Atomic Magnetism

Magnetism of electrons, atoms and ions in solids

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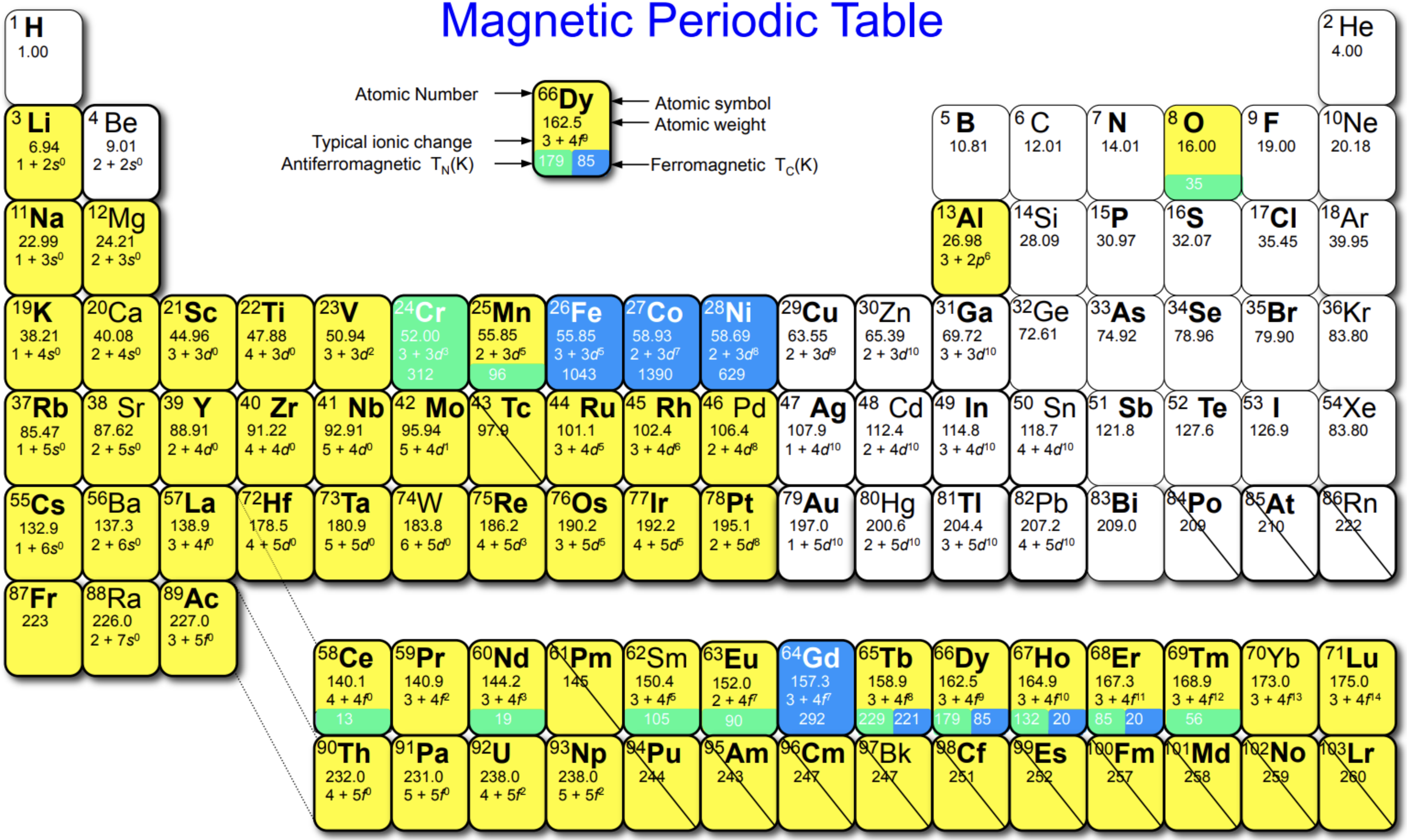
ATOMIC ORIGIN OF MAGNETISM IN MATERIALS

- Single electrons: Spin, Angular Momentum, orbits and spin-orbit coupling
- Many electrons – the magical power of Pauli
- Non-magnetic magnetism : dia-magnetism and Van Vleck paramagnetism
- Hund’s rules and effective moment : a 4f lanthanide success story
- Crystal field effect : the case of 3d transition metals
- Jahn-Teller effect

Slides by Ivica Zivkovic and previous ESM lectures

Magnetic Periodic Table



1 **H** 1.00																	2 He 4.00
3 **Li** 6.94 $1 + 2s^0$	4 Be 9.01 $2 + 2s^0$											5 **B** 10.81	6 C 12.01	7 **N** 14.01	8 **O** 16.00 35	9 **F** 19.00	10 Ne 20.18
11 **Na** 22.99 $1 + 3s^0$	12 Mg 24.21 $2 + 3s^0$											13 **Al** 26.98 $3 + 2p^6$	14 Si 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 Ar 39.95
19 **K** 38.21 $1 + 4s^0$	20 Ca 40.08 $2 + 4s^0$	21 **Sc** 44.96 $3 + 3d^0$	22 **Ti** 47.88 $4 + 3d^0$	23 **V** 50.94 $3 + 3d^2$	24 **Cr** 52.00 $3 + 3d^3$ 312	25 **Mn** 55.85 $2 + 3d^5$ 96	26 **Fe** 55.85 $3 + 3d^5$ 1043	27 **Co** 58.93 $2 + 3d^7$ 1390	28 **Ni** 58.69 $2 + 3d^8$ 629	29 **Cu** 63.55 $2 + 3d^9$	30 Zn 65.39 $2 + 3d^{10}$	31 **Ga** 69.72 $3 + 3d^{10}$	32 Ge 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 Kr 83.80
37 **Rb** 85.47 $1 + 5s^0$	38 Sr 87.62 $2 + 5s^0$	39 **Y** 88.91 $2 + 4d^0$	40 **Zr** 91.22 $4 + 4d^0$	41 **Nb** 92.91 $5 + 4d^0$	42 **Mo** 95.94 $5 + 4d^1$	43 **Tc** 97.9	44 **Ru** 101.1 $3 + 4d^5$	45 **Rh** 102.4 $3 + 4d^6$	46 Pd 106.4 $2 + 4d^8$	47 **Ag** 107.9 $1 + 4d^{10}$	48 Cd 112.4 $2 + 4d^{10}$	49 **In** 114.8 $3 + 4d^{10}$	50 Sn 118.7 $4 + 4d^{10}$	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 Xe 83.80
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Most atoms are magnetic

⬜ Diamagnet
🟨 Paramagnet
BOLD Magnetic atom

🟦 Ferromagnet T_C > 290K
🟩 Antiferromagnet with T_N > 290K
⬜ Antiferromagnet/Ferromagnet with T_N/T_C < 290 K

Few materials are magnetic

SPIN MAGNETIC MOMENT

- Intrinsic property of electrons (and other subatomic particles).
- Demonstrated experimentally by Stern & Gerlach (1922),
- Analogous (but inaccurate!) to a charged particle spinning around its axis.
- Electrons, and fermions, can only have two spin states: $\sigma = \pm 1/2$

Analogously to the orbital magnetic momentum:

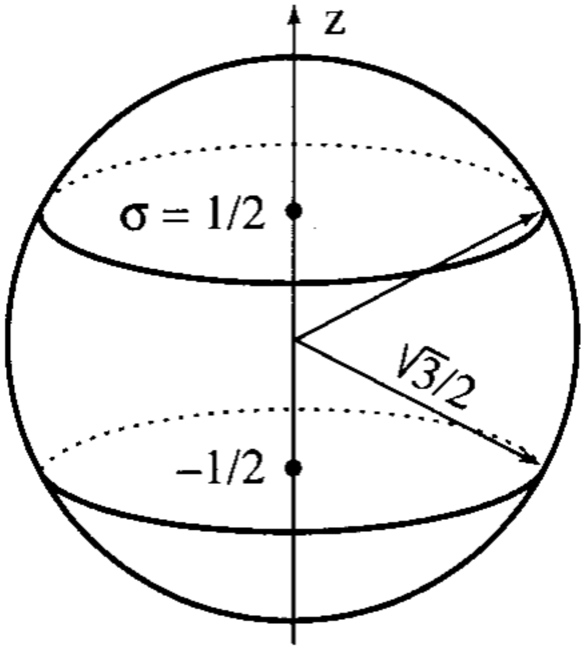
$$\boldsymbol{L}_{\boldsymbol{s}} = \hbar s$$

$$\langle s^2 \rangle = s(s+1)$$

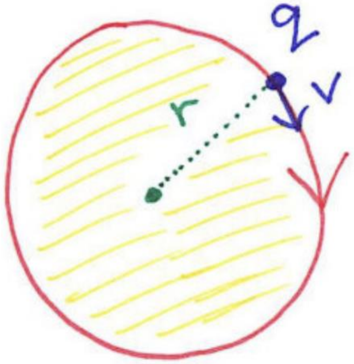
$$\langle s_z \rangle = \pm 1/2$$

$$\boldsymbol{m}_{\boldsymbol{s}} = -2\mu_B \boldsymbol{s}$$

Then, $\langle (m_s)_z \rangle = \pm 1 \mu_B$



ORBITAL ANGULAR MOMENTUM



$$I = \frac{q}{2\pi r / v}$$

Magnetic moment $\mu = I\pi r^2 = \boxed{\frac{q}{2m}} \overbrace{L}^{mvr}$

GYROMAGNETIC RATIO γ

LINEAR MOMENTUM

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x}$$

e^{ikx} eigenfunction

$\hbar k$ eigenvalue

ANGULAR MOMENTUM

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$e^{im\phi}$ eigenfunction

$m\hbar$ eigenvalue

INTEGER $\nearrow m$

$\because \; e^{im(\phi+2\pi)} = e^{im\phi}$

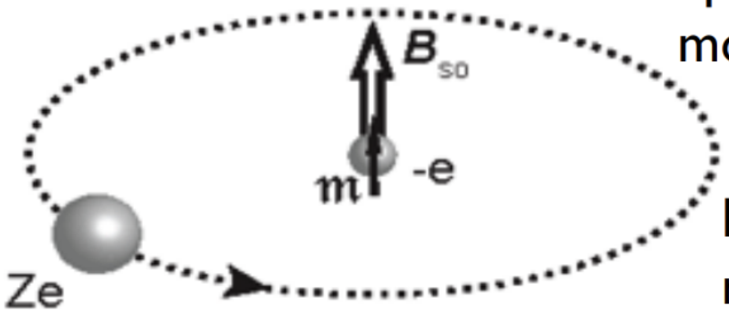
$$\hat{\underline{L}} = \hat{\underline{r}} \times \hat{\underline{p}} = -i\hbar\, \underline{r} \times \nabla$$

$$\hat{L}_z = i\hbar \left[y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y} \right] = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{L}_z |\ell, m\rangle = m\hbar |\ell, m\rangle \qquad \hat{L}^2 |\ell, m\rangle = \ell(\ell+1)\hbar^2 |\ell, m\rangle$$

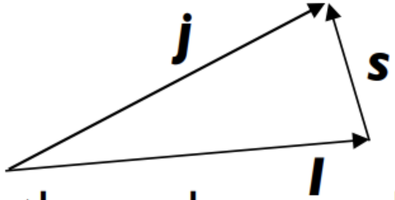
$$\langle \theta, \phi | \ell, m \rangle = \underset{\text{SPHERICAL HARMONICS}}{Y_\ell^m(\theta, \phi)} \propto \underset{\text{ASSOCIATED LEGENDRE POLYNOMIAL}}{P_\ell^m(\cos\theta)}\, e^{im\phi}$$

Spin-Orbit Coupling



Spin and angular momentum coupled to create total angular momentum ***j***. $\boldsymbol{J} = \boldsymbol{l} + \boldsymbol{s}$

$$\boldsymbol{m} = \gamma \boldsymbol{j}$$



From the electron's point of view, the nucleus revolves round it with speed v ⇒ current loop. It is a relativistic effect

$$I = Zev/2\pi r$$

which produces a magnetic field $\mu_0 I/2r$ at the centre

$$B_{so} = \mu_0 Zev/4\pi r^2 \quad [\sim 10\,\mathrm{T} \text{ for B or C}]$$

$E = -\, \boldsymbol{m}.\boldsymbol{B}$ $\qquad E_{so} = -\, \mu_B B_{so}$

Since $r \approx a_0/Z$ and $m_e v r \approx \hbar$

$$\boxed{E_{so} \approx -\mu_0 \mu_B^2 Z^4/4\pi a_0^3}$$

The spin – orbit Hamiltonian for a single electron is of the form:

$$\boxed{\mathcal{H}_{so} = \lambda \hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}}}$$

in general $\mathcal{H}_{so} = (1/2m_e^2c^2r)dV/dr\ \boldsymbol{l}.\boldsymbol{s}$

The total magnetic moment is thus:

$$\boldsymbol{m}_t = \boldsymbol{m}_o + \boldsymbol{m}_s$$

Which needs not be collinear with the total angular momentum:

$$\boldsymbol{L}_t = \hbar(\boldsymbol{l} + \boldsymbol{s})$$

✓ Every particle has a magnetic moment, and an intrinsic angular momentum;

- Proton: $\boldsymbol{m}_p = g_p \left(\frac{\hbar e}{2 m_p} \right) \hbar \boldsymbol{L}, \quad g_p = 2.793$
- Neutron: does not carry electric charge, but it has both an intrinsic angular momentum and a magnetic moment:

$$\boldsymbol{m}_n = g_n \left(\frac{\hbar e}{2 m_n} \right) \hbar \boldsymbol{L}, \quad g_p = 1.913$$

✓ These magnetic moments are much smaller than that of the electron, due to the different masses.

Electron in a H-atom

- One electron and a symmetric potential, (e.g. H-atom)

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) + V(r)\Psi(\mathbf{r},t)$$

with stationary states

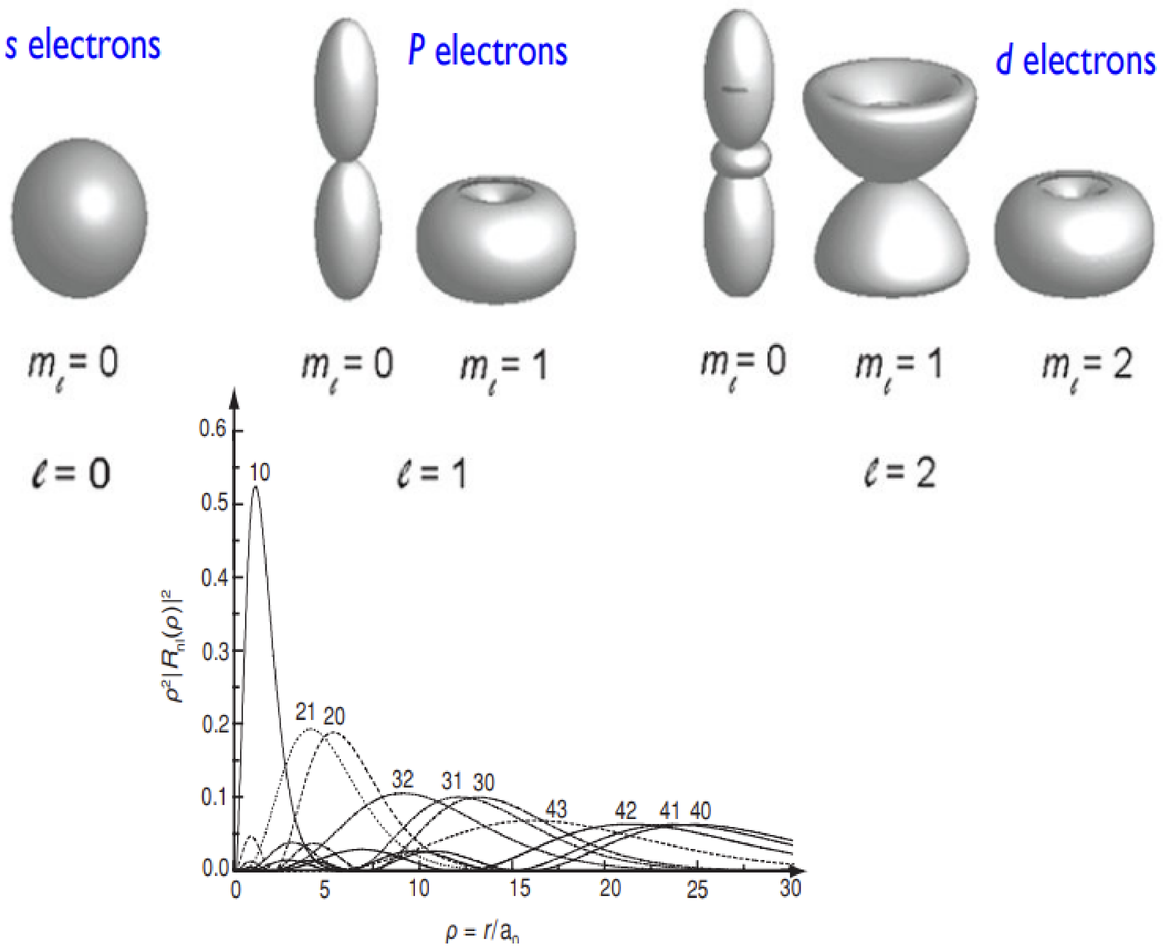
$$\Psi(\mathbf{r},t) = \Phi_{n,l,m}(r,\theta,\phi)u_\sigma e^{-iE_nt/\hbar}$$

where

$$\Phi_{n,l,m}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

and principal, $n = 1, 2, \cdots$, angular momentum, $l = 0, 1, \cdots, n-1$ and $m = -l, -l+1, \cdots, l$ and spin, $\sigma = \uparrow, \downarrow$, quantum numbers.

- H-atom: $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$, $E_n = -\frac{13.6}{n^2}$ eV.



$$H_0 = \sum_i \left[-\left(\frac{\hbar^2}{2 m_e} \right) \nabla^2 - \frac{Z e^2}{4 \pi \varepsilon_0 r_i} \right] + \underbrace{\sum_{i<j} \frac{e^2}{4 \pi \varepsilon_0 r_{ij}}}_{\text{repulsion between electrons}}$$

This Hamiltonian is insoluble.

Approximation: average effective potential with spherical symmetry.

➔ The degeneracy of energy levels with equal *n* is lifted:

Energy depends on *l*: $E(2p_{+1}) \neq E(2p_0) \neq E(2p_{-1})$

Filling sequence of electronic levels!

L-S coupling scheme: (important for most ions of interest in magnetism)

Individual spin and angular momenta add to give resultant quantum numbers:

$$S = \sum s_i, \quad M_S = \sum m_{si}, \quad L = \sum l_i, \quad M_L = \sum m_{li}$$

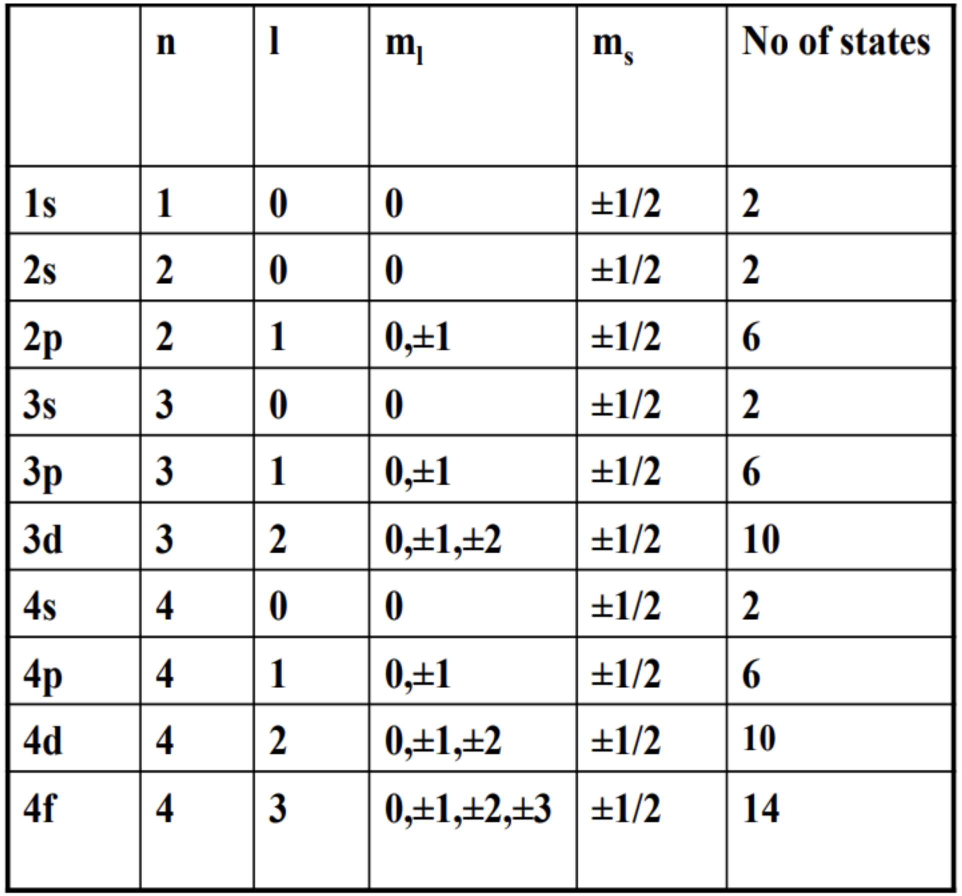
(Alternatively, when LS coupling is very strong, l_i and s_i first couple for each electron to yield j_i: $\boldsymbol{j} - \boldsymbol{j}$ coupling scheme)

Many electrons in atoms

- 2 electrons in same spatial state occupy different spin states (S=0), electrons with ‘parallel’ spins (S=1) tend to avoid each other --- spin correlation. Magnetic properties of matter.
- Many electron wavefunctions as Slater determinants of 1-electron wavefunctions.
- Each electron in effective potential set up by nucleus and other electrons, l degeneracy broken.
- Products of states labelled as 1s2, 2s2, 2p6,…

Filled states cancel S and L to effective (almost) zero magnetic moment

In solids, ions share or swap electrons to create filled shells => eliminating magnetic moments



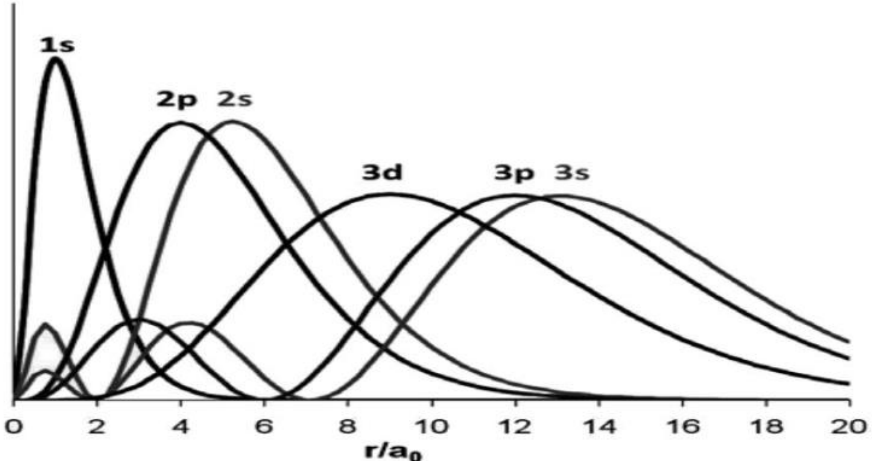
	n	l	m_l	m_s	No of states
1s	1	0	0	±1/2	2
2s	2	0	0	±1/2	2
2p	2	1	0,±1	±1/2	6
3s	3	0	0	±1/2	2
3p	3	1	0,±1	±1/2	6
3d	3	2	0,±1,±2	±1/2	10
4s	4	0	0	±1/2	2
4p	4	1	0,±1	±1/2	6
4d	4	2	0,±1,±2	±1/2	10
4f	4	3	0,±1,±2,±3	±1/2	14

One-electron hydrogenic states

The three quantum number n ,l m_l denote an orbital.

Orbitals are denoted nx_{ml}, x = s, p, d, f... for l = 0,1,2, 3,...

Each orbital can accommodate at most two electrons* (m_s=±1/2)

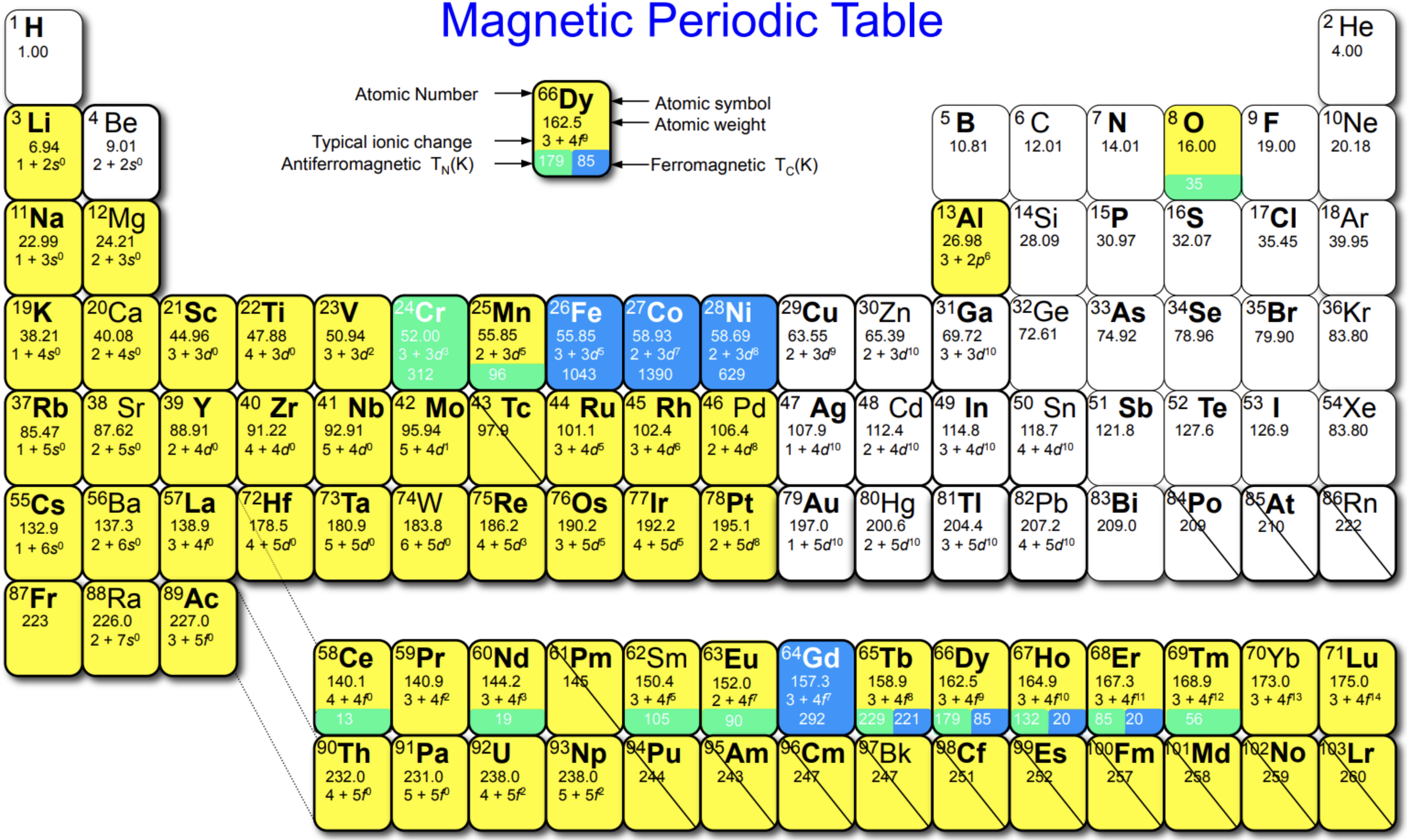


	n	l	m_l	m_s	No of states
1s	1	0	0	±1/2	2
2s	2	0	0	±1/2	2
2p	2	1	0,±1	±1/2	6
3s	3	0	0	±1/2	2
3p	3	1	0,±1	±1/2	6
3d	3	2	0,±1,±2	±1/2	10
4s	4	0	0	±1/2	2
4p	4	1	0,±1	±1/2	6
4d	4	2	0,±1,±2	±1/2	10
4f	4	3	0,±1,±2,±3	±1/2	14

*The Pauli exclusion principle: No two electrons can have the same four quantum numbers.

⇒ Two electrons in the same orbital must have opposite spin.

Magnetic Periodic Table



Atomic Number → 66 **Dy** ← Atomic symbol
162.5 ← Atomic weight
Typical ionic change → $3 + 4f^9$
Antiferromagnetic T_N(K) → 179 | 85 ← Ferromagnetic T_C(K)

1 **H** 1.00																	2 He 4.00
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				90 **Th** 232.0 $4 + 5f^0$	91 **Pa** 231.0 $5 + 5f^0$	92 **U** 238.0 $4 + 5f^2$	93 **Np** 238.0 $5 + 5f^2$	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 Bk 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 259	103 **Lr** 260

Most atoms are magnetic

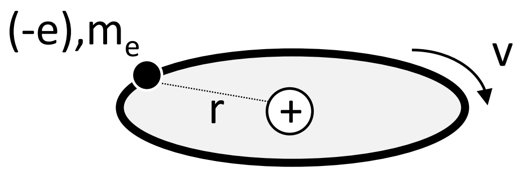
⬜ Diamagnet
🟨 Paramagnet
BOLD Magnetic atom

🟦 Ferromagnet T_C > 290K
🟩 Antiferromagnet with T_N > 290K
🟩🟦 Antiferromagnet/Ferromagnet with T_N/T_C < 290 K

Few materials are magnetic

ISOLATED MAGNETIC MOMENTS

an atom in a magnetic field



<u>not one but several electrons</u>

$$\vec{L} = \vec{r} \times \vec{p} \rightarrow \sum_i \vec{r}_i \times \vec{p}_i$$

<u>kinetic energy</u>

$$E_k = \frac{1}{2} m\boldsymbol{v}^2 = \frac{1}{2m}\boldsymbol{p}^2$$

$$\overset{B>0}{=} \frac{1}{2m}(\boldsymbol{p} - q\boldsymbol{A})^2$$

q = -e

<u>applying magnetic field</u>

$$\mathcal{H}_0 = \sum_i \left(\frac{\boldsymbol{p}_i^2}{2m} + V_i\right) \rightarrow \sum_i \left(\frac{[\boldsymbol{p}_i + e\boldsymbol{A}]^2}{2m} + V_i\right) + g\mu_B \boldsymbol{BS}$$

choice of gauge:

$$\boldsymbol{A} = \frac{1}{2}\boldsymbol{B} \times \boldsymbol{r}$$

$$\boxed{\mathcal{H} = \mathcal{H}_0 + \mu_B(\boldsymbol{L} + g\boldsymbol{S})\boldsymbol{B} + \frac{e^2}{8m}\sum_i (\boldsymbol{B} \times \boldsymbol{r}_i)^2}$$

“Non-magnet magnetism 1” : diamagnetism

Filled shells

$$\mathcal{H} = \mathcal{H}_0 + \mu_B\cancel{(\boldsymbol{L}+g\boldsymbol{S})}\boldsymbol{B} + \boxed{\frac{e^2}{8m}\sum_i(\boldsymbol{B}\times\boldsymbol{r}_i)^2}$$

small perturbation

dominant contribution

$$\mathcal{H}_0|\Psi_i\rangle = E_i|\Psi_i\rangle$$

$$\underset{\text{ground state}}{E_0} < \underbrace{E_1 < E_2 < E_3\cdots}_{\text{excited states}}$$

perturbation theory

1. order $\quad \Delta E_0 = \langle 0|\mathcal{H}_{pert}|0\rangle$

2. order $\quad \Delta E_0 = \sum_i \frac{\langle 0|\mathcal{H}_{pert}|i\rangle\langle i|\mathcal{H}_{pert}|0\rangle}{E_0 - E_i}$

$$\Delta E^{dia} = \left\langle 0\left|\frac{e^2}{8m}\sum_i(\boldsymbol{B}\times\boldsymbol{r}_i)^2\right|0\right\rangle$$

$$B \parallel z \Rightarrow \boldsymbol{B} = \begin{pmatrix}0\\0\\B\end{pmatrix} \qquad \boldsymbol{r}_i = \begin{pmatrix}x_i\\y_i\\z_i\end{pmatrix} \qquad (\boldsymbol{B}\times\boldsymbol{r}_i) = B\begin{pmatrix}-y_i\\x_i\\0\end{pmatrix}$$

$$\Delta E^{dia} = \frac{e^2B^2}{8m}\sum_i\langle 0|x_i^2+y_i^2|0\rangle = \frac{e^2B^2}{12m}\sum_i\langle 0|r_i^2|0\rangle$$

spherical symmetry

$$\langle 0|x_i^2|0\rangle = \langle 0|y_i^2|0\rangle = \langle 0|z_i^2|0\rangle = \frac{1}{3}\langle 0|r_i^2|0\rangle$$

$$\chi_{dia} = \frac{M}{H} \sim \frac{1}{H}\frac{\partial \Delta E^{dia}}{\partial B} \sim \sum_i\langle 0|r_i^2|0\rangle$$

$$\boxed{\chi_{dia} \sim Z_{out}r^2}$$

“Non-magnet magnetism 2” : Van Vleck paramagnetism

Filled shell in the ground state

$$\mathcal{H} = \mathcal{H}_0 + \mu_B \cancel{(\boldsymbol{L} + g\boldsymbol{S})}\boldsymbol{B} + \boxed{\frac{e^2}{8m}\sum_i (\boldsymbol{B} \times \boldsymbol{r}_i)^2}$$

small perturbation

dominant contribution

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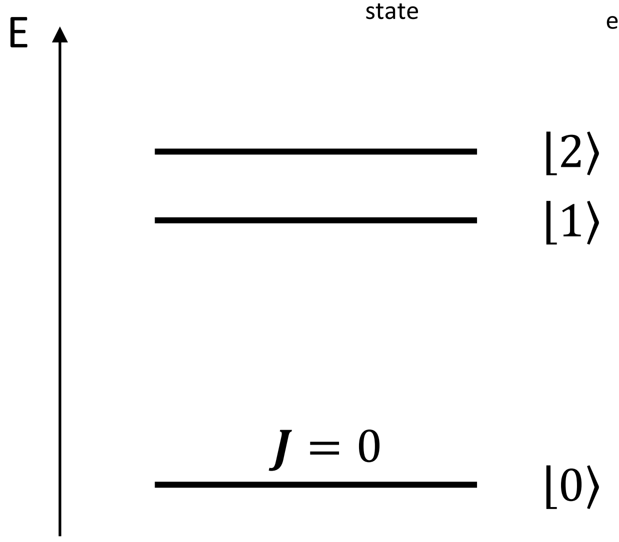


$$\Delta E^{(1)} = \langle 0|\boldsymbol{J}|0\rangle = 0$$

$$\Delta E^{(2)} \sim \sum_{i \geq 1} \frac{|\langle 0|(\boldsymbol{L} + g\boldsymbol{S})\boldsymbol{B}|i\rangle|^2}{E_i - E_0}$$

$$\boxed{\chi_{VV} \sim \sum_{i \geq 1} \frac{|\langle 0|(L_z + gS_z)|i\rangle|^2}{E_i - E_0} > 0}$$

temperature and field independent

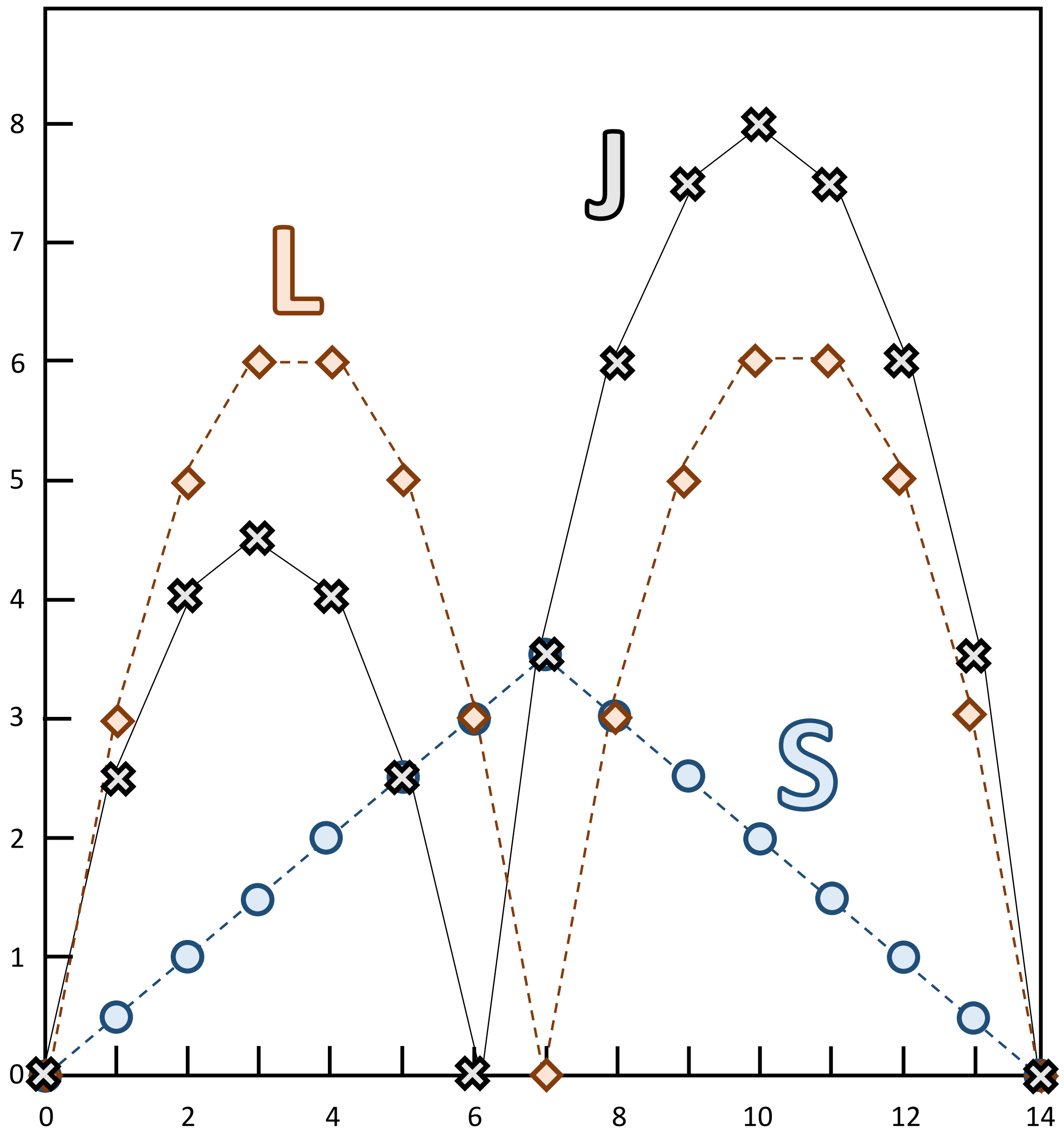
Unfilled shells – 4f example : Hund's rules

1 Maximize S

2 Maximize L

3 subtract/add

ion	N	S	L	J	3
La^{3+}	0	0	0	0	J = |L-S|
Ce^{3+}	1	1/2	3	5/2	
Pr^{3+}	2	1	5	4	
Nd^{3+}	3	3/2	6	9/2	
Pm^{3+}	4	2	6	4	
Sm^{3+}	5	5/2	5	5/2	
Eu^{3+}	6	3	3	0	
Gd^{3+}	7	7/2	0	7/2	
Tb^{3+}	8	3	3	6	J = |L+S|
Dy^{3+}	9	5/2	5	15/2	
Ho^{3+}	10	2	6	8	
Er^{3+}	11	3/2	6	15/2	
Tm^{3+}	12	1	5	6	
Yb^{3+}	13	1/2	3	7/2	
Lu^{3+}	14	0	0	0	



Landé g-factor

total (measured) moment

$$\hat{\boldsymbol{\mu}} = g_J \mu_B \hat{\boldsymbol{J}} = \mu_B (g_L \hat{\boldsymbol{L}} + g_S \hat{\boldsymbol{S}})$$

$$g_J \hat{\boldsymbol{J}}^2 = (g_L \hat{\boldsymbol{L}}\hat{\boldsymbol{J}} + g_S \hat{\boldsymbol{S}}\hat{\boldsymbol{J}})$$

total angular momentum

$\vec{\boldsymbol{J}} = \vec{\boldsymbol{L}} + \vec{\boldsymbol{S}}$ → but also operators!

$$\vec{\boldsymbol{L}} = \vec{\boldsymbol{J}} - \vec{\boldsymbol{S}} \qquad \vec{\boldsymbol{S}} = \vec{\boldsymbol{J}} - \vec{\boldsymbol{L}}$$

$$\vec{\boldsymbol{S}}^2 = (\vec{\boldsymbol{J}} - \vec{\boldsymbol{L}})^2 = \vec{\boldsymbol{J}}^2 - \vec{\boldsymbol{L}}^2 - 2\vec{\boldsymbol{J}}\vec{\boldsymbol{L}}$$

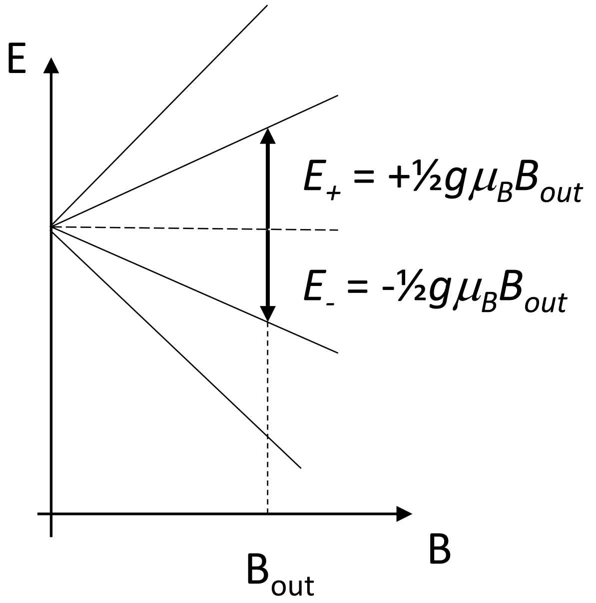
$$g_J = g_L \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} + g_S \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

for $g_L = 1, g_S = 2$

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

Landé g-factor

ISOLATED MAGNETIC MOMENTS



$E_+ = +½g\mu_B B_{out}$

$E_- = -½g\mu_B B_{out}$

$\Delta E = E_+ - E_- = g\mu_B B_{out}$

the principle of ESR (EPR)

<u>thermodynamics through the partition function:</u>

$$Z = \sum_i e^{\frac{E_i}{k_B T}} = \sum_{m_J=-J}^{J} e^{\frac{m_J g_J \mu_B B}{k_B T}}$$

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

$$M = n g_J \mu_B \langle m_J \rangle = n g_J \mu_B \frac{\sum_{m_J=-J}^{J} m_J e^{m_J x}}{\sum_{m_J=-J}^{J} e^{m_J x}}$$

$$x = \frac{g_J \mu_B J B_{out}}{k_B T}$$

$$M = n g_J \mu_B J B_J(x)$$

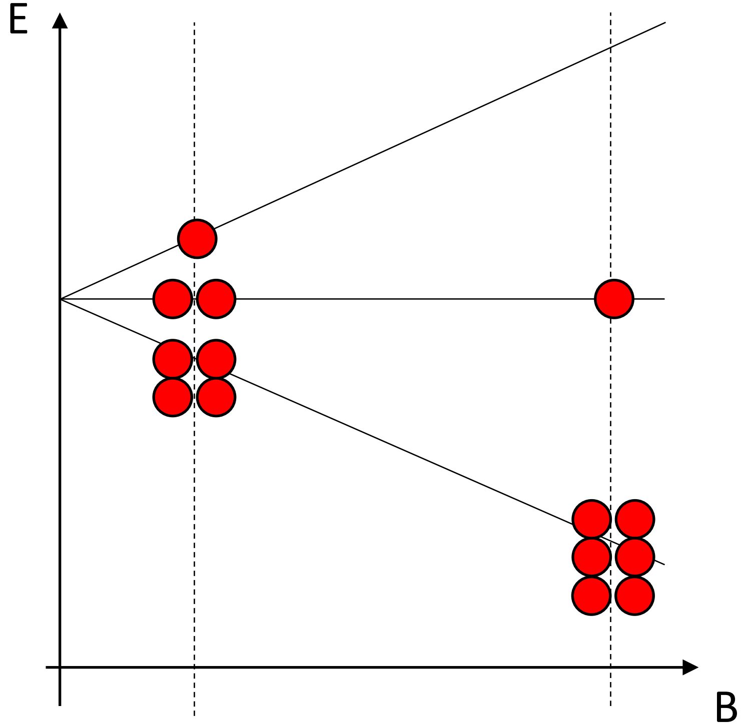
$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J} x\right)$$

Brillouin function

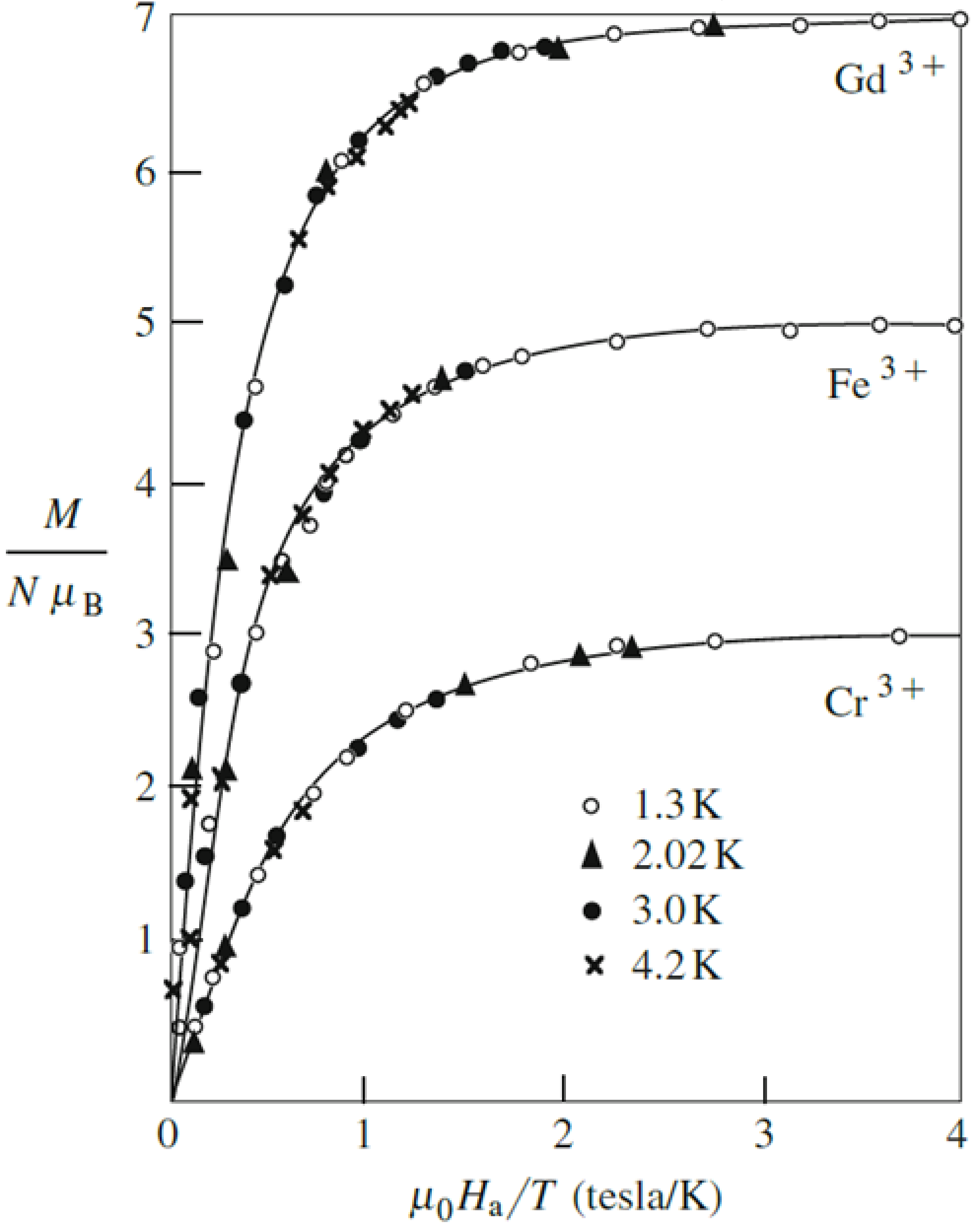
ISOLATED MAGNETIC MOMENTS

$$M = \underbrace{n g_J \mu_B J}_{\text{saturation value}} B_J(x) \qquad x = \frac{g_J \mu_B J B_{out}}{k_B T}$$

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right)$$



PhysRev 88, 559 (1952)



ISOLATED MAGNETIC MOMENTS

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right)$$

$\underline{J \to \infty}$

$$B_\infty(x) \to L(x) = \coth x - \frac{1}{x}$$

Langevin function

ISOLATED MAGNETIC MOMENTS

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right)$$

$J \to \infty$

$$B_\infty(x) \to L(x) = \coth x - \frac{1}{x}$$

Langevin function

$x \ll 1$

$$B_J(x) \approx \frac{J+1}{3J}x \to M = f(T)B$$

$$\chi = \frac{N_A \mu_0 g_J^2 \mu_B^2 J(J+1)}{3k_B T} = \frac{C}{T}$$

Curie law

ISOLATED MAGNETIC MOMENTS

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right)$$

$\underline{J \to \infty}$

$$B_\infty(x) \to L(x) = \coth x - \frac{1}{x}$$

Langevin function

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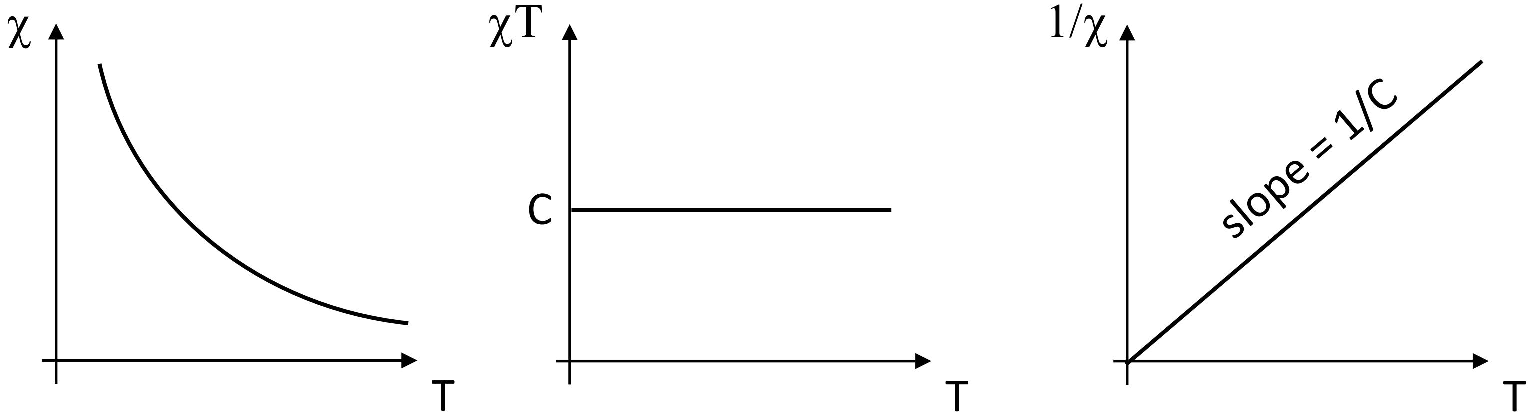
Curie law

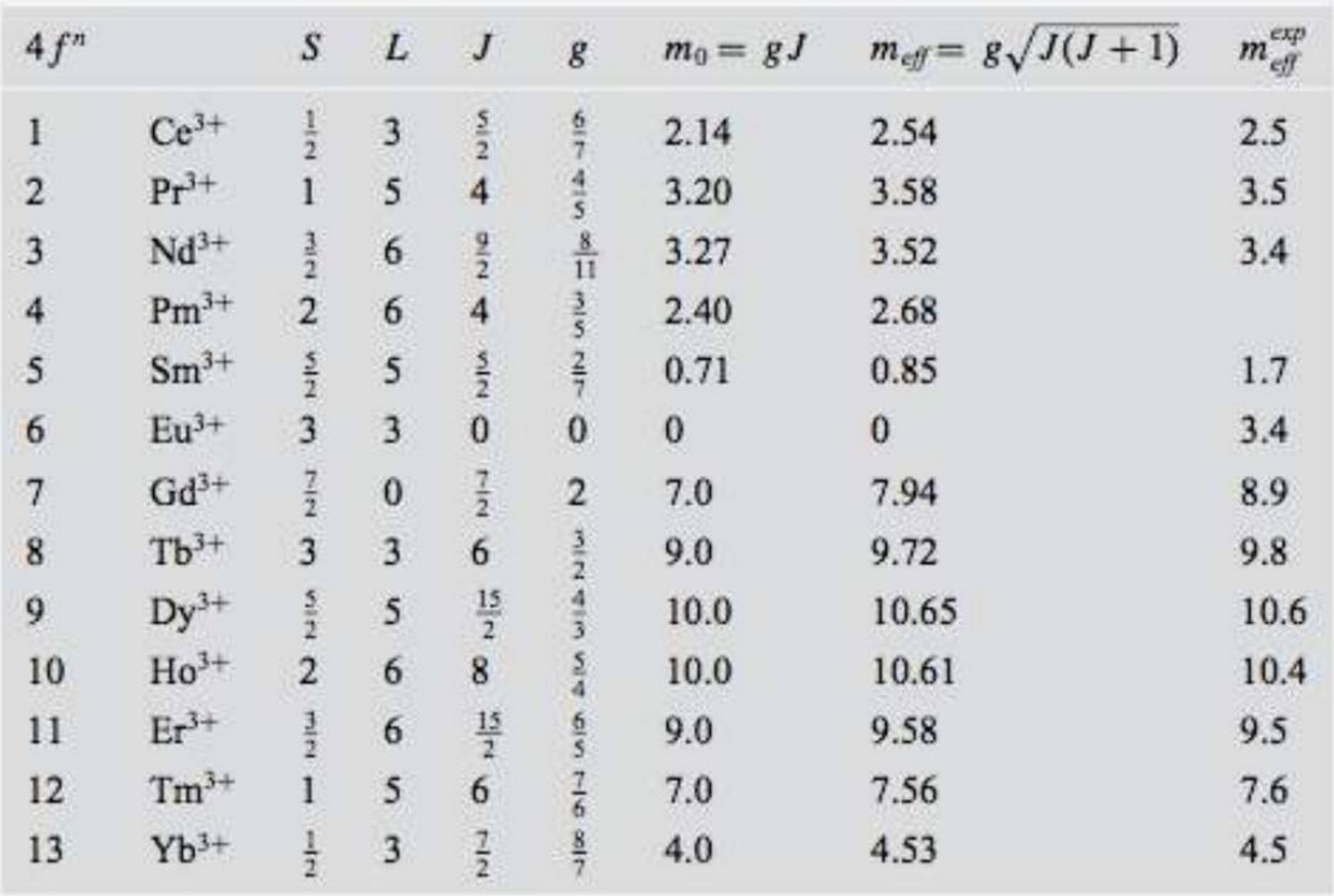
$$\chi = \frac{N_A \mu_0 g_J^2 \mu_B^2 J(J+1)}{3k_B T} = \frac{C}{T} = \frac{N_A \mu_0 \mu_{eff}^2}{3k_B T}$$

$$\mu_{eff}^2 = g_J^2 \mu_B^2 J(J+1)$$



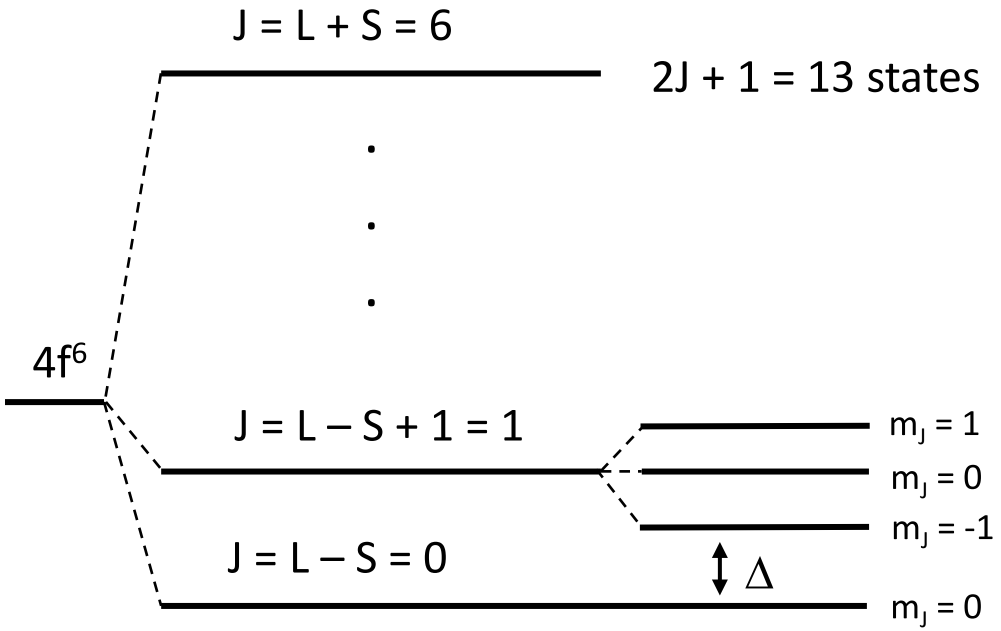
ISOLATED MAGNETIC MOMENTS

Hund's rules



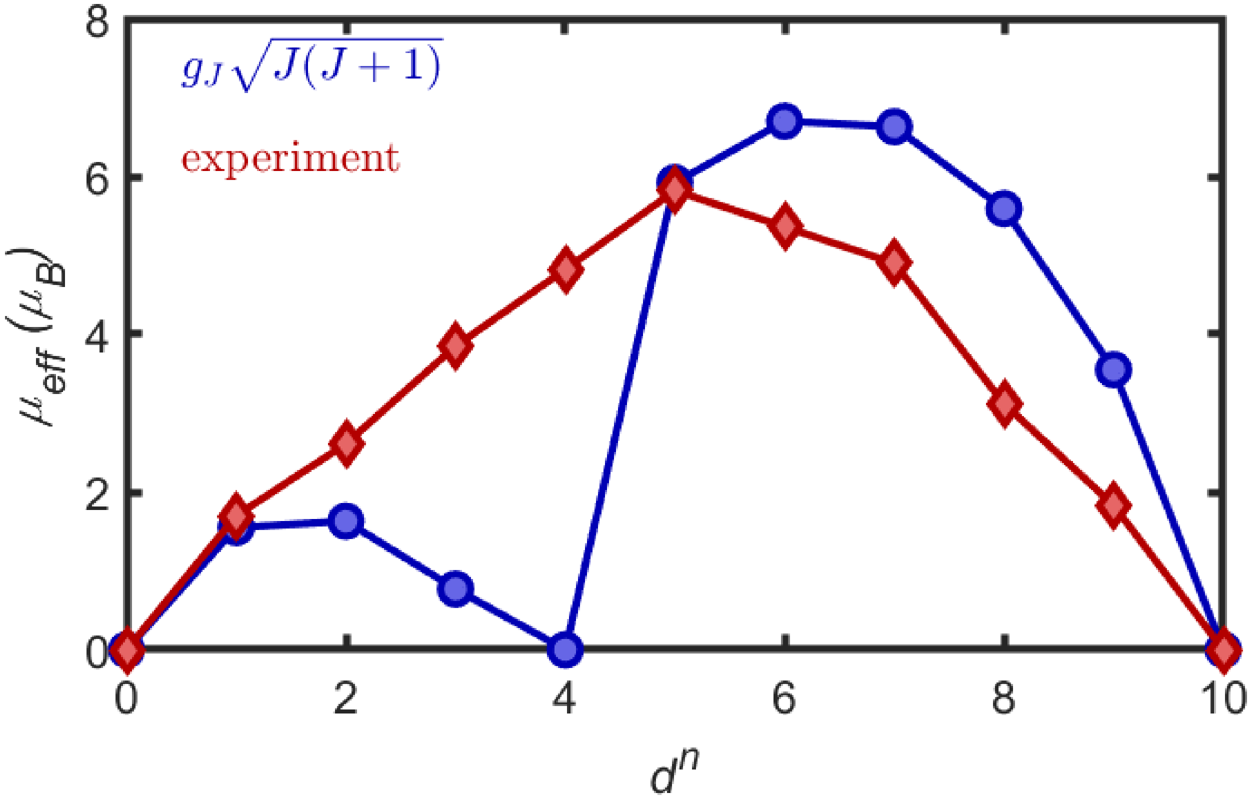
$4f^n$		S	L	J	g	$m_0 = gJ$	$m_{eff} = g\sqrt{J(J+1)}$	m_{eff}^{exp}
1	Ce^{3+}	$\frac{1}{2}$	3	$\frac{5}{2}$	$\frac{6}{7}$	2.14	2.54	2.5
2	Pr^{3+}	1	5	4	$\frac{4}{5}$	3.20	3.58	3.5
3	Nd^{3+}	$\frac{3}{2}$	6	$\frac{9}{2}$	$\frac{8}{11}$	3.27	3.52	3.4
4	Pm^{3+}	2	6	4	$\frac{3}{5}$	2.40	2.68	
5	Sm^{3+}	$\frac{5}{2}$	5	$\frac{5}{2}$	$\frac{2}{7}$	0.71	0.85	1.7
6	Eu^{3+}	3	3	0	0	0	0	3.4
7	Gd^{3+}	$\frac{7}{2}$	0	$\frac{7}{2}$	2	7.0	7.94	8.9
8	Tb^{3+}	3	3	6	$\frac{3}{2}$	9.0	9.72	9.8
9	Dy^{3+}	$\frac{5}{2}$	5	$\frac{15}{2}$	$\frac{4}{3}$	10.0	10.65	10.6
10	Ho^{3+}	2	6	8	$\frac{5}{4}$	10.0	10.61	10.4
11	Er^{3+}	$\frac{3}{2}$	6	$\frac{15}{2}$	$\frac{6}{5}$	9.0	9.58	9.5
12	Tm^{3+}	1	5	6	$\frac{7}{6}$	7.0	7.56	7.6
13	Yb^{3+}	$\frac{1}{2}$	3	$\frac{7}{2}$	$\frac{8}{7}$	4.0	4.53	4.5

deviations (Sm, Eu)



when $k_B T \sim \Delta$, $\mu > 0$

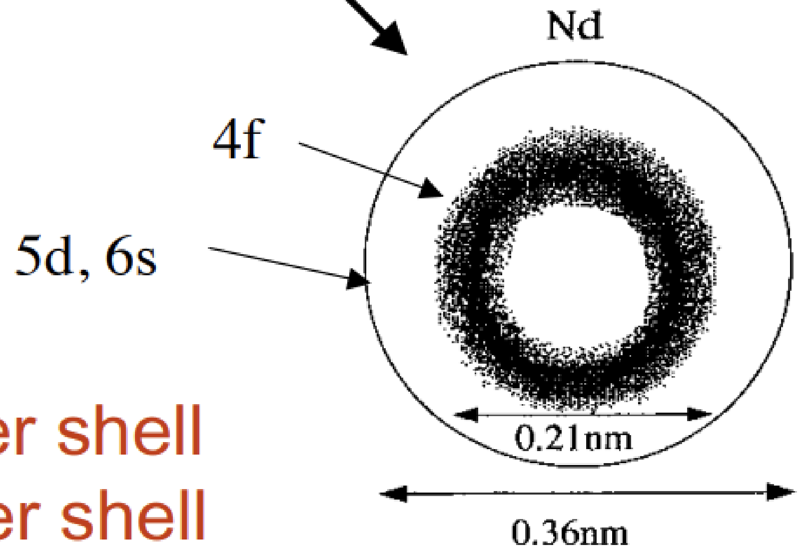
The failure of 3D transition metals

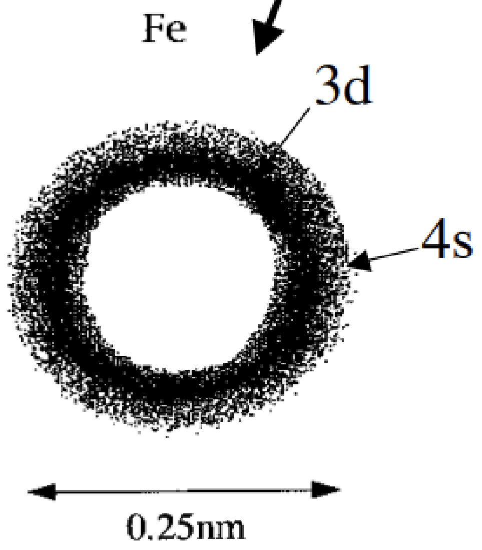


The 2 main series of magnetic elements

Rare-earth element

Transition-metal element

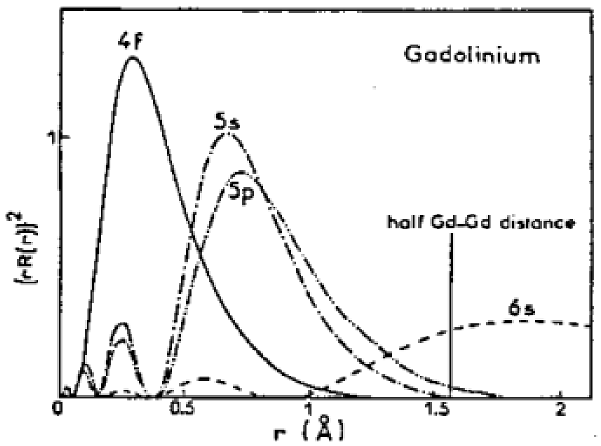


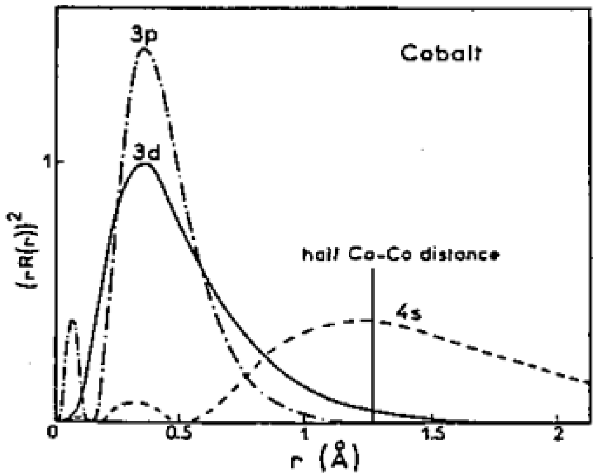


4f electrons : inner shell

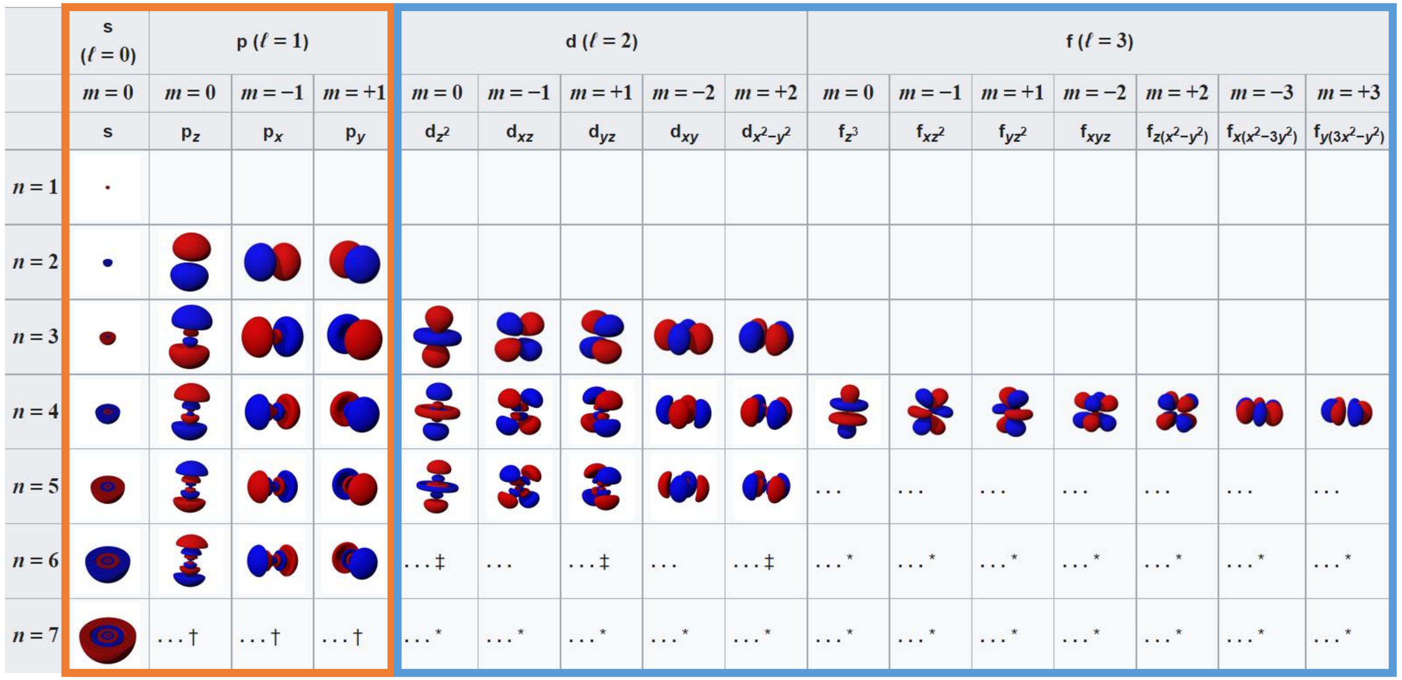
3d electrons : outer shell

leads to very different behaviours





CRYSTAL FIELD EFFECTS



	s ($\ell = 0$)	p ($\ell = 1$)			d ($\ell = 2$)					f ($\ell = 3$)						
	$m = 0$	$m = 0$	$m = -1$	$m = +1$	$m = 0$	$m = -1$	$m = +1$	$m = -2$	$m = +2$	$m = 0$	$m = -1$	$m = +1$	$m = -2$	$m = +2$	$m = -3$	$m = +3$
	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	f_{z^3}	f_{xz^2}	f_{yz^2}	f_{xyz}	$f_{z(x^2-y^2)}$	$f_{x(x^2-3y^2)}$	$f_{y(3x^2-y^2)}$
$n = 1$																
$n = 2$																
$n = 3$																
$n = 4$																
$n = 5$										. . .	. . .	. . .	. . .	. . .	. . .	. . .
$n = 6$					. . . ‡	. . .	. . . ‡	. . .	. . . ‡	. . . *	. . . *	. . . *	. . . *	. . . *	. . . *	. . . *
$n = 7$		. . . †	. . . †	. . . †	. . . *	. . . *	. . . *	. . . *	. . . *	. . . *	. . . *	. . . *	. . . *	. . . *	. . . *	. . . *

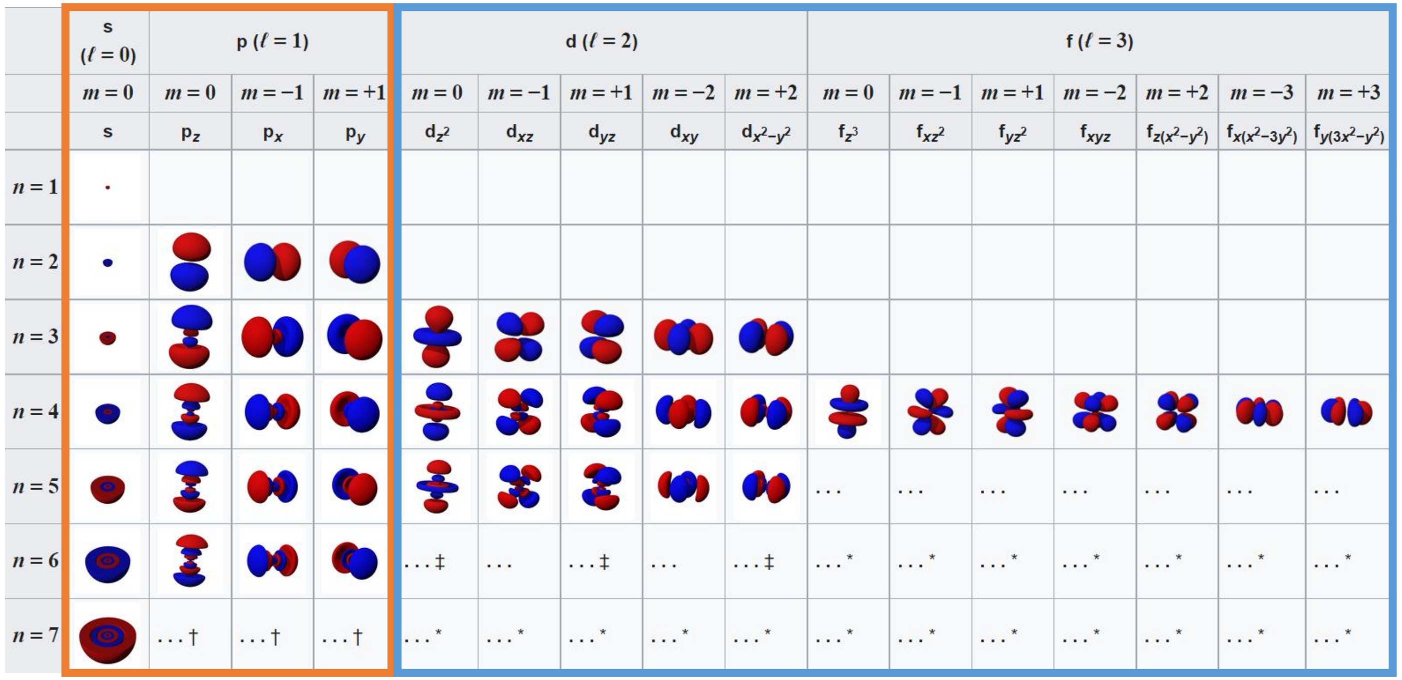
bonding

magnetism

- ❖ based on hydrogen
- ❖ visualization is not straight-forward
- ❖ radial and spherical coordinates
- ❖ complex value

image source: wikimedia.org

CRYSTAL FIELD EFFECTS



	s ($\ell = 0$)	p ($\ell = 1$)			d ($\ell = 2$)					f ($\ell = 3$)						
	$m = 0$	$m = 0$	$m = -1$	$m = +1$	$m = 0$	$m = -1$	$m = +1$	$m = -2$	$m = +2$	$m = 0$	$m = -1$	$m = +1$	$m = -2$	$m = +2$	$m = -3$	$m = +3$
	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	f_{z^3}	f_{xz^2}	f_{yz^2}	f_{xyz}	$f_{z(x^2-y^2)}$	$f_{x(x^2-3y^2)}$	$f_{y(3x^2-y^2)}$
$n = 1$																
$n = 2$																
$n = 3$																
$n = 4$																
$n = 5$										…	…	…	…	…	…	…
$n = 6$					…‡	…	…‡	…	…‡	…*	…*	…*	…*	…*	…*	…*
$n = 7$		…†	…†	…†	…*	…*	…*	…*	…*	…*	…*	…*	…*	…*	…*	…*

- based on hydrogen
- radial and angular coordinates
- complex value
- visualization is not straight-forward

bonding

magnetism

$$p_0 = R_{n,l=1} Y_{l=1,m=0}$$

$$p_1 = R_{n,l=1} Y_{l=1,m=1}$$

$$p_{-1} = R_{n,l=1} Y_{l=1,m=-1}$$

$$p_x = \frac{1}{\sqrt{2}}(-p_1 + p_{-1})$$

$$p_y = \frac{i}{\sqrt{2}}(p_1 + p_{-1})$$

$$p_z = p_0$$

$$d_0 = R_{n,l=2} Y_{l=2,m=0}$$

$$d_1 = R_{n,l=2} Y_{l=2,m=1}$$

$$d_{-1} = R_{n,l=2} Y_{l=2,m=-1}$$

$$d_2 = R_{n,l=2} Y_{l=2,m=2}$$

$$d_{-2} = R_{n,l=2} Y_{l=2,m=-2}$$

$$d_{3z^2-r^2} = d_0$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(d_2 + d_{-2})$$

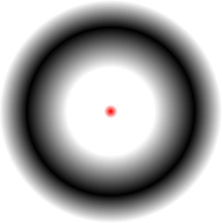
$$d_{xy} = \frac{-i}{\sqrt{2}}(d_2 - d_{-2})$$

$$d_{xz} = \frac{-1}{\sqrt{2}}(d_1 - d_{-1})$$

$$d_{yz} = \frac{i}{\sqrt{2}}(d_1 + d_{-1})$$

image source: wikimedia.org

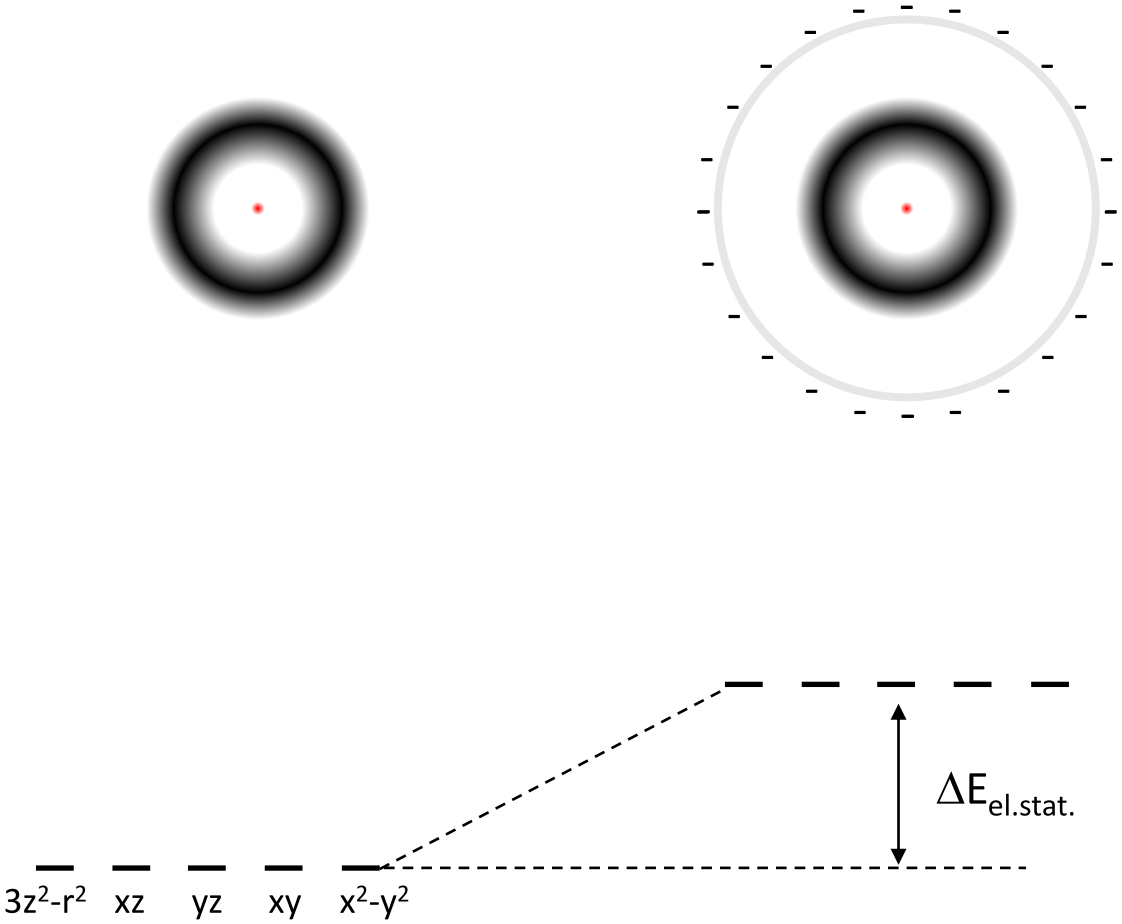
CRYSTAL FIELD EFFECTS



$3z^2-r^2$ xz yz xy x^2-y^2

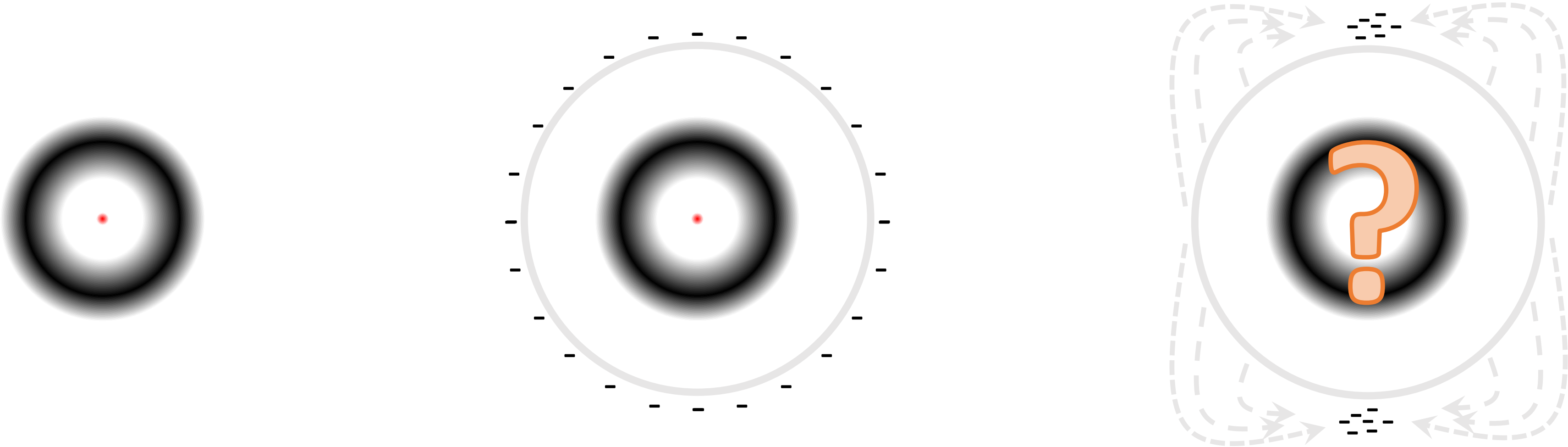
CRYSTAL FIELD EFFECTS

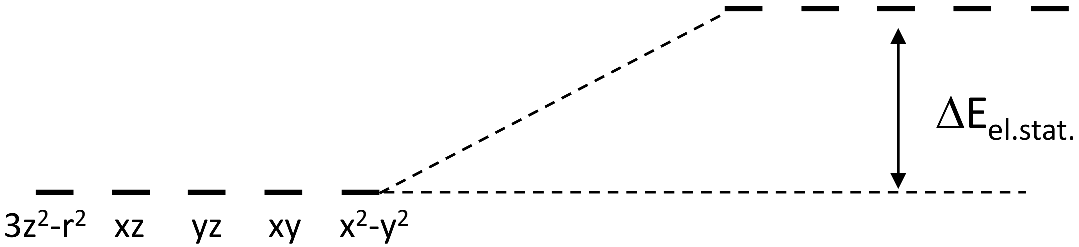
charged environment



CRYSTAL FIELD EFFECTS

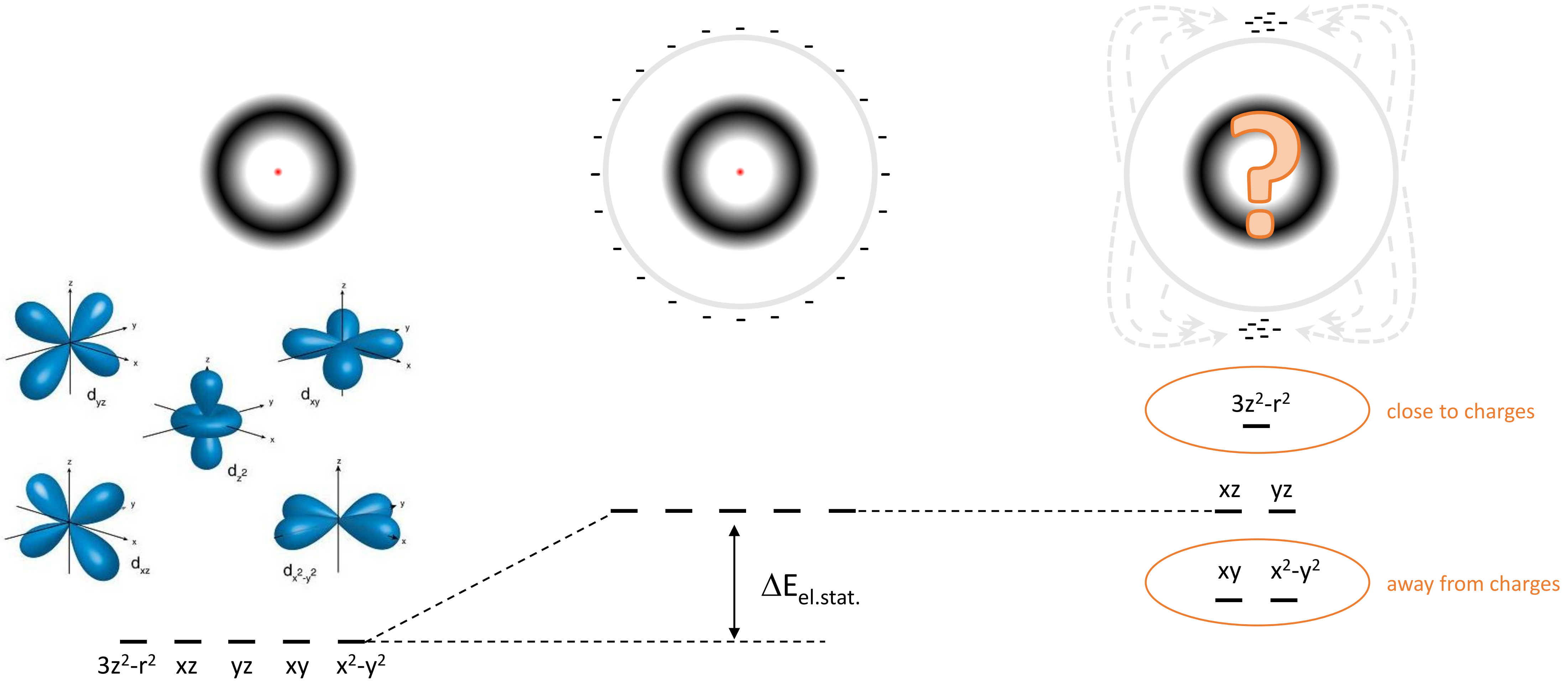
charged environment





CRYSTAL FIELD EFFECTS

charged environment



$3z^2$-r^2 xz yz xy x^2-y^2

$\Delta E_{el.stat.}$

$3z^2$-r^2

close to charges

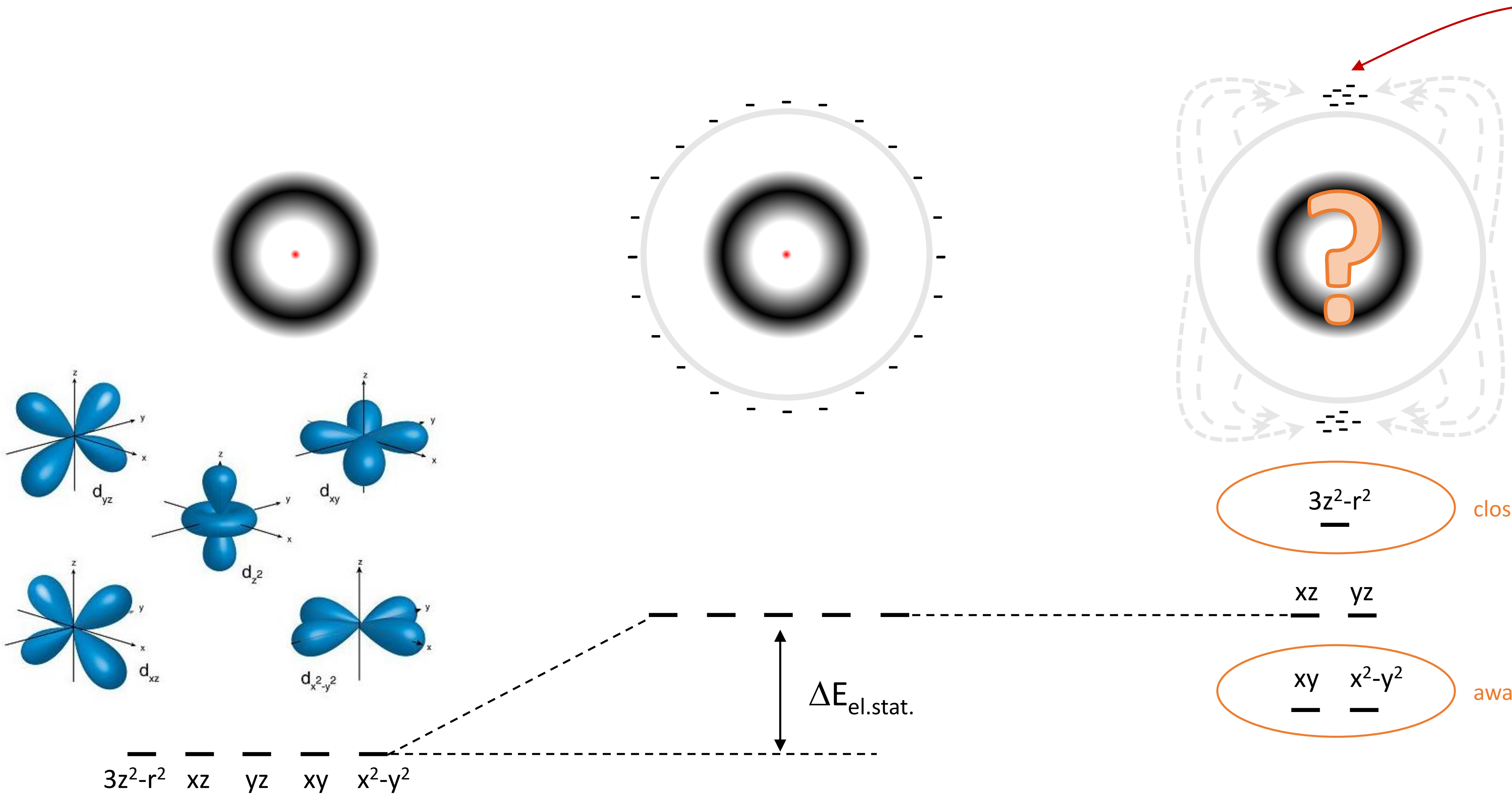
xz yz

xy x^2-y^2

away from charges

CRYSTAL FIELD EFFECTS

charged environment



$3z^2$-r^2 xz yz xy x^2-y^2

$\Delta E_{el.stat.}$

point-charges
(crystal field theory)

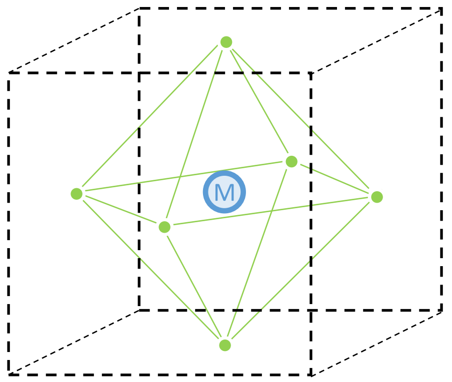
cation-anion orbital mixing
(ligand field theory)

$3z^2$-r^2 close to charges

xz yz

xy x^2-y^2 away from charges

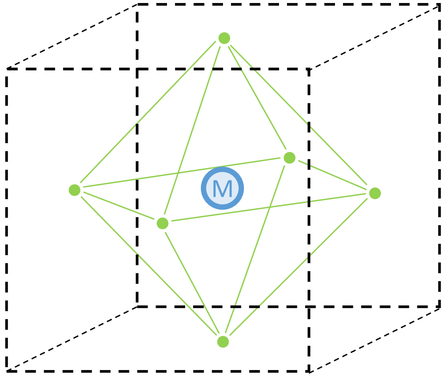
- 6 point charges
- equal distance from the magnetic ion (ideal case)



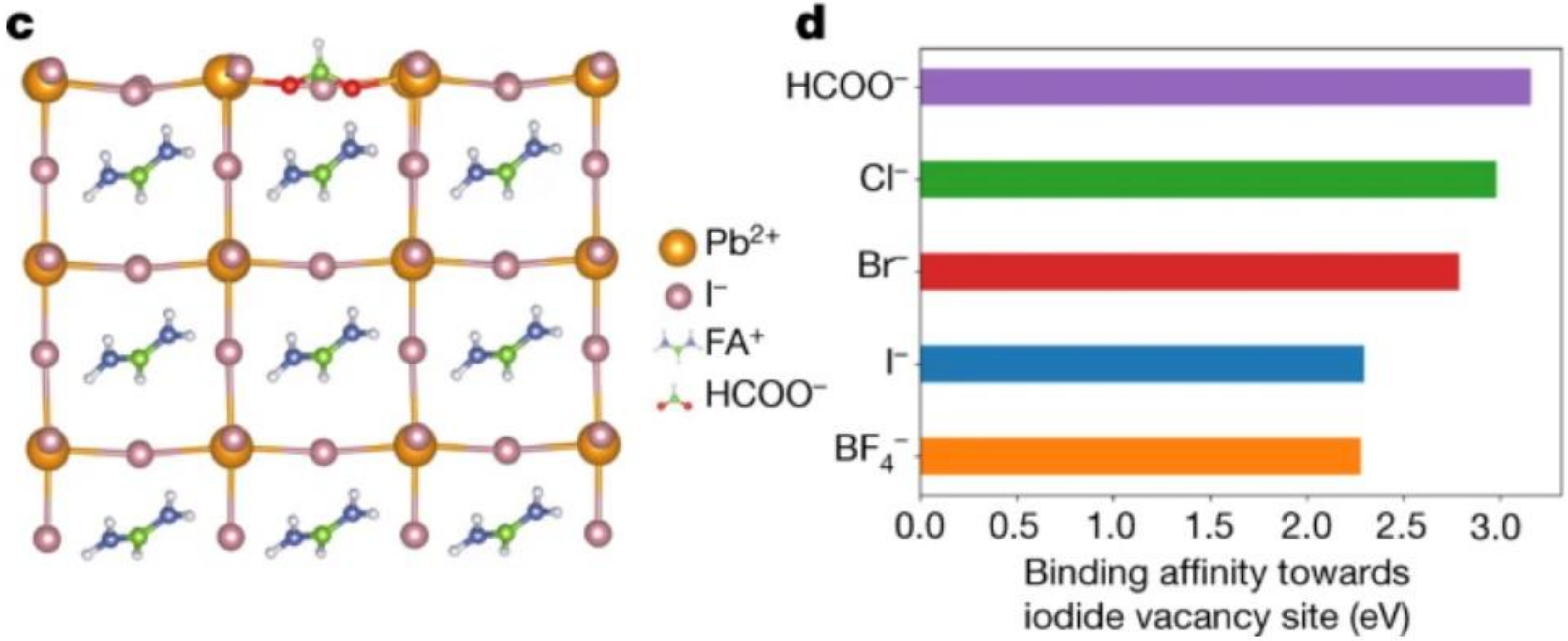
CRYSTAL FIELD EFFECTS

octahedral environment

- 6 point charges
- equal distance from the magnetic ion (ideal case)
- ABO_3 (perovskites, new solar-cell materials)



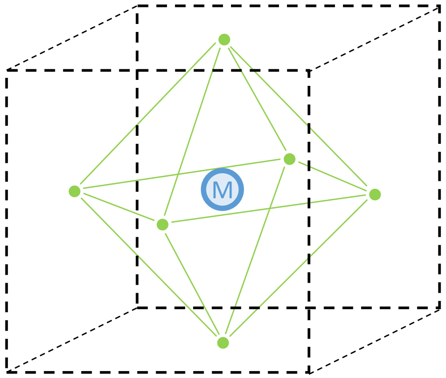
Nature 592, 381 (2021)

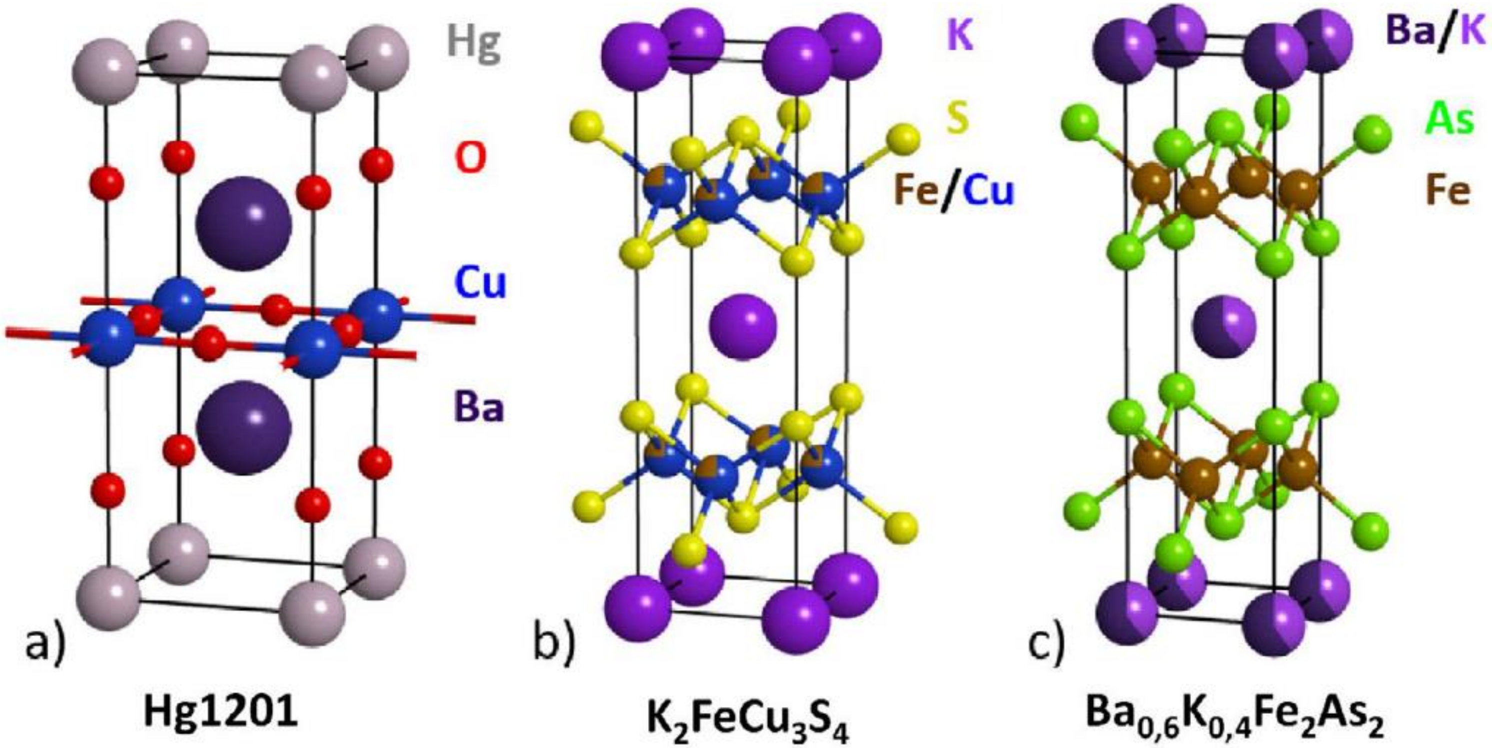


CRYSTAL FIELD EFFECTS

octahedral environment

- 6 point charges
- equal distance from the magnetic ion (ideal case)
- ABO_3 (perovskites, new solar-cell materials)
- high-Tc superconductivity in cuprates





a) Hg1201

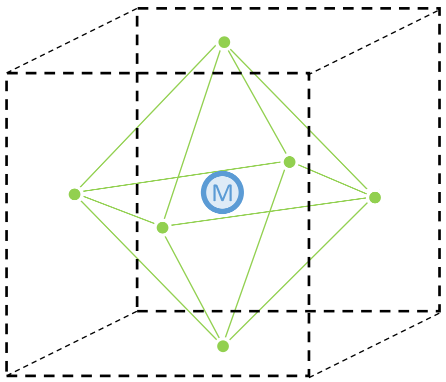
b) $K_2FeCu_3S_4$

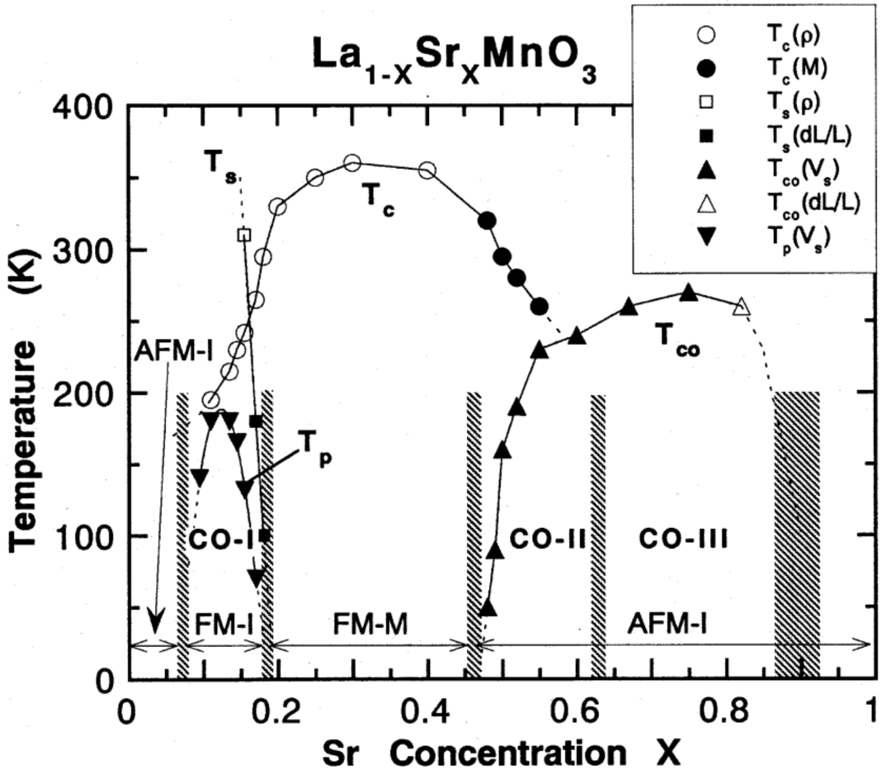
c) $Ba_{0,6}K_{0,4}Fe_2As_2$

CRYSTAL FIELD EFFECTS

octahedral environment

- 6 point charges
- equal distance from the magnetic ion (ideal case)
- ABO_3 (perovskites, new solar-cell materials)
- high-Tc superconductivity in cuprates
- colossal magnetoresistance in manganites





J. Phys. Soc. Jpn. 67, 2582 (1998)

CRYSTAL FIELD EFFECTS

octahedral environment

- ❖ 6 point charges
- ❖ equal distance from the magnetic ion (ideal case)
- ❖ ABO_3 (perovskites, new solar-cell materials)
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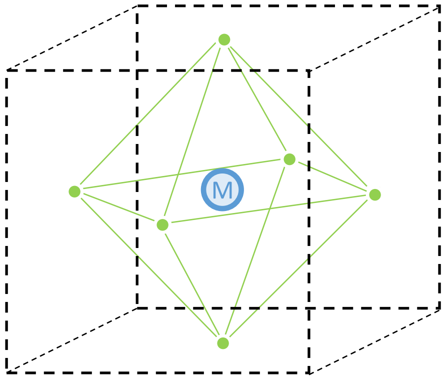

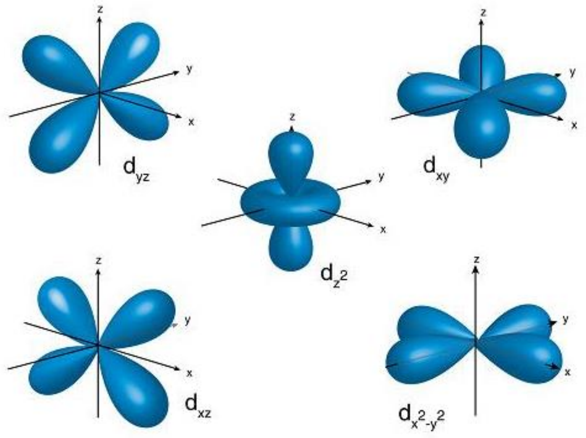

$3z^2-r^2$ xz yz xy x^2-y^2

image source: wikimedia.org

CRYSTAL FIELD EFFECTS

octahedral environment

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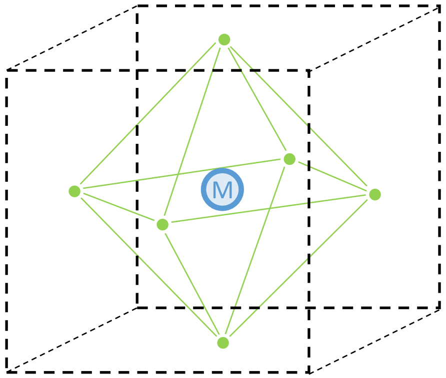
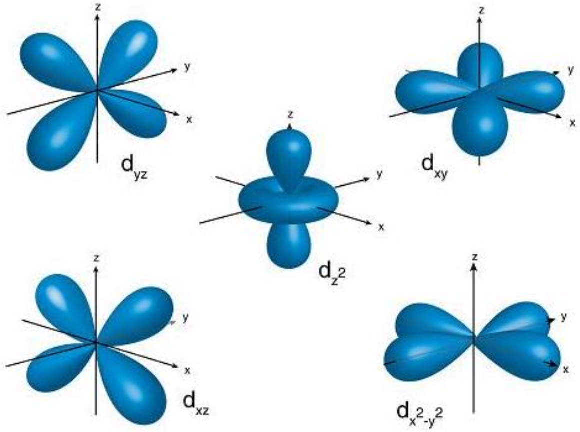
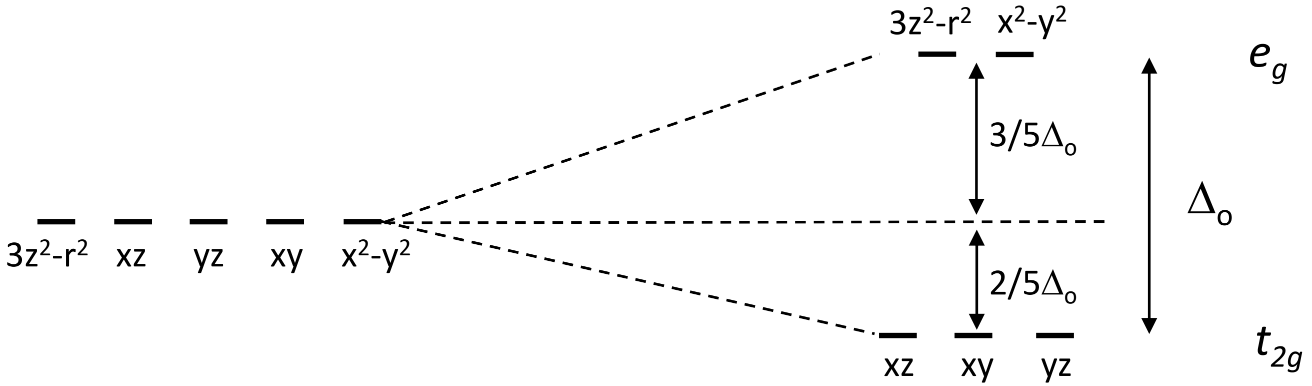






$3z^2-r^2$ x^2-y^2 e_g

$3/5\Delta_o$

Δ_o

$3z^2-r^2$ xz yz xy x^2-y^2

$2/5\Delta_o$

xz xy yz t_{2g}

image source: wikimedia.org

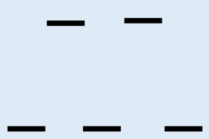
CRYSTAL FIELD EFFECTS

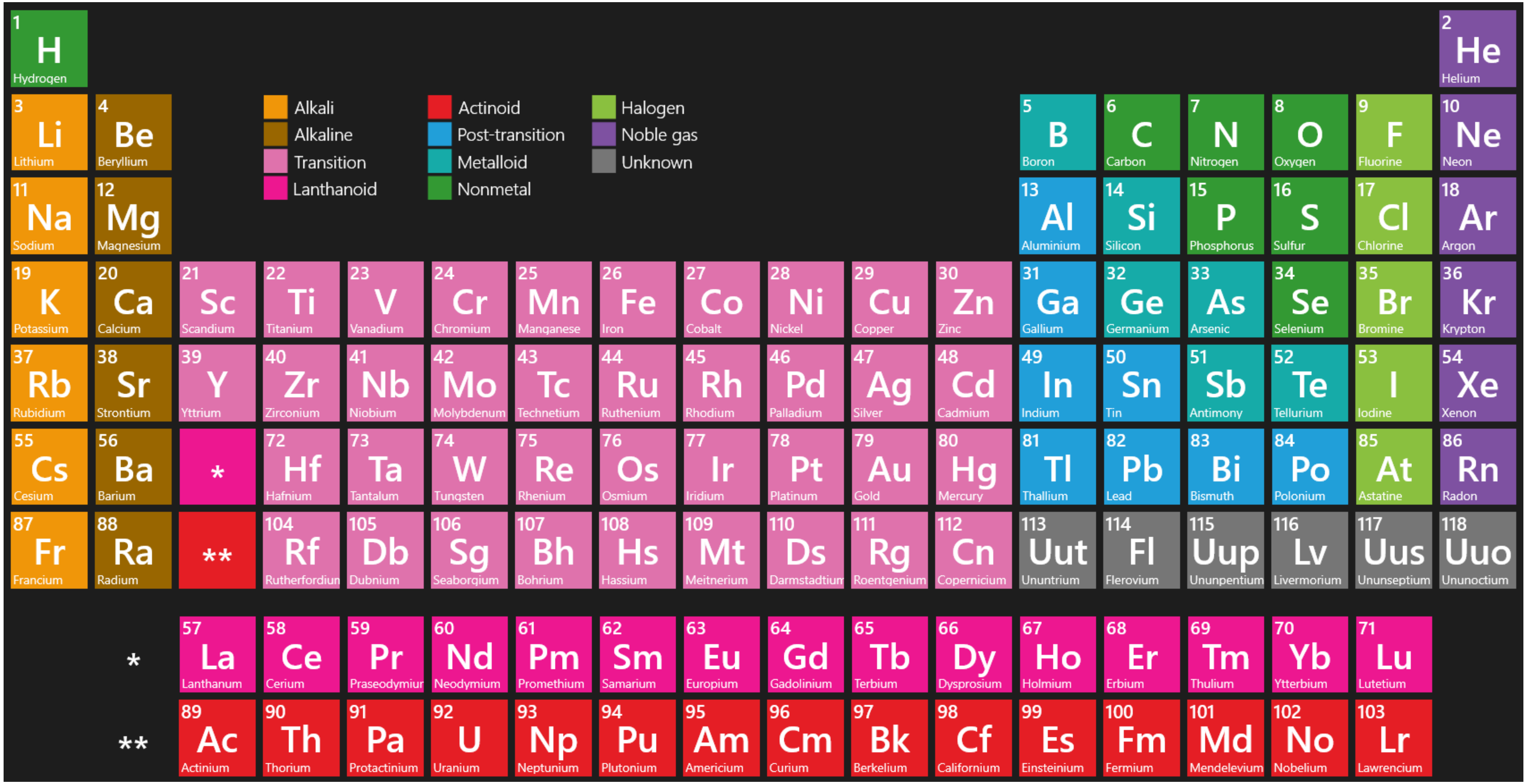
octahedral environment

d^0

$Sc^{3+}/Ti^{4+}/V^{5+}$

$S = 0$





- Alkali
- Alkaline
- Transition
- Lanthanoid
- Actinoid
- Post-transition
- Metalloid
- Nonmetal
- Halogen
- Noble gas
- Unknown

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
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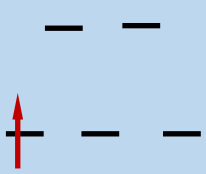
CRYSTAL FIELD EFFECTS

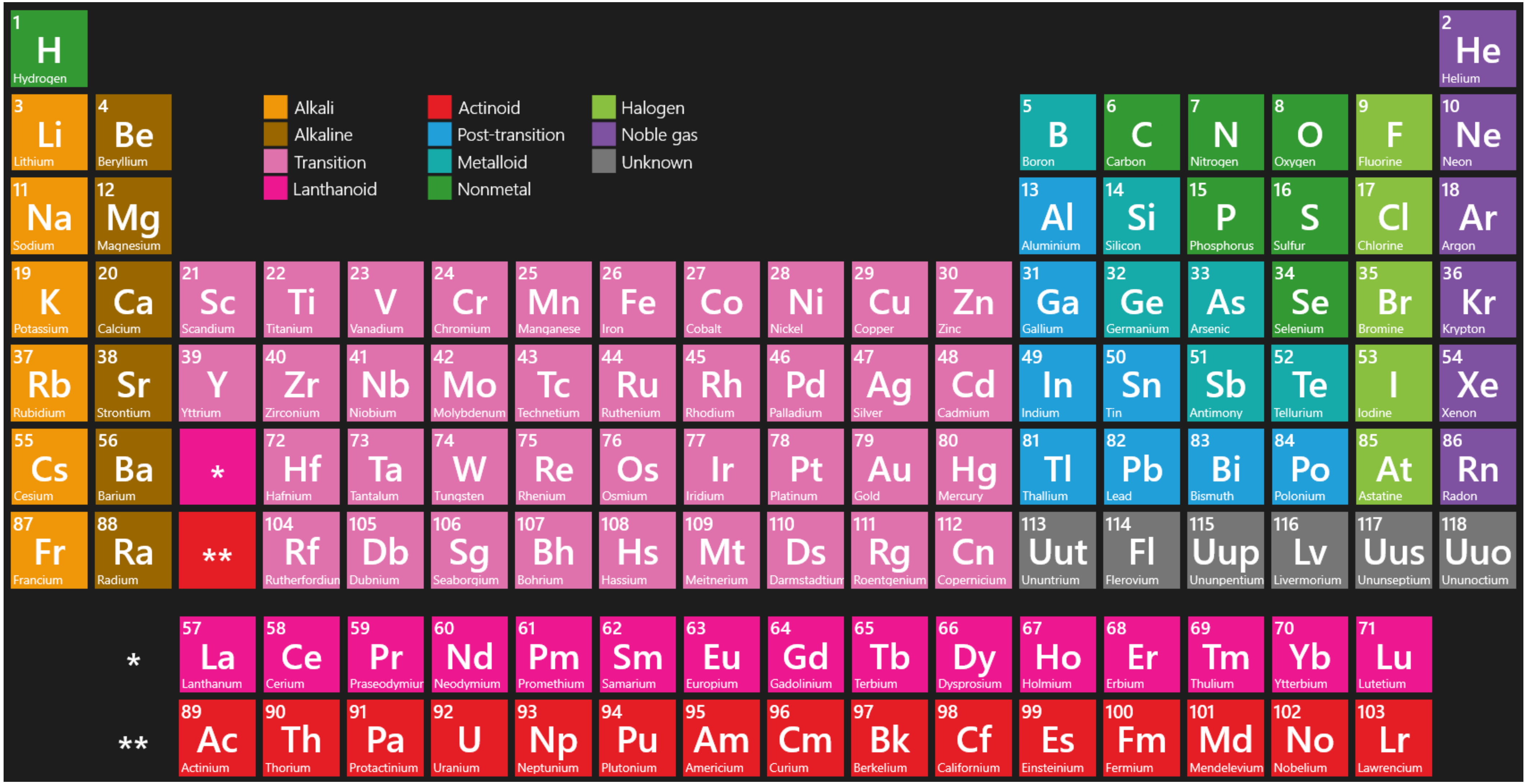
octahedral environment

d^1

$Sc^{2+}/Ti^{3+}/V^{4+}/Cr^{5+}$

S = 1/2





■ Alkali
■ Alkaline
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■ Lanthanoid
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■ Nonmetal
■ Halogen
■ Noble gas
■ Unknown

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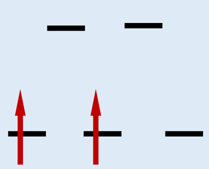
CRYSTAL FIELD EFFECTS

octahedral environment

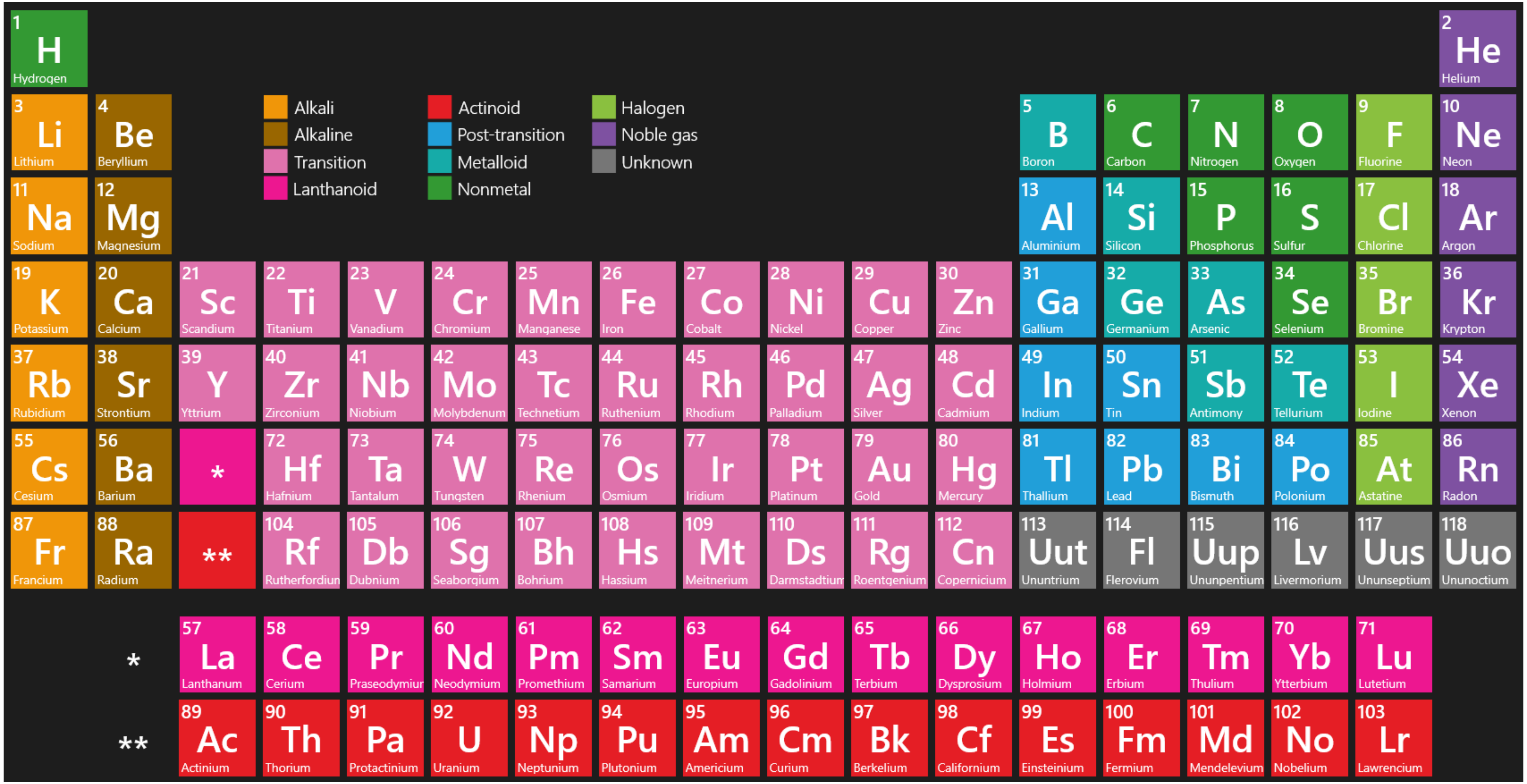
d^2

$Ti^{2+}/V^{3+}/Cr^{4+}$

S = 1



!!! maximize S !!!



- 🟧 Alkali
- 🟫 Alkaline
- ▨ Transition
- ▨ Lanthanoid
- 🟥 Actinoid
- 🟦 Post-transition
- ▨ Metalloid
- 🟩 Nonmetal
- ▨ Halogen
- 🟪 Noble gas
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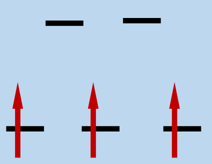
CRYSTAL FIELD EFFECTS

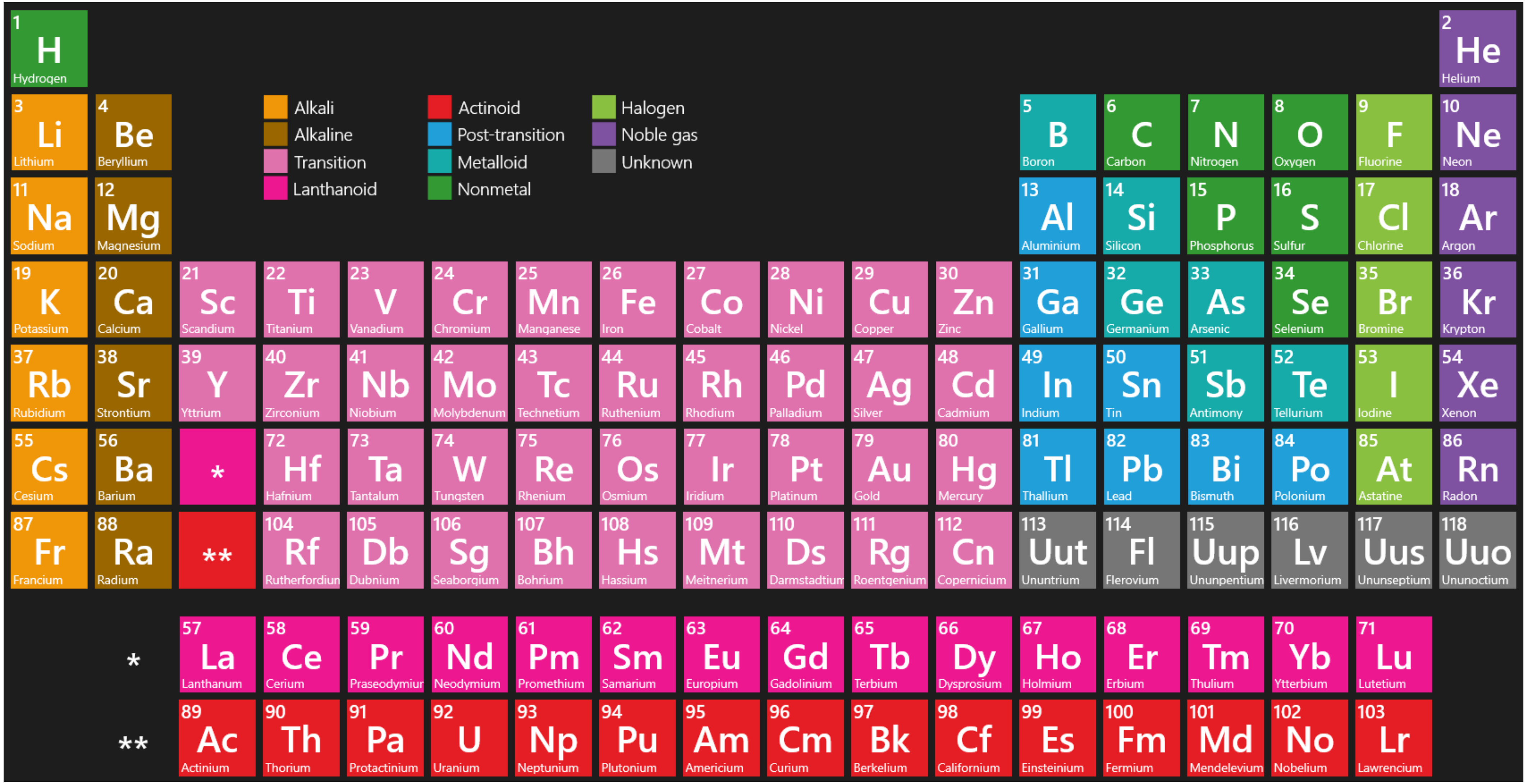
octahedral environment

d^3

$V^{2+}/Cr^{3+}/Mn^{4+}$

$S = 3/2$





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■ Alkaline
■ Transition
■ Lanthanoid
■ Actinoid
■ Post-transition
■ Metalloid
■ Nonmetal
■ Halogen
■ Noble gas
■ Unknown

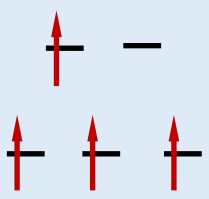
CRYSTAL FIELD EFFECTS

octahedral environment

d^4

Cr^{2+}/Mn^{3+}

S = 2



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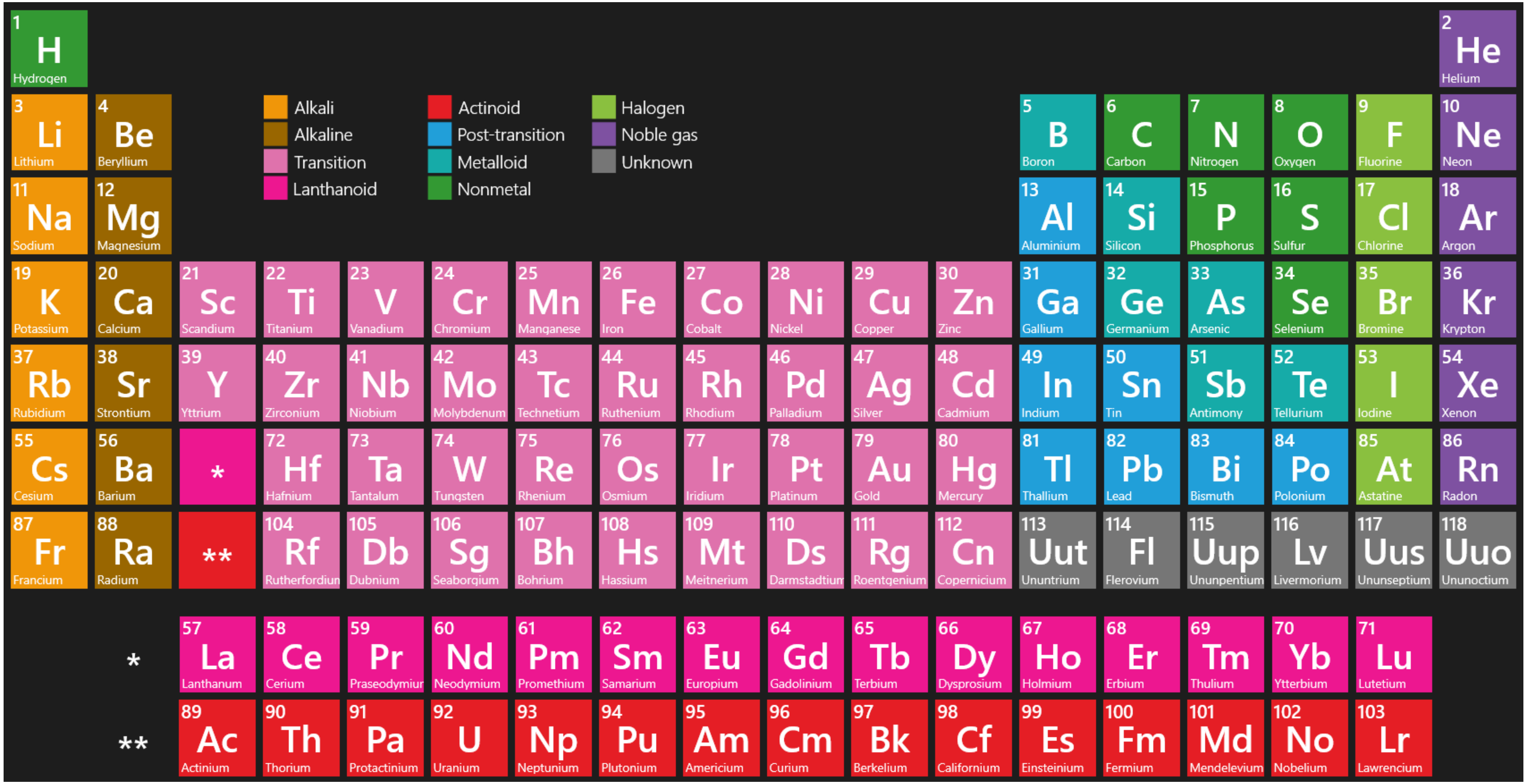

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🟧 Alkali	🟥 Actinoid	🟩 Halogen
🟫 Alkaline	🟦 Post-transition	🟪 Noble gas
▨ Transition	▨ Metalloid	⬜ Unknown
▨ Lanthanoid	🟩 Nonmetal	

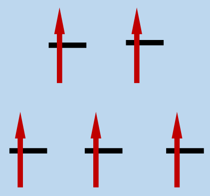
CRYSTAL FIELD EFFECTS

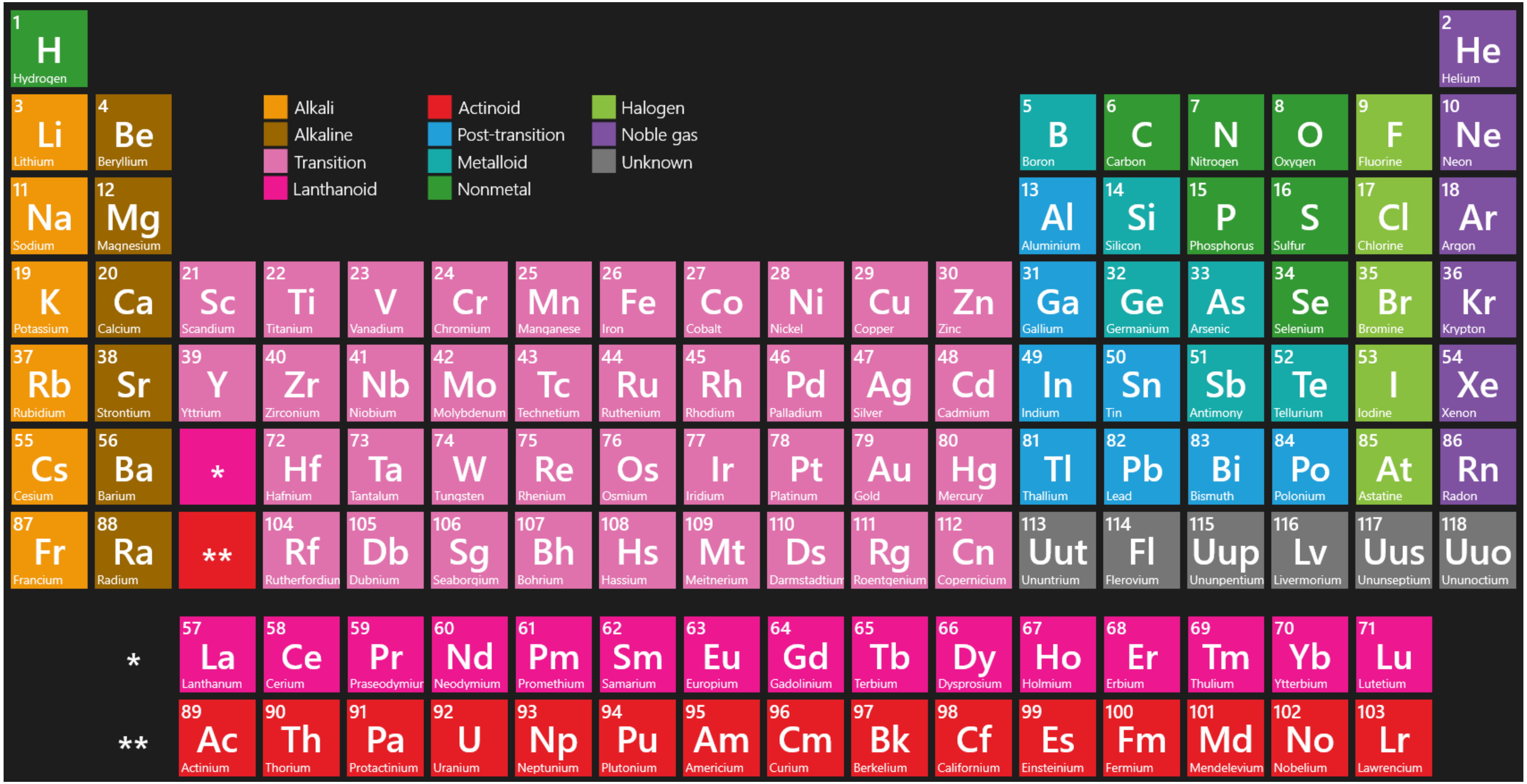
octahedral environment

d^5

Mn^{2+}/Fe^{3+}

S = 5/2





- 🟧 Alkali
- 🟫 Alkaline
- 🟪 Transition
- 🟥 Lanthanoid
- 🟥 Actinoid
- 🟦 Post-transition
- 🟦 Metalloid
- 🟩 Nonmetal
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- 🟪 Noble gas
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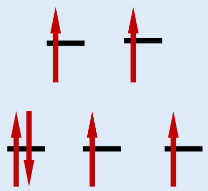
CRYSTAL FIELD EFFECTS

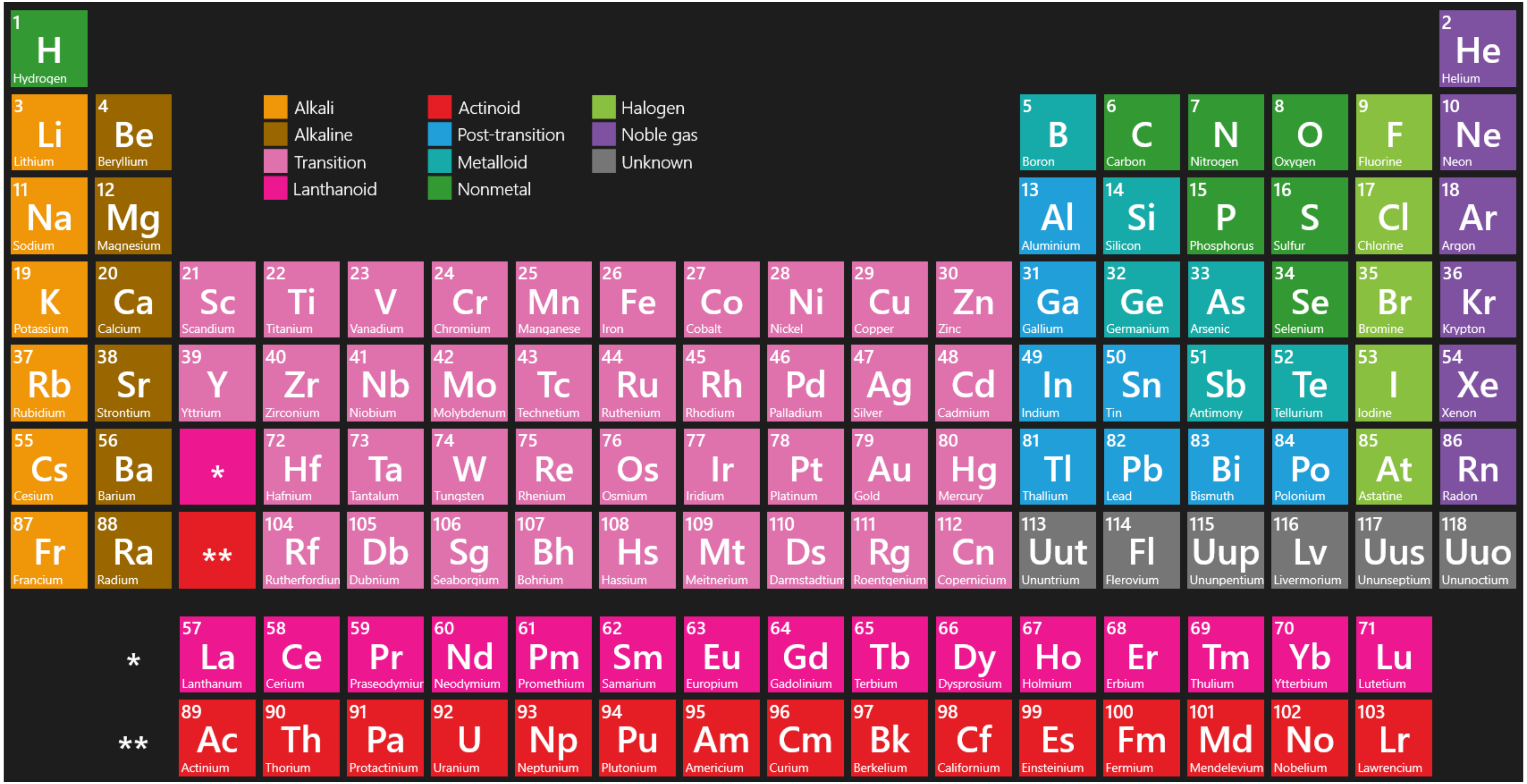
octahedral environment

d^6

Fe^{2+}/Co^{3+}

S = 2





🟧 Alkali
🟫 Alkaline
▨ Transition
▨ Lanthanoid
🟥 Actinoid
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▨ Halogen
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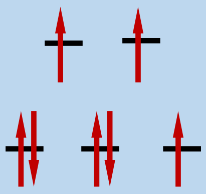
CRYSTAL FIELD EFFECTS

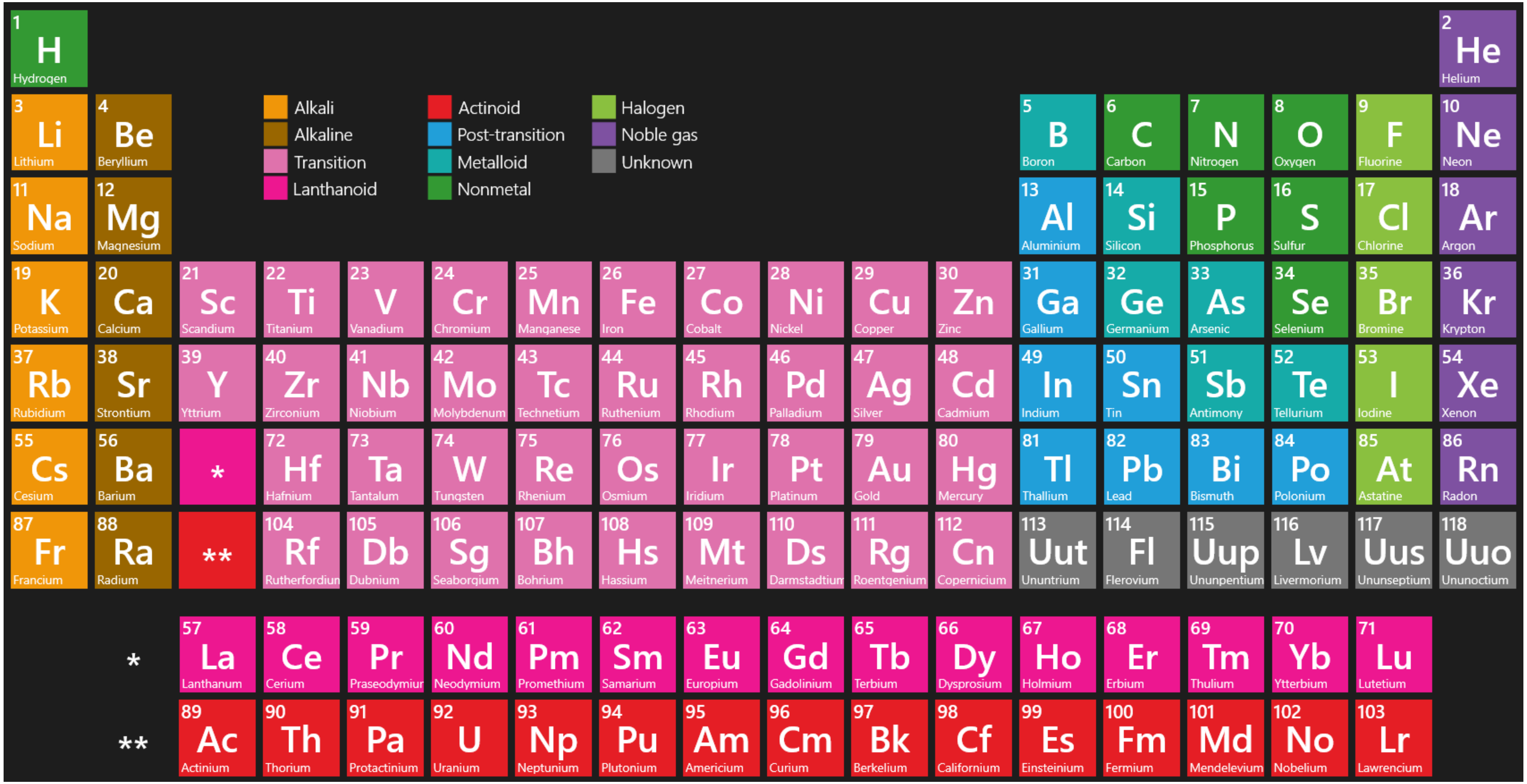
octahedral environment

d^7

Co^{2+}

S = 3/2





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87 Fr Francium	88 Ra Radium	**	104 Rf Rutherfordiun	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtiur	111 Rg Roentgenium	112 Cn Copernicium	113 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium
	*	57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymiur	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium	
	**	89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium	

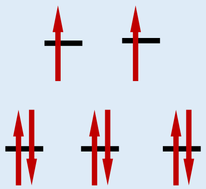
CRYSTAL FIELD EFFECTS

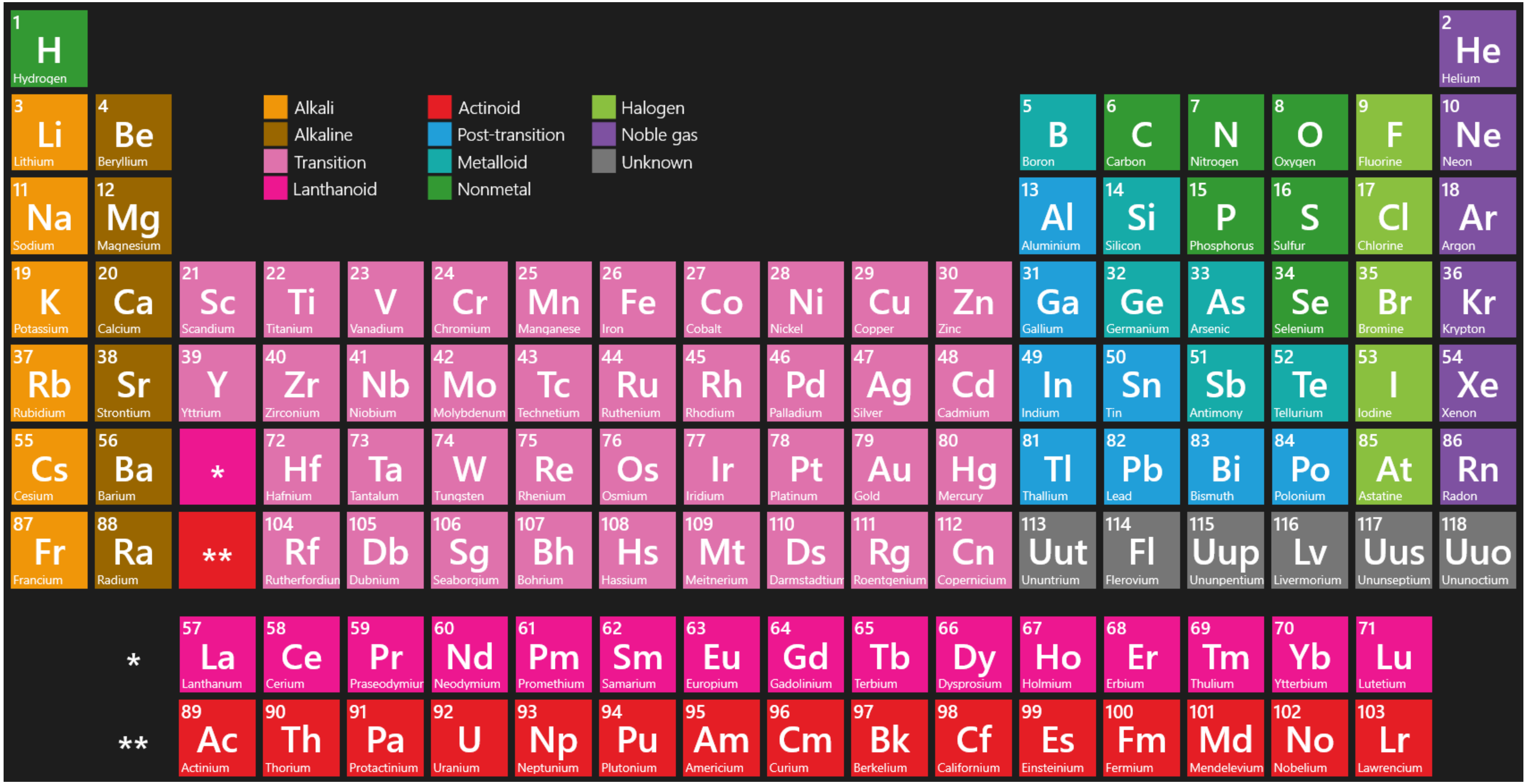
octahedral environment

d^8

Ni^{2+}

S = 1





1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
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- Alkali
- Alkaline
- Transition
- Lanthanoid
- Actinoid
- Post-transition
- Metalloid
- Nonmetal
- Halogen
- Noble gas
- Unknown

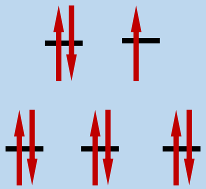
CRYSTAL FIELD EFFECTS

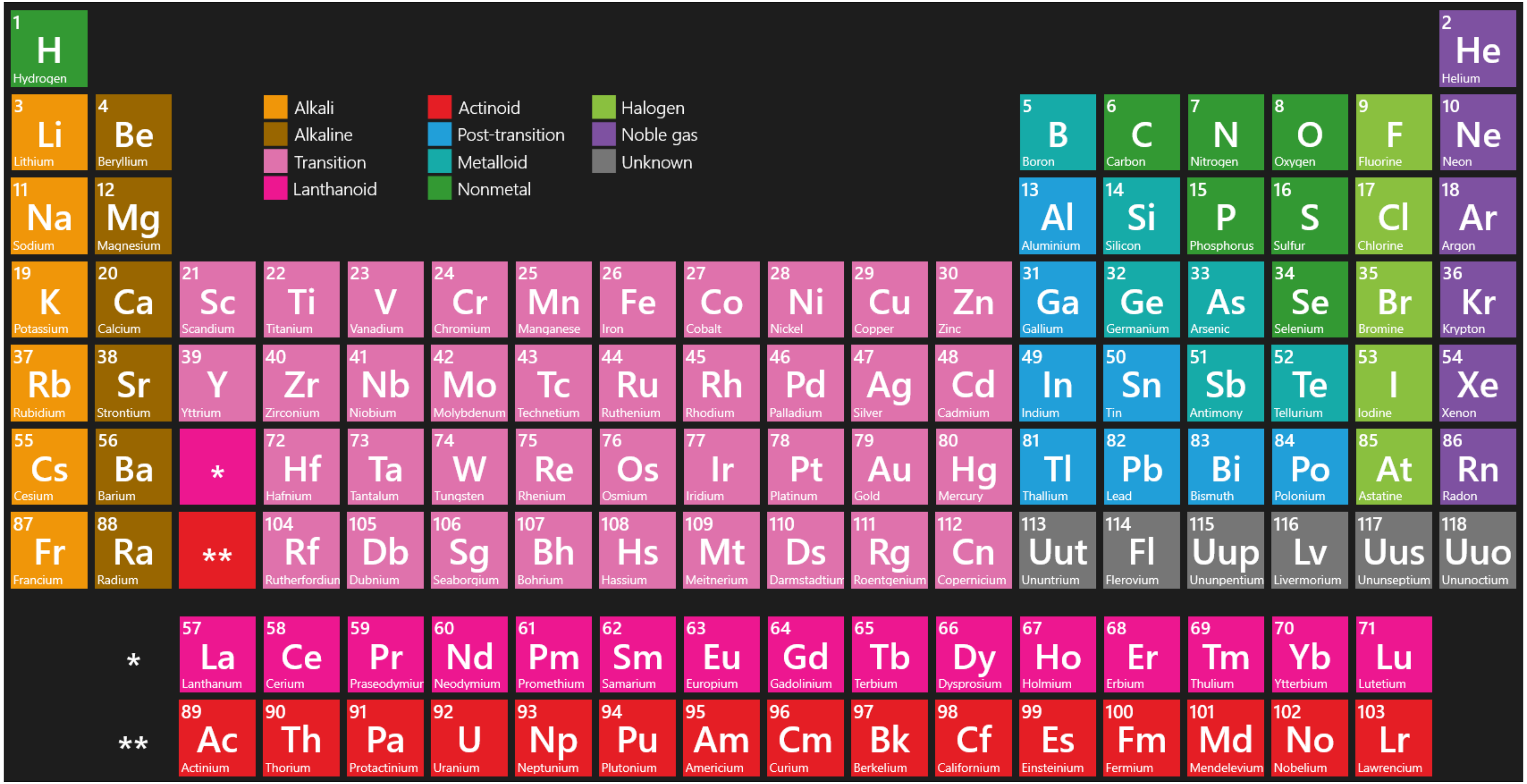
octahedral environment

d^9

Cu^{2+}

S = 1/2





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- 🟧 Alkali
- 🟫 Alkaline
- 🟪 Transition
- 🟥 Lanthanoid
- 🟥 Actinoid
- 🟦 Post-transition
- 🟦 Metalloid
- 🟩 Nonmetal
- 🟩 Halogen
- 🟪 Noble gas
- ⬜ Unknown

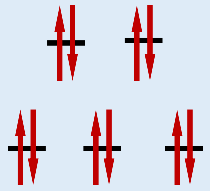
CRYSTAL FIELD EFFECTS

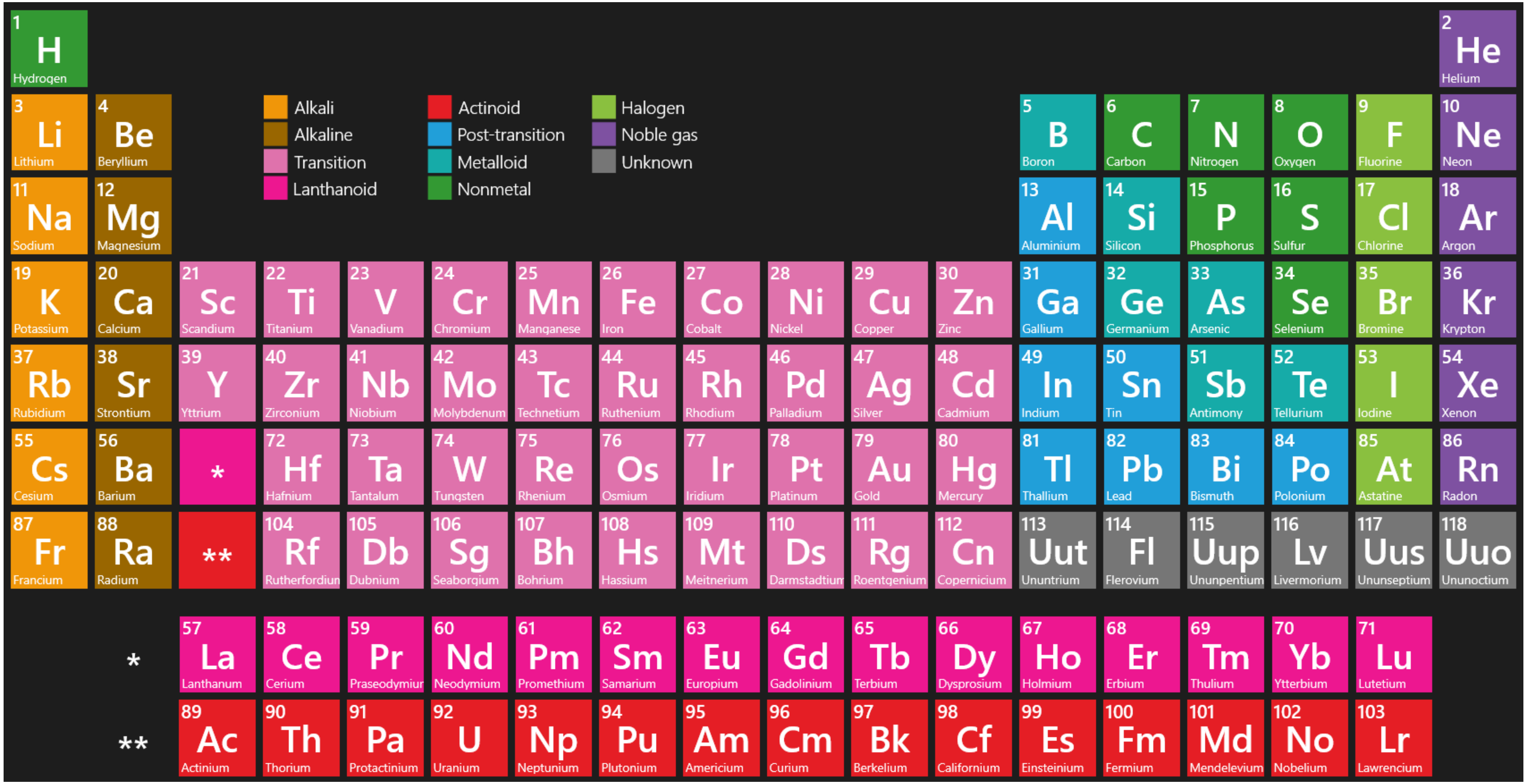
octahedral environment

d^{10}

Cu^{1+}/Zn^{2+}

S = 0





■ Alkali
■ Alkaline
■ Transition
■ Lanthanoid
■ Actinoid
■ Post-transition
■ Metalloid
■ Nonmetal
■ Halogen
■ Noble gas
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55 Cs Cesium	56 Ba Barium	*	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
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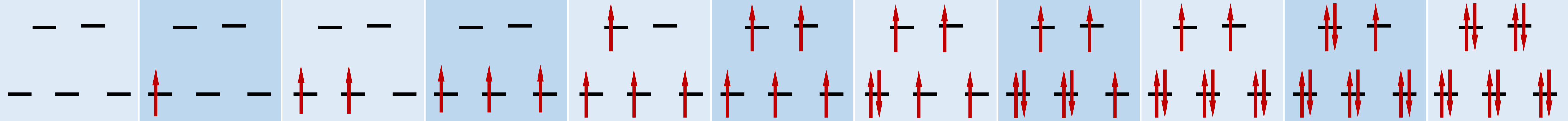
CRYSTAL FIELD EFFECTS

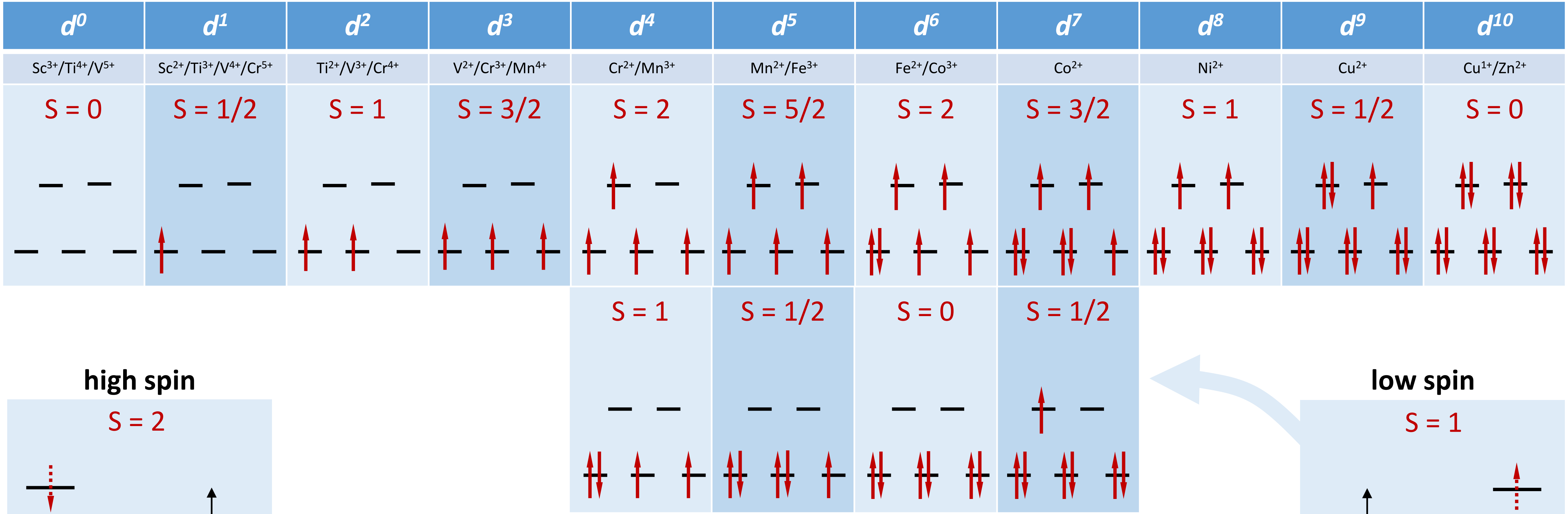
octahedral environment

d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
$Sc^{3+}/Ti^{4+}/V^{5+}$	$Sc^{2+}/Ti^{3+}/V^{4+}/Cr^{5+}$	$Ti^{2+}/V^{3+}/Cr^{4+}$	$V^{2+}/Cr^{3+}/Mn^{4+}$	Cr^{2+}/Mn^{3+}	Mn^{2+}/Fe^{3+}	Fe^{2+}/Co^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cu^{1+}/Zn^{2+}
S = 0	S = 1/2	S = 1	S = 3/2	S = 2	S = 5/2	S = 2	S = 3/2	S = 1	S = 1/2	S = 0



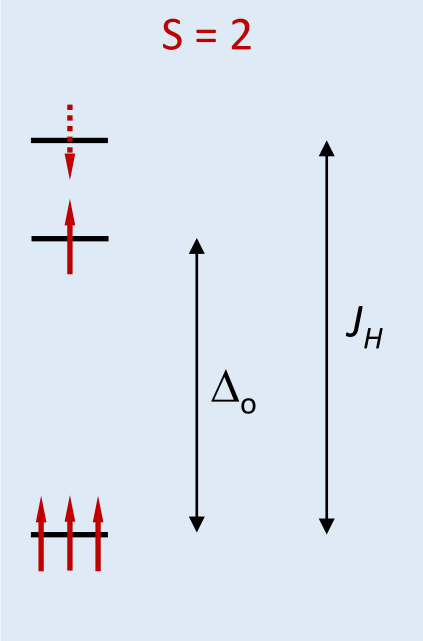
CRYSTAL FIELD EFFECTS

high spin/low spin

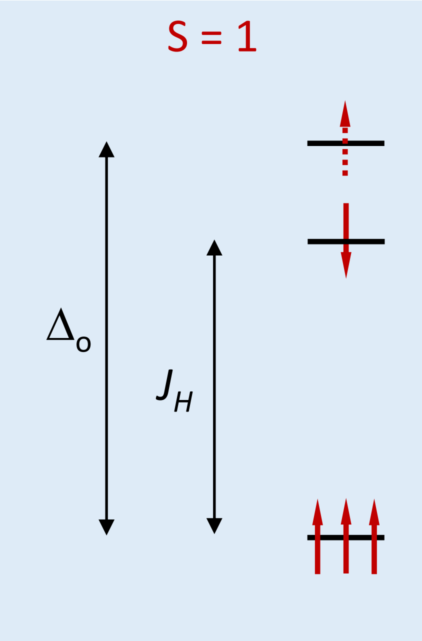


d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
$Sc^{3+}/Ti^{4+}/V^{5+}$	$Sc^{2+}/Ti^{3+}/V^{4+}/Cr^{5+}$	$Ti^{2+}/V^{3+}/Cr^{4+}$	$V^{2+}/Cr^{3+}/Mn^{4+}$	Cr^{2+}/Mn^{3+}	Mn^{2+}/Fe^{3+}	Fe^{2+}/Co^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cu^{1+}/Zn^{2+}
S = 0	S = 1/2	S = 1	S = 3/2	S = 2	S = 5/2	S = 2	S = 3/2	S = 1	S = 1/2	S = 0
				S = 1	S = 1/2	S = 0	S = 1/2			

high spin



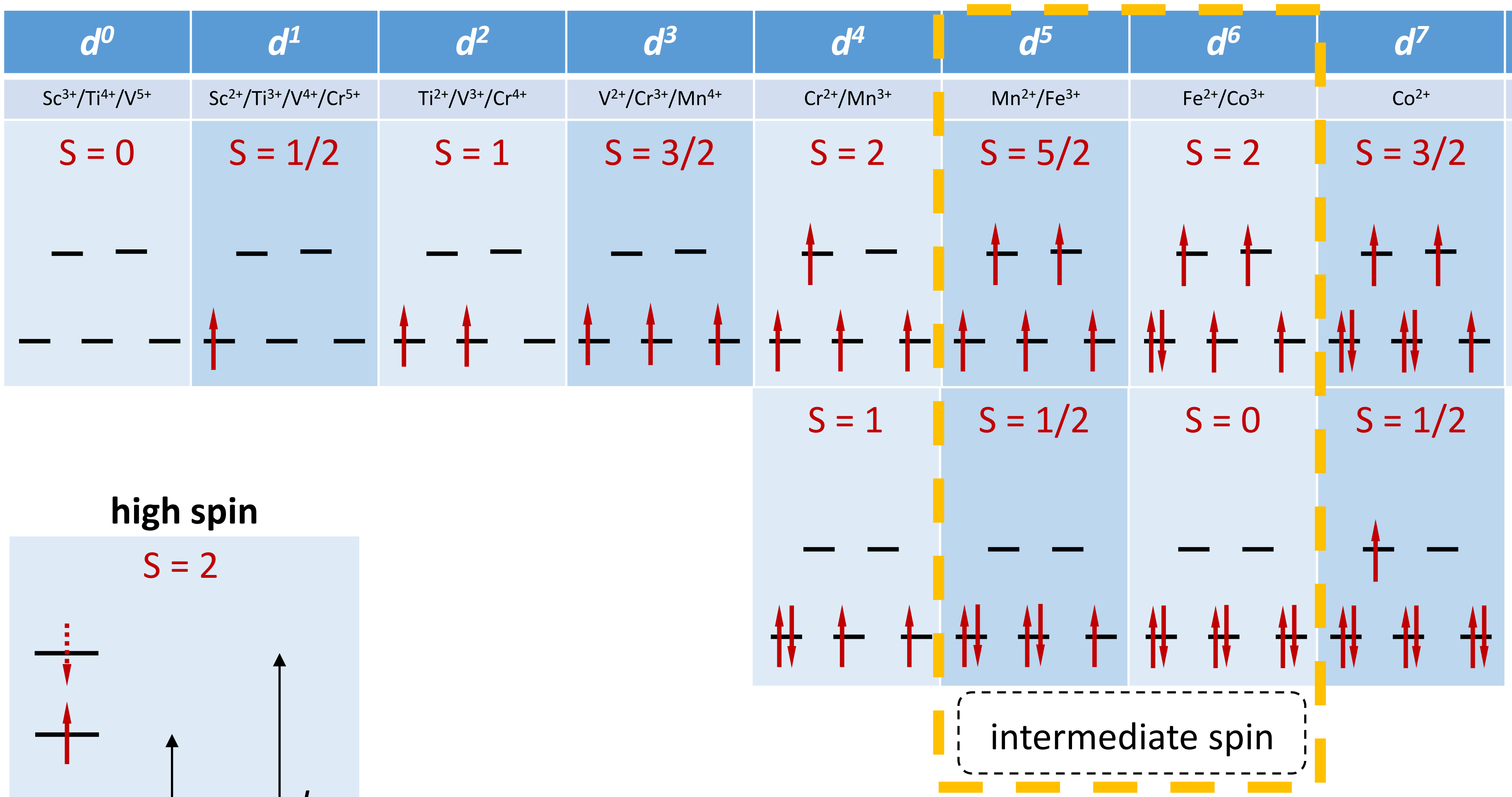
low spin



- ❖ if there would be no electron-electron repulsion ($J_H = 0$) → S = 1
- ❖ if $J_H > 0$ but $J_H < \Delta_o \rightarrow S = 1$
- ❖ if $J_H > \Delta_o \rightarrow S = 2$

CRYSTAL FIELD EFFECTS

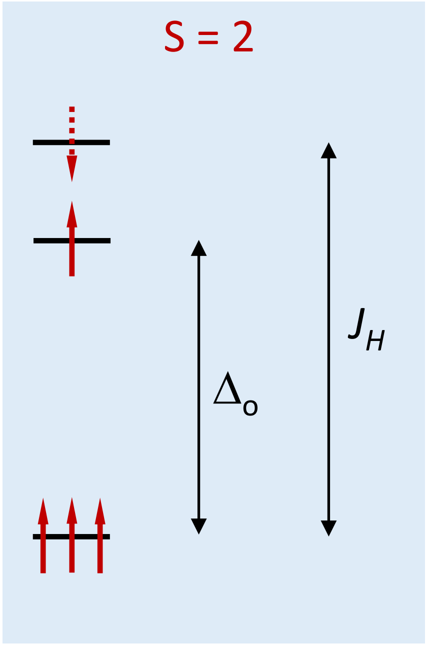
high spin/low spin



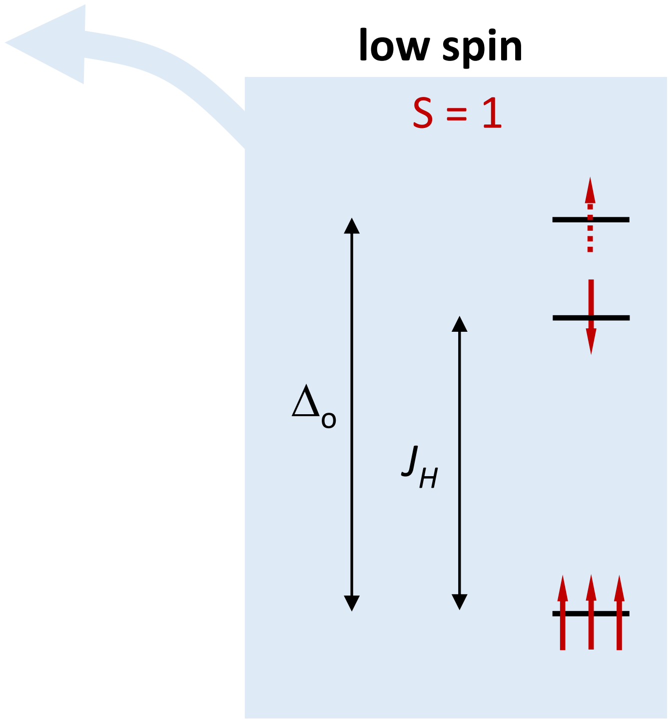
d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
$Sc^{3+}/Ti^{4+}/V^{5+}$	$Sc^{2+}/Ti^{3+}/V^{4+}/Cr^{5+}$	$Ti^{2+}/V^{3+}/Cr^{4+}$	$V^{2+}/Cr^{3+}/Mn^{4+}$	Cr^{2+}/Mn^{3+}	Mn^{2+}/Fe^{3+}	Fe^{2+}/Co^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cu^{1+}/Zn^{2+}
S = 0	S = 1/2	S = 1	S = 3/2	S = 2	S = 5/2	S = 2	S = 3/2	S = 1	S = 1/2	S = 0
				S = 1	S = 1/2	S = 0	S = 1/2			

intermediate spin

high spin

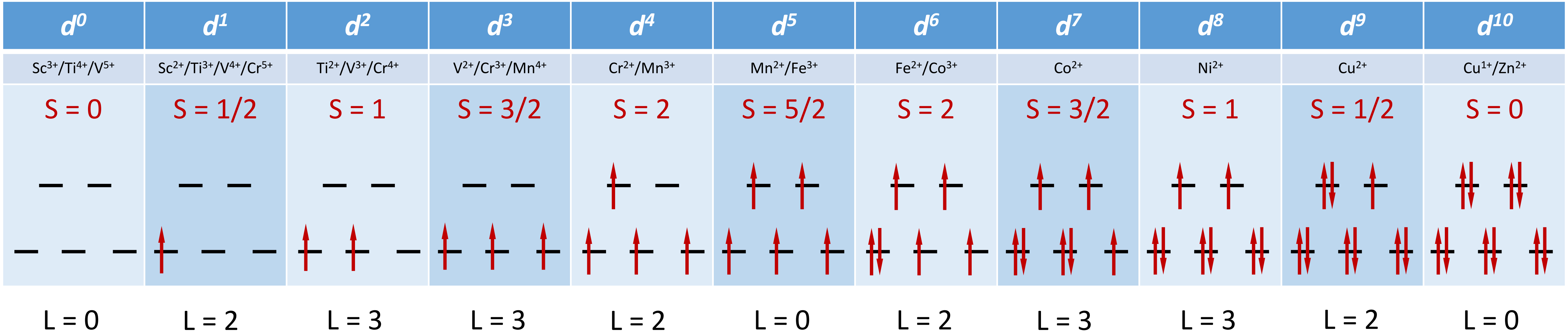


low spin

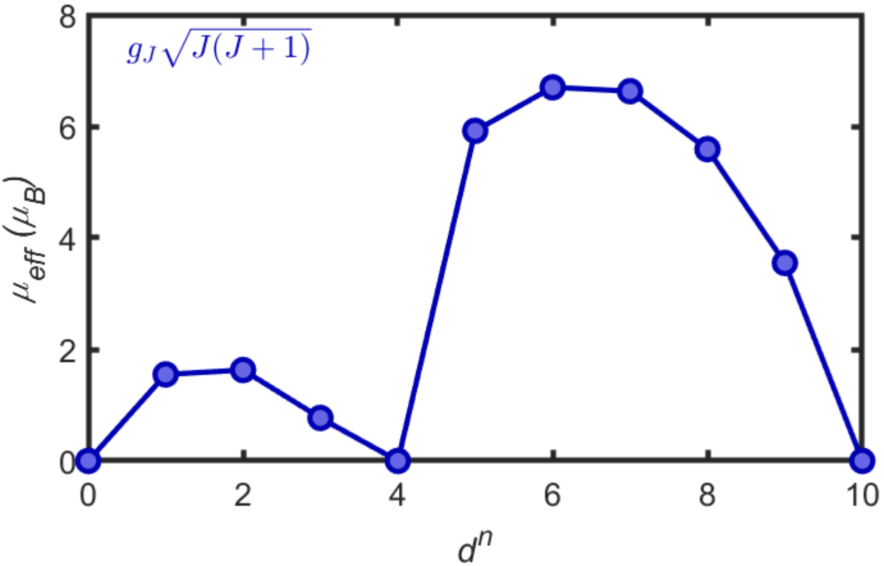


CRYSTAL FIELD EFFECTS

orbital quenching



d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc^{3+}/Ti^{4+}/V^{5+}	Sc^{2+}/Ti^{3+}/V^{4+}/Cr^{5+}	Ti^{2+}/V^{3+}/Cr^{4+}	V^{2+}/Cr^{3+}/Mn^{4+}	Cr^{2+}/Mn^{3+}	Mn^{2+}/Fe^{3+}	Fe^{2+}/Co^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cu^{1+}/Zn^{2+}
S = 0	S = 1/2	S = 1	S = 3/2	S = 2	S = 5/2	S = 2	S = 3/2	S = 1	S = 1/2	S = 0
L = 0	L = 2	L = 3	L = 3	L = 2	L = 0	L = 2	L = 3	L = 3	L = 2	L = 0

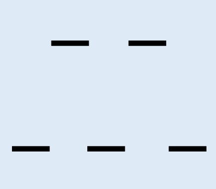
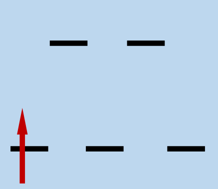
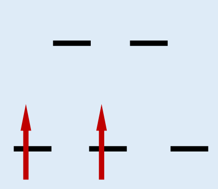
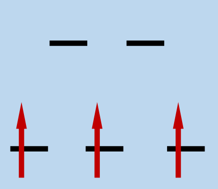
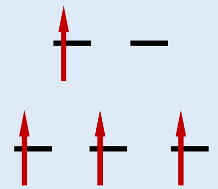
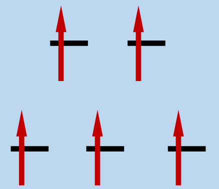
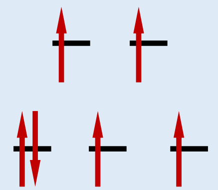
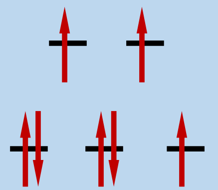
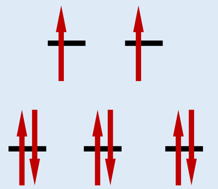
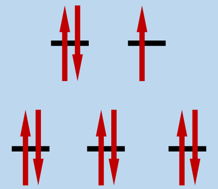
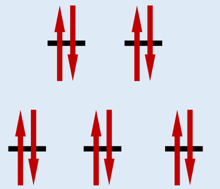


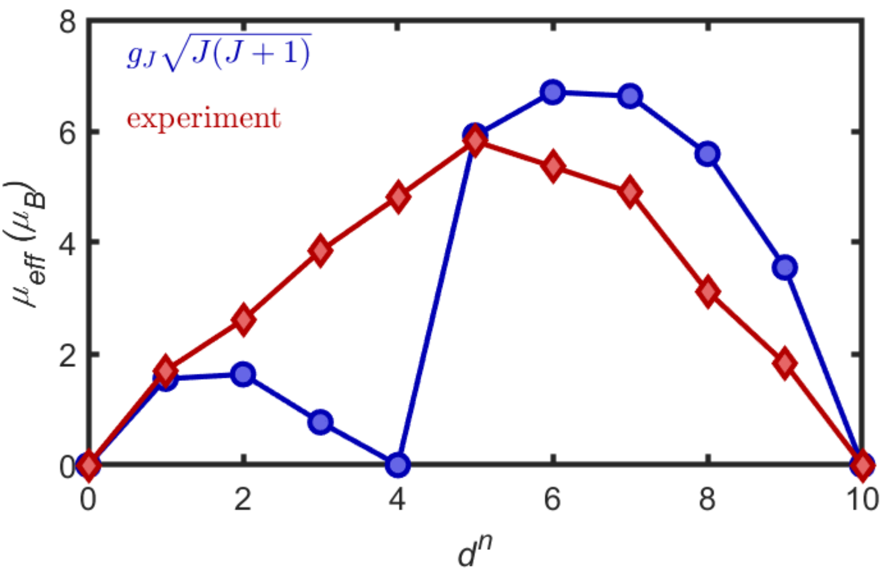
$$\chi = \frac{N_A \mu_0 g_J^2 \mu_B^2 J(J+1)}{3k_B T} = \frac{C}{T} = \frac{N_A \mu_0 \mu_{eff}^2}{3k_B T}$$

$$\mu_{eff}^2 = g_J^2 \mu_B^2 J(J+1)$$

CRYSTAL FIELD EFFECTS

orbital quenching

d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
$Sc^{3+}/Ti^{4+}/V^{5+}$	$Sc^{2+}/Ti^{3+}/V^{4+}/Cr^{5+}$	$Ti^{2+}/V^{3+}/Cr^{4+}$	$V^{2+}/Cr^{3+}/Mn^{4+}$	Cr^{2+}/Mn^{3+}	Mn^{2+}/Fe^{3+}	Fe^{2+}/Co^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cu^{1+}/Zn^{2+}
S = 0	S = 1/2	S = 1	S = 3/2	S = 2	S = 5/2	S = 2	S = 3/2	S = 1	S = 1/2	S = 0
										
L = 0	L = 2	L = 3	L = 3	L = 2	L = 0	L = 2	L = 3	L = 3	L = 2	L = 0



CRYSTAL FIELD EFFECTS

orbital quenching

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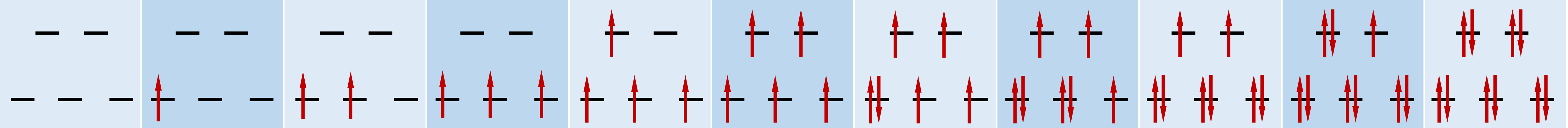
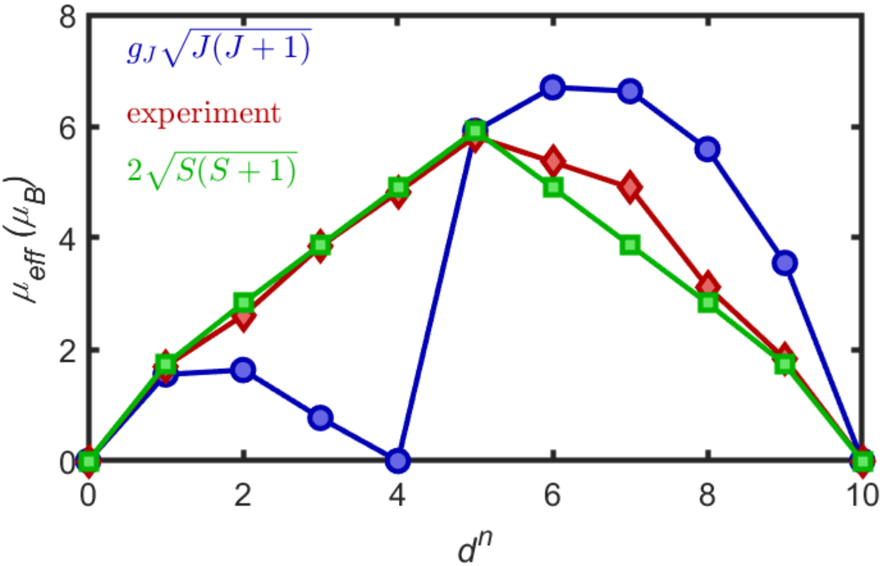
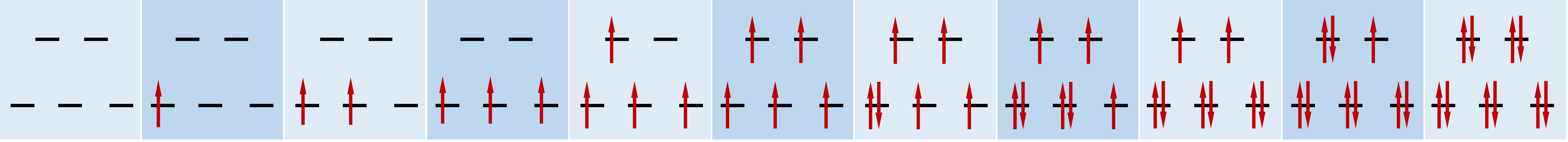
$Sc^{3+}/Ti^{4+}/V^{5+}$	$Sc^{2+}/Ti^{3+}/V^{4+}/Cr^{5+}$	$Ti^{2+}/V^{3+}/Cr^{4+}$	$V^{2+}/Cr^{3+}/Mn^{4+}$	Cr^{2+}/Mn^{3+}	Mn^{2+}/Fe^{3+}	Fe^{2+}/Co^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cu^{1+}/Zn^{2+}
S = 0	S = 1/2	S = 1	S = 3/2	S = 2	S = 5/2	S = 2	S = 3/2	S = 1	S = 1/2	S = 0
L = 0	L = 2	L = 3	L = 3	L = 2	L = 0	L = 2	L = 3	L = 3	L = 2	L = 0



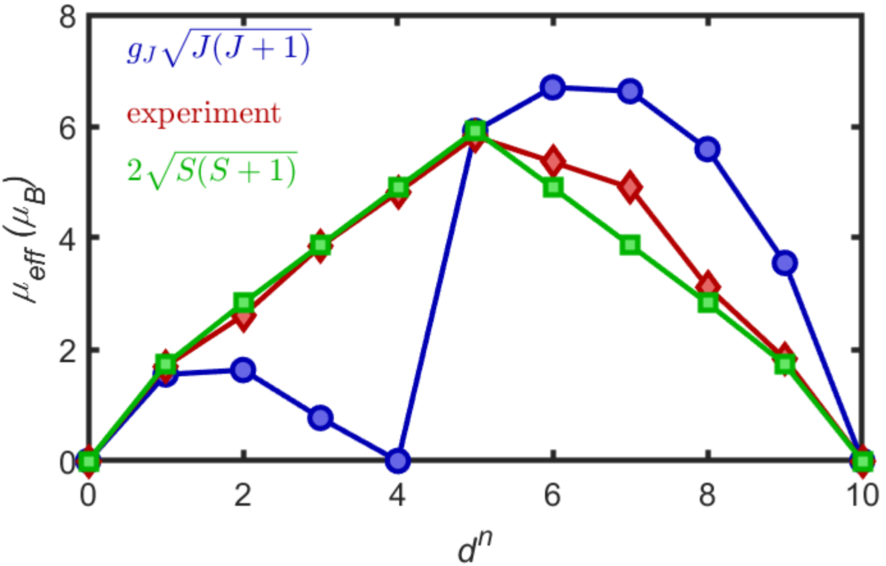


CRYSTAL FIELD EFFECTS

orbital quenching



d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
$Sc^{3+}/Ti^{4+}/V^{5+}$	$Sc^{2+}/Ti^{3+}/V^{4+}/Cr^{5+}$	$Ti^{2+}/V^{3+}/Cr^{4+}$	$V^{2+}/Cr^{3+}/Mn^{4+}$	Cr^{2+}/Mn^{3+}	Mn^{2+}/Fe^{3+}	Fe^{2+}/Co^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cu^{1+}/Zn^{2+}
S = 0	S = 1/2	S = 1	S = 3/2	S = 2	S = 5/2	S = 2	S = 3/2	S = 1	S = 1/2	S = 0
L = 0	L = 2	L = 3	L = 3	L = 2	L = 0	L = 2	L = 3	L = 3	L = 2	L = 0



- ❖ **J = L + S** does not work $\qquad \mathcal{H}_0 > \mathcal{H}_{CF} > \mathcal{H}_{SO} \gg \mathcal{H}_Z$
- ❖ L is 'quenched'
- ❖ point charges break the rotational symmetry

$$V_{CF}^{oct}(r) \sim x^4 + y^4 + z^4 - \frac{3}{5}r^4$$

real

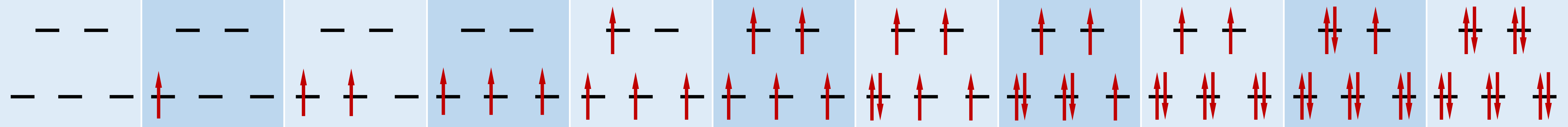
$$\hat{\boldsymbol{L}} = -i\hat{\boldsymbol{r}}\times\nabla \xrightarrow{\text{imaginary}}$$

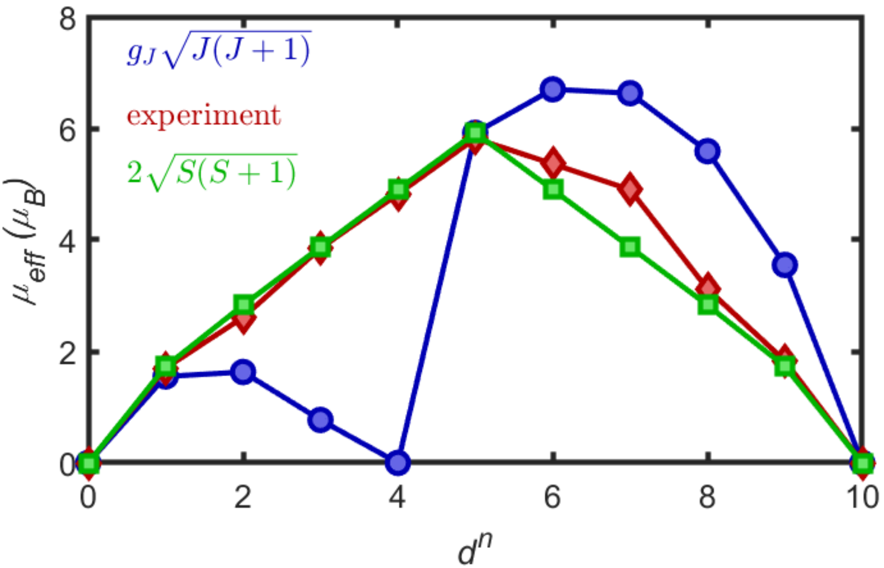
Hermitian, so $\langle 0|\hat{\boldsymbol{L}}|0\rangle \in \mathbb{R}$ only if $\langle 0|\hat{\boldsymbol{L}}|0\rangle = 0$

CRYSTAL FIELD EFFECTS

orbital quenching

d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
$Sc^{3+}/Ti^{4+}/V^{5+}$	$Sc^{2+}/Ti^{3+}/V^{4+}/Cr^{5+}$	$Ti^{2+}/V^{3+}/Cr^{4+}$	$V^{2+}/Cr^{3+}/Mn^{4+}$	Cr^{2+}/Mn^{3+}	Mn^{2+}/Fe^{3+}	Fe^{2+}/Co^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cu^{1+}/Zn^{2+}
S = 0	S = 1/2	S = 1	S = 3/2	S = 2	S = 5/2	S = 2	S = 3/2	S = 1	S = 1/2	S = 0
L = 0	L = 2	L = 3	L = 3	L = 2	L = 0	L = 2	L = 3	L = 3	L = 2	L = 0





❖ in practice: incomplete quenching

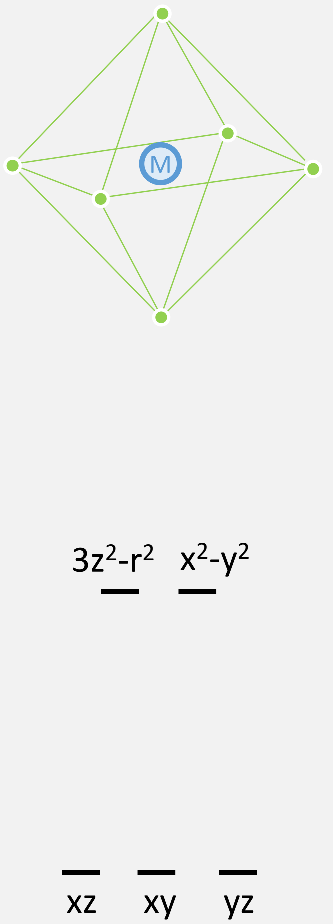
- t_{2g} subset (*n*=1,2,6,7), 'effective' $L = 1$
- spin-orbit coupling

❖ reflected in $g > 2$ and often anisotropic

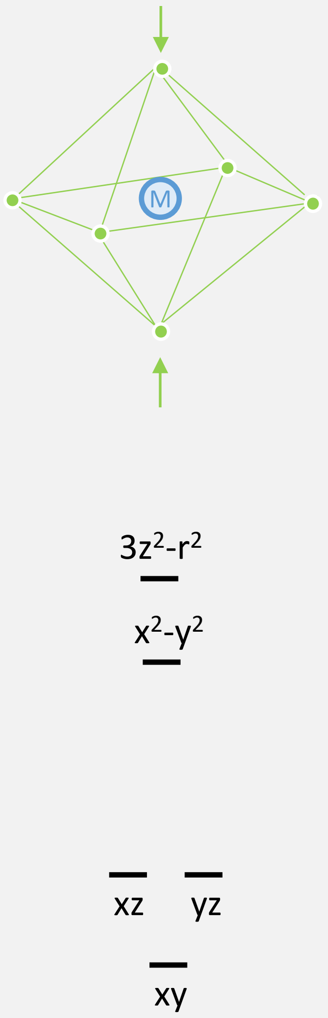
CRYSTAL FIELD EFFECTS

other environments

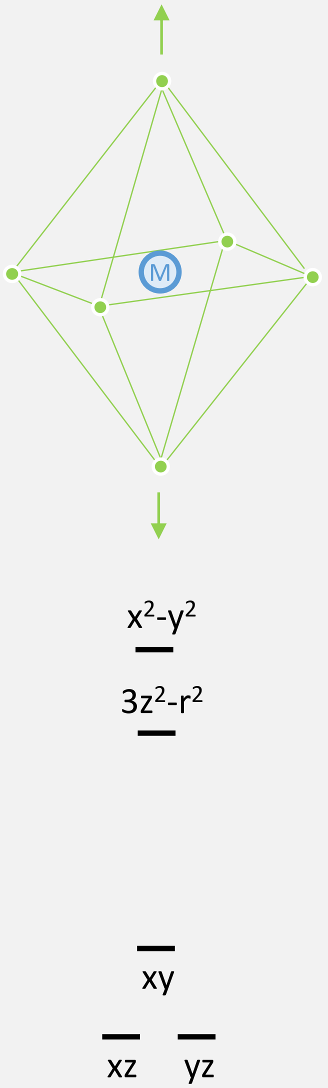
octahedral



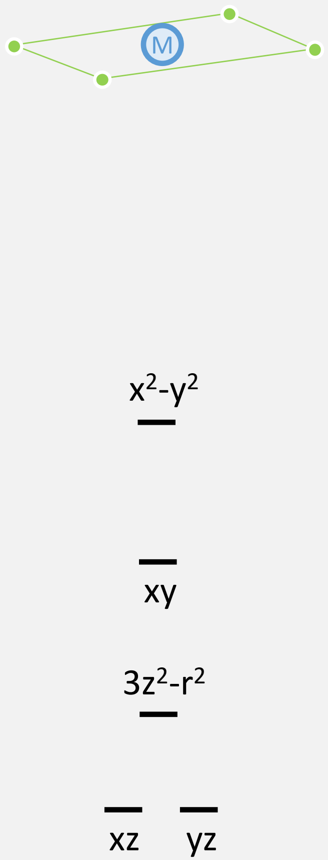
tetragonal compression



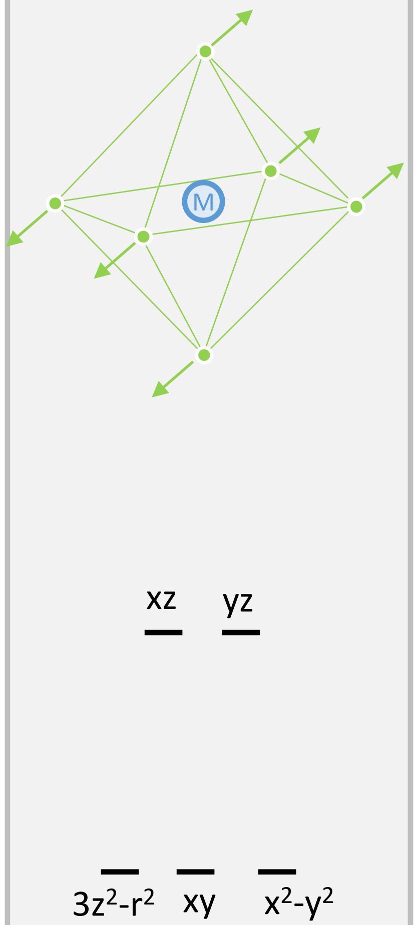
tetragonal elongation



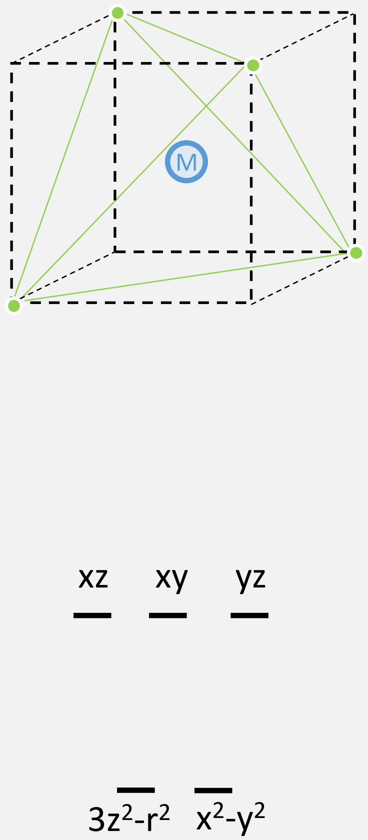
square planar



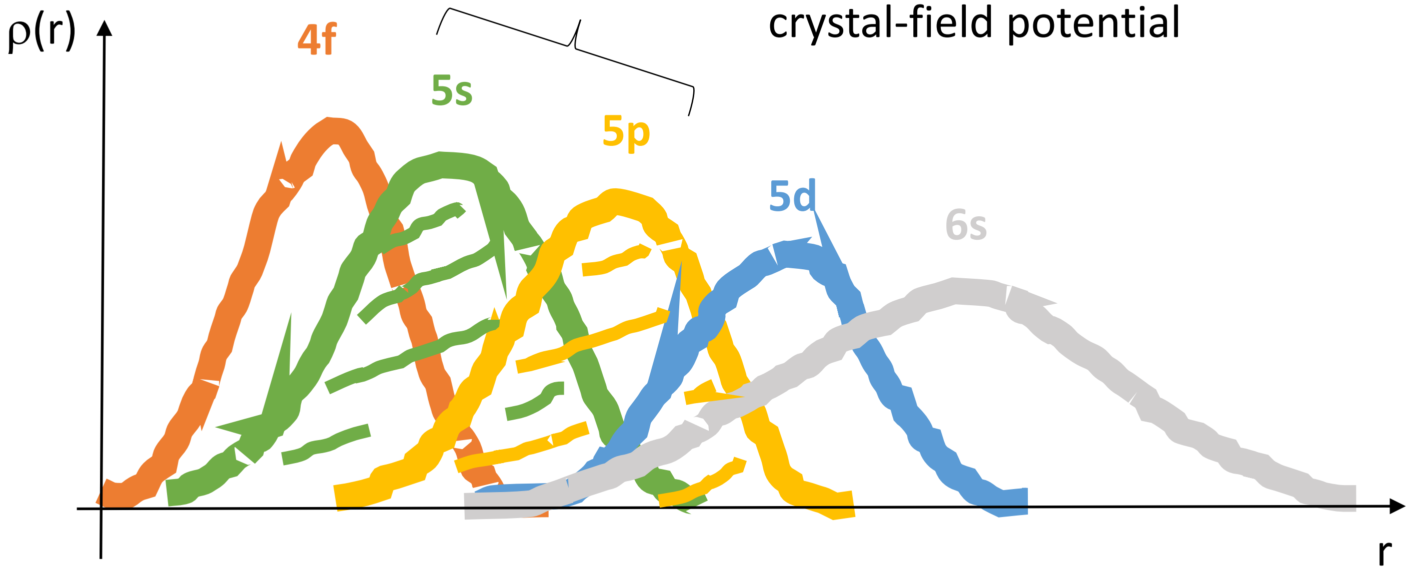
trigonal prism



tetrahedral



$$\mathcal{H}_0 > \mathcal{H}_{SO} > \mathcal{H}_{CF} > \mathcal{H}_Z$$

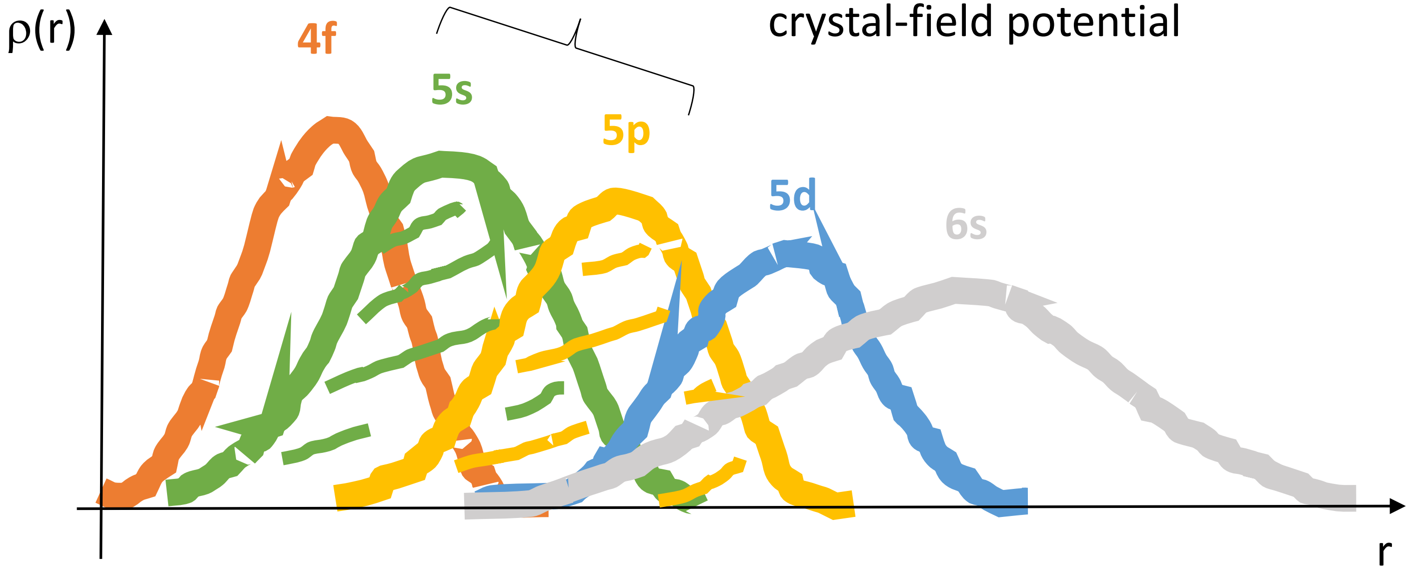


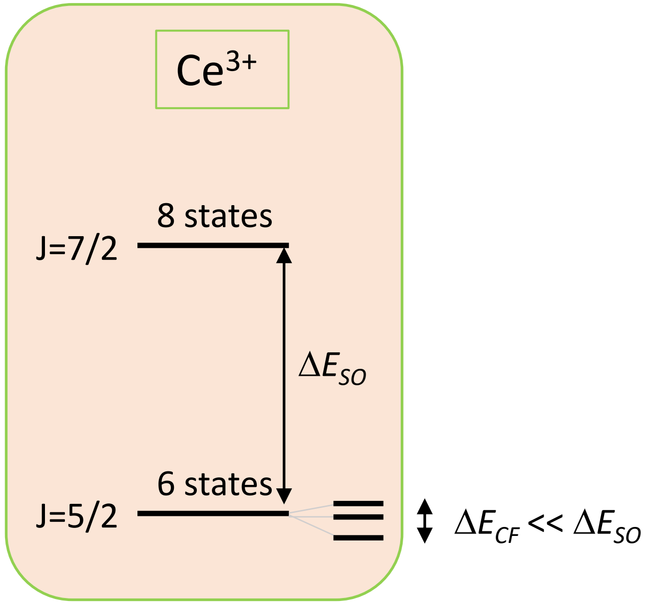
CRYSTAL FIELD EFFECTS

4f orbitals

$$\mathcal{H}_0 > \mathcal{H}_{SO} > \mathcal{H}_{CF} > \mathcal{H}_Z$$

shielding of 4f electrons from the crystal-field potential





Ce^{3+}

8 states

J=7/2

ΔE_{SO}

6 states

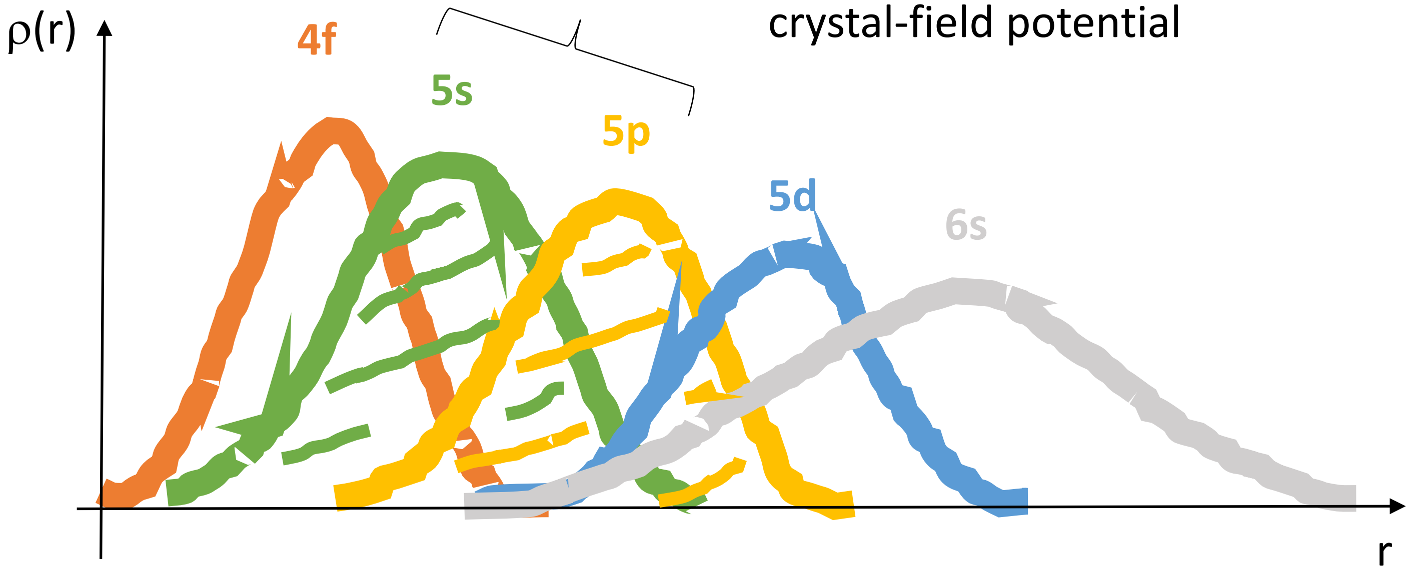
J=5/2

$\Delta E_{CF} << \Delta E_{SO}$

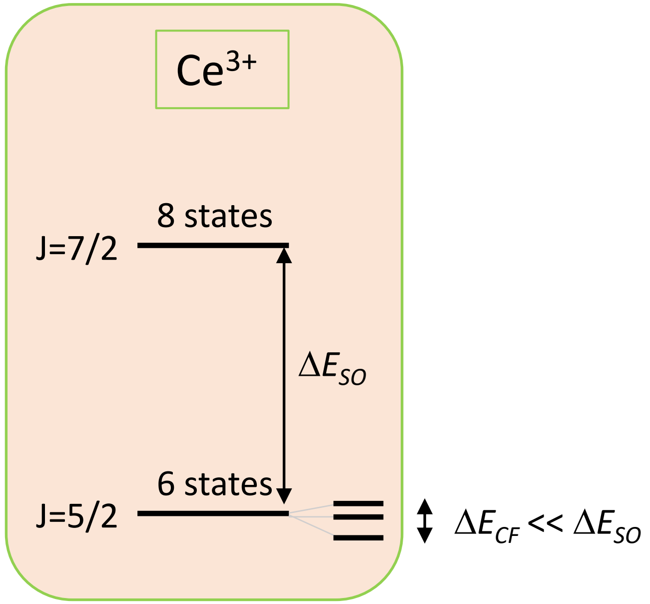
CRYSTAL FIELD EFFECTS

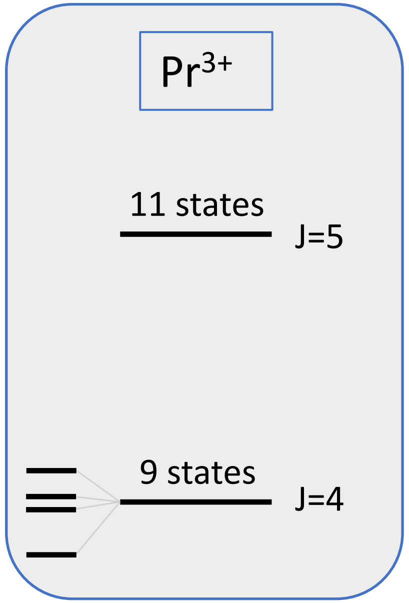
4f orbitals

$$\mathcal{H}_0 > \mathcal{H}_{SO} > \mathcal{H}_{CF} > \mathcal{H}_Z$$



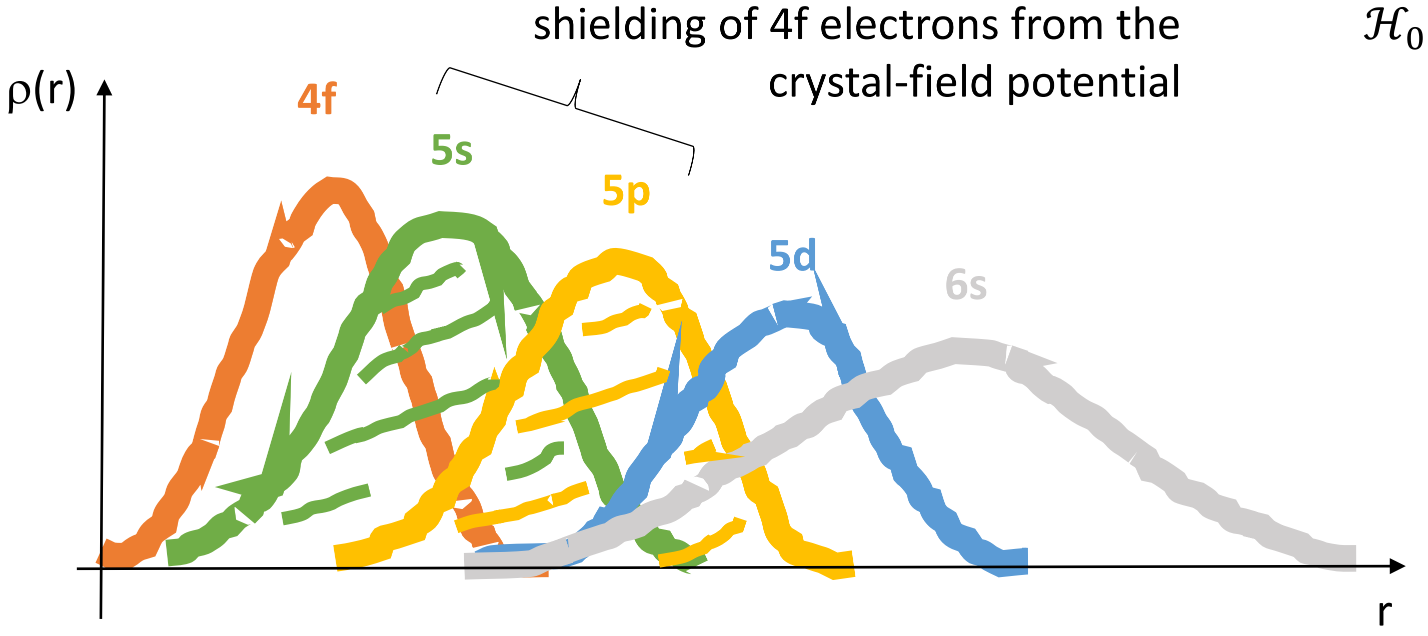
shielding of 4f electrons from the crystal-field potential



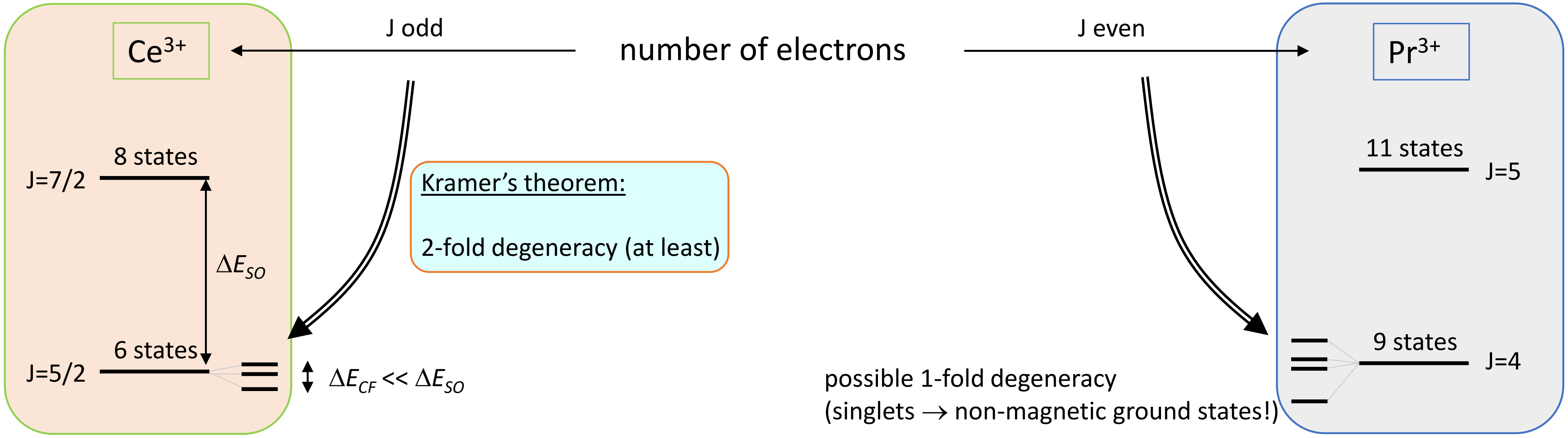


CRYSTAL FIELD EFFECTS

$$\mathcal{H}_0 > \mathcal{H}_{SO} > \mathcal{H}_{CF} > \mathcal{H}_Z$$



shielding of 4f electrons from the crystal-field potential



number of electrons

J odd

J even

Ce^{3+}

J=7/2 — 8 states

ΔE_{SO}

J=5/2 — 6 states

$\Delta E_{CF} << \Delta E_{SO}$

<u>Kramer's theorem:</u>

2-fold degeneracy (at least)

Pr^{3+}

11 states — J=5

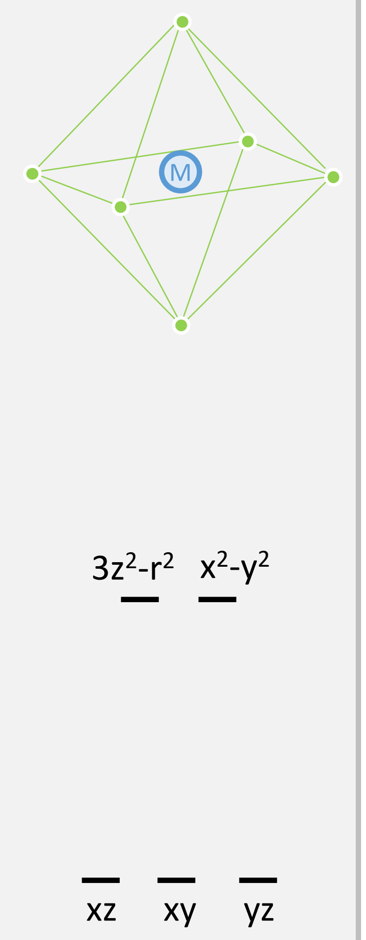
9 states — J=4

possible 1-fold degeneracy
(singlets → non-magnetic ground states!)

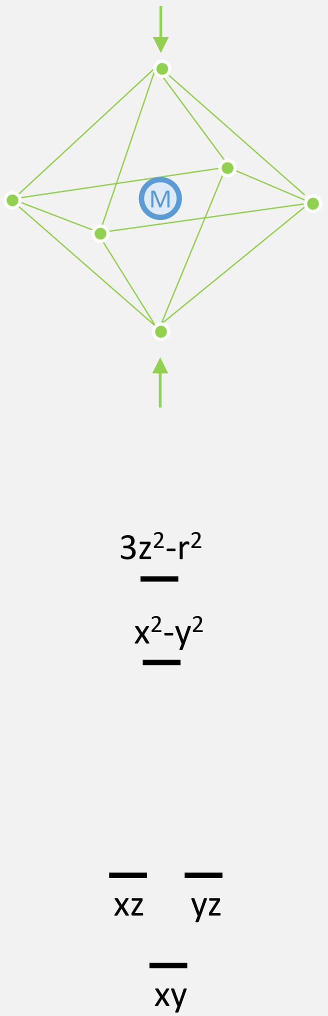
CRYSTAL FIELD EFFECTS

other environments

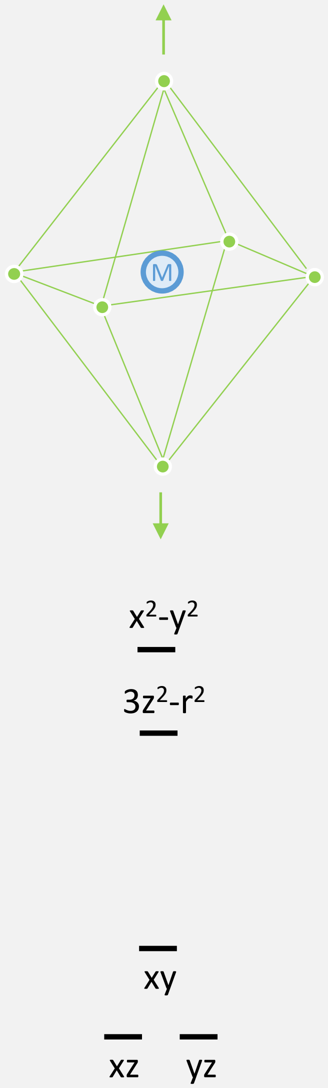
octahedral



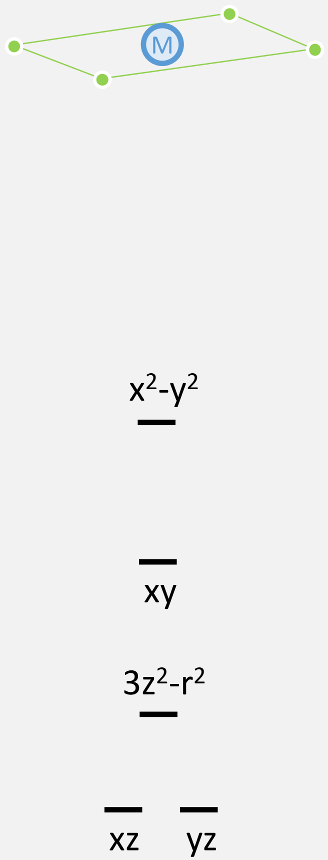
tetragonal compression



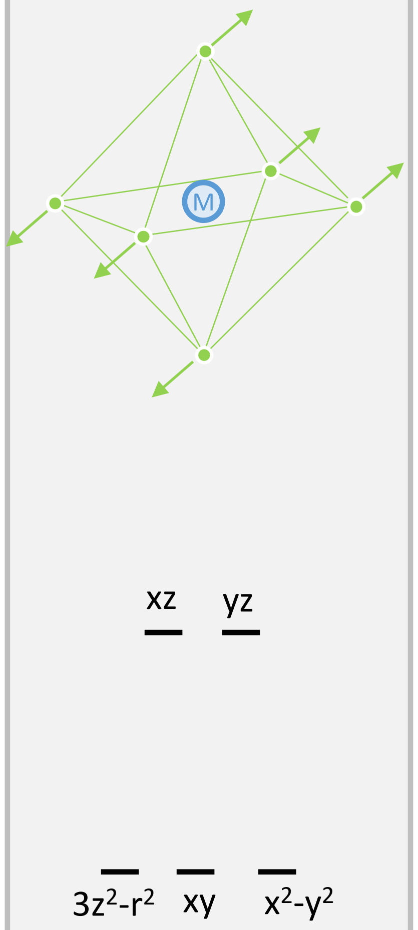
tetragonal elongation



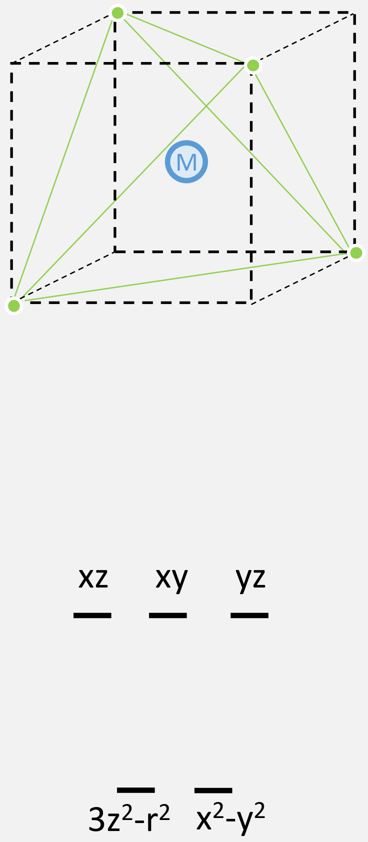
square planar



trigonal prism

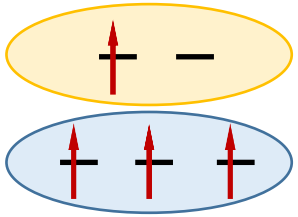


tetrahedral



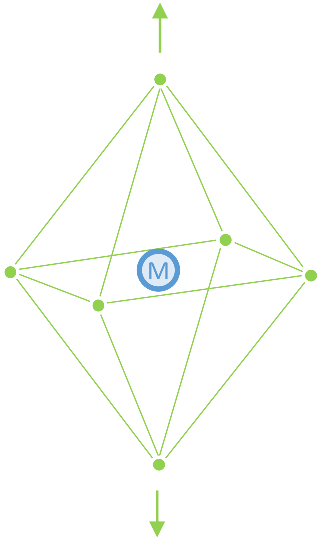
CRYSTAL FIELD EFFECTS

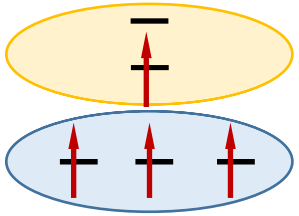
Jahn-Teller effect



doubly degenerate

no degeneracy





no degeneracy

no degeneracy

Orbital energy gain

one orbital up

$$\Delta E_d = f(z - z_0) = \pm a(z - z_0) + \cancel{b(z - z_0)^2} + \cdots$$

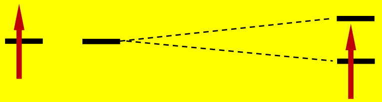
one orbital down

$$z - z_0 = \xi \ll z_0$$

$$E_{tot} = \pm a\xi + \frac{1}{2}k\xi^2$$

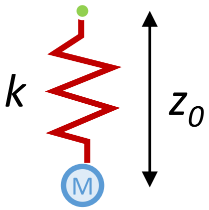
$$\frac{dE_{tot}}{d\xi} = \pm a + k\xi = 0$$

$$\xi_{JT} = \pm\frac{a}{k}$$



static JT

Elastic energy cost



$$E_{elas} = \frac{1}{2}k(z - z_0)^2$$

Magneto-elastic effects

ATOMIC ORIGIN OF MAGNETISM IN MATERIALS

- Single electrons: Spin, Angular Momentum, orbits and spin-orbit coupling
- Many electrons – the magical power of Pauli
- Non-magnetic magnetism : dia-magnetism and Van Vleck paramagnetism
- Hund's rules and effective moment : a 4f lanthanide success story
- Crystal field effect : the case of 3d transition metals
- Jahn-Teller effect

Slides by Ivica Zivkovic and previous ESM lectures