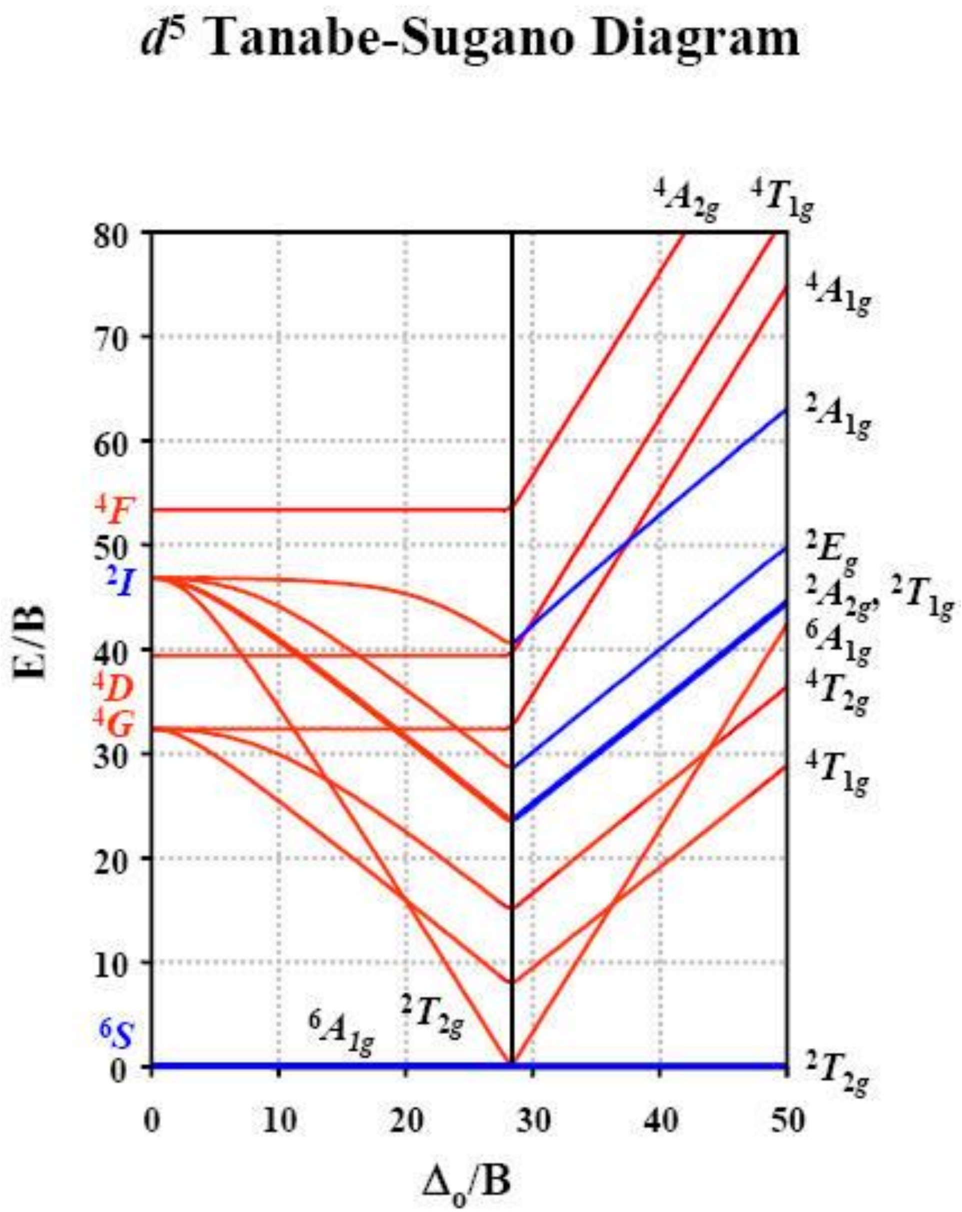




Tanabe-Sugano diagrams – octahedral field – d^4,d^6






d^5 Tanabe-Sugano Diagram
E/B
Δ_o/B
0
10
20
30
40
50
60
70
80
^4F
^2I
^4D
^4G
^6S
$^6A_{1g}$
$^2T_{2g}$
$^4A_{2g}$
$^4T_{1g}$
$^4A_{1g}$
$^2A_{1g}$
^2E_g
$^2A_{2g}$, $^2T_{1g}$
$^6A_{1g}$
$^4T_{2g}$
$^4T_{1g}$
$^2T_{2g}$

Sr_2YIrO_6 – Ir^{5+}, t_{2g}^4, $^3T_{1g}$.

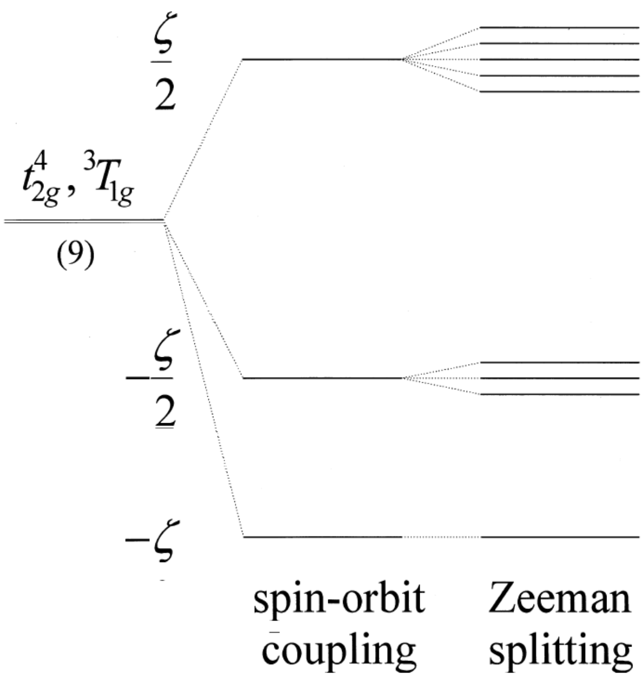


Fig. 5. Energy level diagram for t_{2g}^4 configurations.

Sr_2IrO_4 – Ir^{4+}, t_{2g}^5 , $^2T_{2g}$.

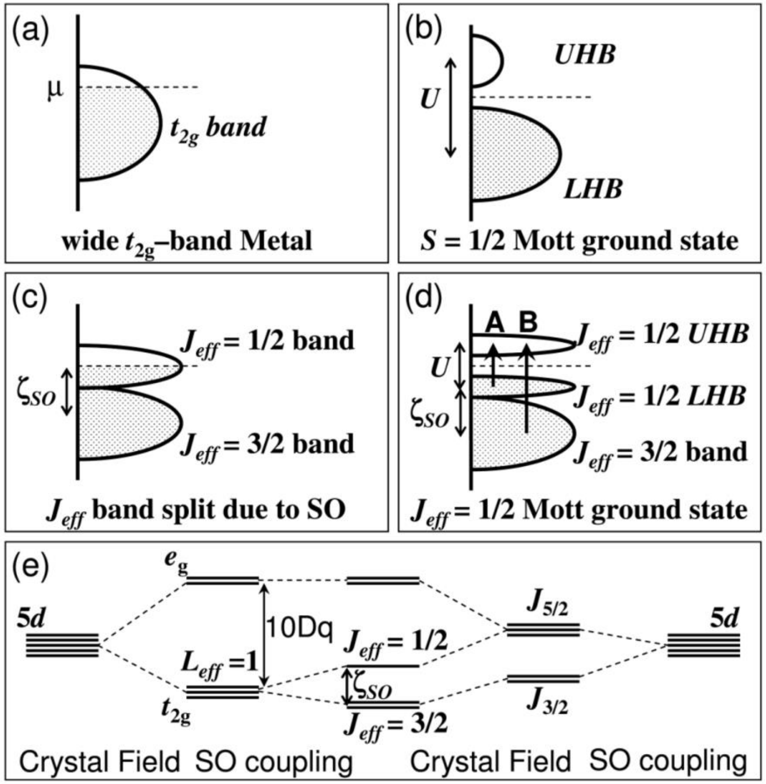
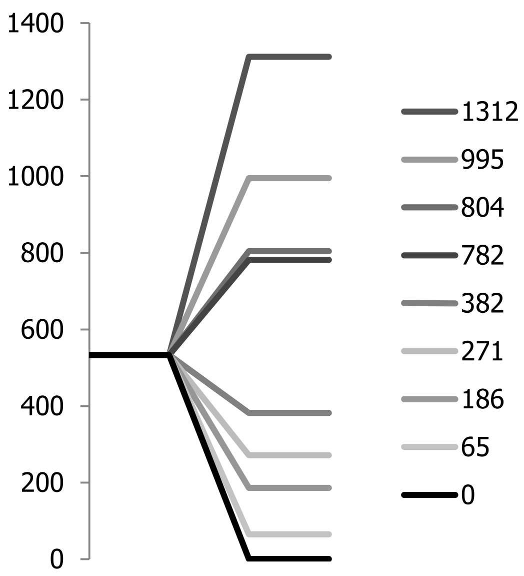


FIG. 1. Schematic energy diagrams for the $5d^5$ (t_{2g}^5) configuration (a) without SO and U, (b) with an unrealistically large U but no SO, (c) with SO but no U, and (d) with SO and U. Possible optical transitions A and B are indicated by arrows. (e) $5d$ level splittings by the crystal field and SO coupling.

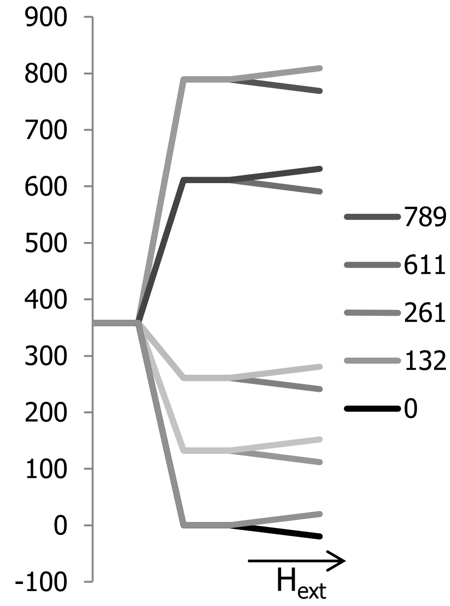
J. Alloys and Comp. 287, 130 (1999).

Phys.Rev.Lett 101, 076402 (2008).

Splitting of the levels of Ln^{3+} in low symmetry crystal field



Pr^{3+} in orthorhombic symmetry



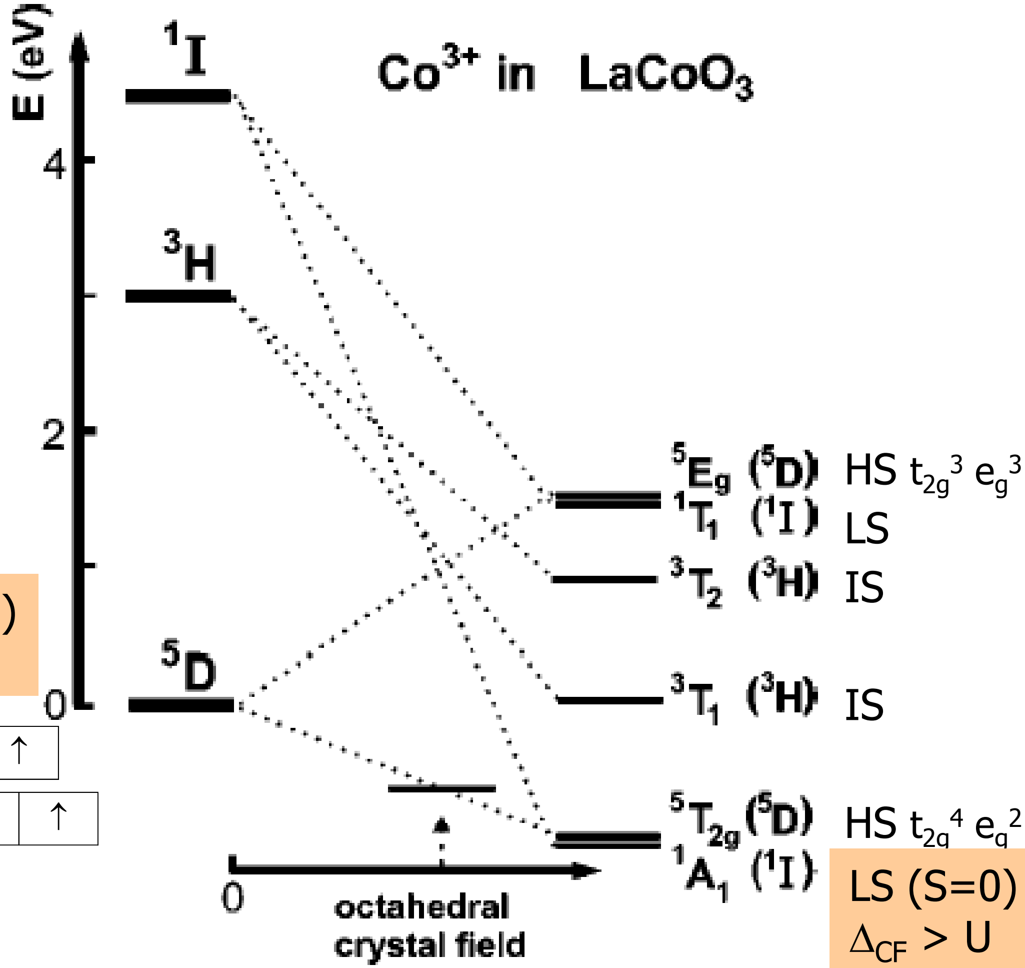
Nd^{3+} in orthorhombic symmetry

Z	val.e	f (3+)	Kramers	3+	4+	d(sing/dubl)		
57	3	0		La	Ce	singlet	1 sing	1S0
58	4	1	Kramers	**Ce**	Pr	dublet	3 dubl	2F5/2
59	5	2	non-Kramers	Pr	Nd	singlet	9 sing	3H4
60	6	3	Kramers	**Nd**	Pm	dublet	5 dubl	4I9/2
61	7	4	non-Kramers	Pm	Sm	singlet	9 sing	5I4
62	8	5	Kramers	**Sm**	Eu	dublet	3 dubl	6H5/2
63	9	6	non-Kramers	Eu	Gd	singlet	1 sing	7F0
64	10	7	Kramers	**Gd**	Tb	dublet	4 dubl	8S7/2
65	11	8	non-Kramers	Tb	Dy	singlet	13 sing	7F6
66	12	9	Kramers	**Dy**	Ho	dublet	8 dubl	6H15/2
67	13	10	non-Kramers	Ho	Er	singlet	17 sing	5I8
68	14	11	Kramers	**Er**	Tm	dublet	8 dubl	4I15/2
69	15	12	non-Kramers	Tm	Yb	singlet	13 sing	3H6
70	16	13	Kramers	**Yb**	Lu	dublet	4 dubl	2F7/2
71	17	14		Lu		singlet	1 sing	1S0

Tanabe-Sugano diagram for d^6 Co^{3+}

LS (S=0)

IS (S=1)



HS (S=2)
$\Delta_{CF} < U$

e_g: ↑ ↑
t_{2g}: ↑↓ ↑ ↑

LS (S=0)
$\Delta_{CF} > U$

e_g: (empty)
t_{2g}: ↑↓ ↑↓ ↑↓

IS (S=1), stabilized due to overlap of Co(d) and O(p) orbitals

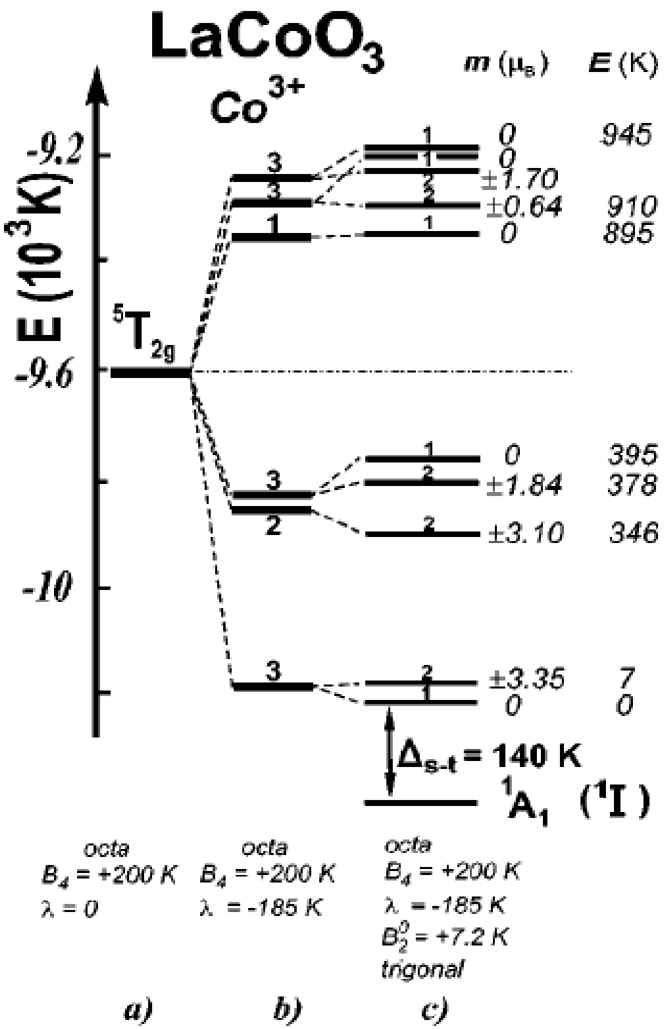
e_g: ↑
t_{2g}: ↑↓ ↑↓ ↑

Co^{3+} ion may exist in 3 spin states in oxides:

1. Low (LS, S=0, $t_{2g}^6 e_g^0$)
2. Intermediate (IS, S=1, $t_{2g}^5 e_g^1$)
3. High (HS, S=2, $t_{2g}^4 e_g^2$)

Because of the different ratios between parameters:

- Crystal field Δ_{CF},
- Coulombic repulsion U,
- Overlap of Co(d) and O(p) orbital.



$^1A_1$: Ground state low spin t_{2g}^6
degeneracy $\nu=1$

$^5T_{2g}$: 1. excited state $t_{2g}^4\, e_g^2$
degeneracy $\nu=5\times3=15$

Splitting due to:

a) octahedral crystal field H_{CF} (B_4) = 200K

b) spin-orbit interaction H_{SO} (λ) = 185K

c) trigonal distortion of octahedra H_{trig} (B_2) = 7.2K

$H_{CF} > H_{SO} > H_{trig}$

Racah parameters A, B, C (>0)

Energy of the state E(L,S) is generally expressed

$E(L,S) = aA + bB + cC$

e.g. d^2 ($\Leftrightarrow d^8$):

$^3F = A - 8B$

$^3P = A + 7B$

$^1G = A + 4B + 2C$

$^1D = A - 3B + 2C$

$^1S = A + 14B + 7C$

$\beta = B / B_o < 1$ Nephelauxetic ratio

B_o: free ion, B: in polyhedra