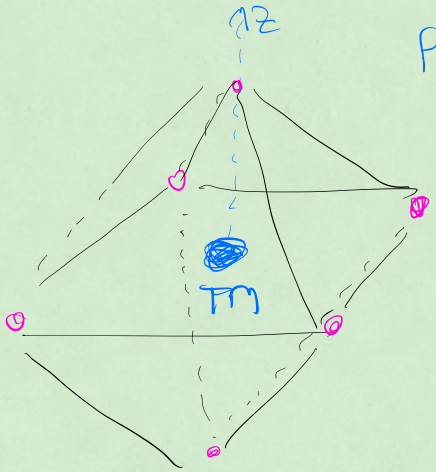
17.10-2022



Perfect octahed.

O_h

$\langle l' m' | \mathcal{H}_{CF} | l m \rangle$

$$\rightarrow = \begin{pmatrix} a & & & & & d \\ & b & & & & \\ & & c & & & \\ & & & b & & \\ d & & & & a & \end{pmatrix}$$

Diagonalization ⇝

eigenstates $|d \ldots\rangle$

Symmetry adapted w.f.

O_h

$SO(3)$

free ion

into SOLID

e_g — —

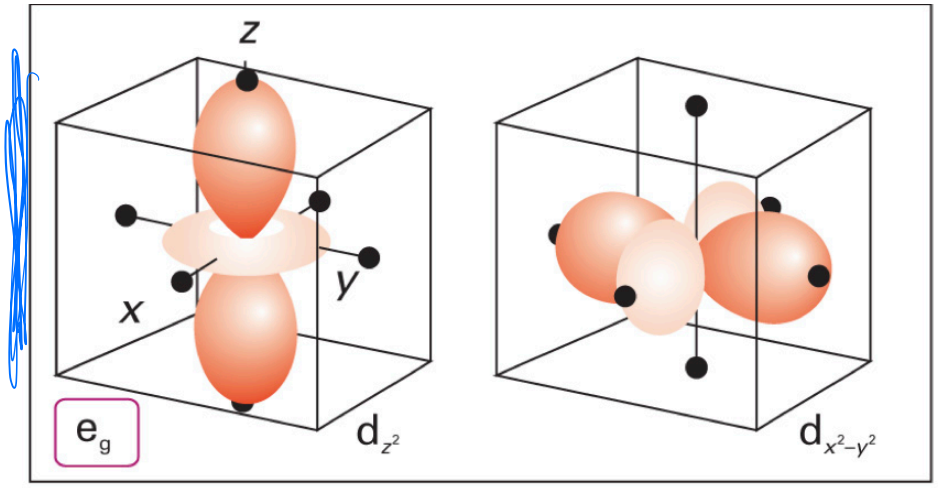
t_{2g} — — —

$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{ee} + \mathcal{H}_{CF} + \ldots$

$\mathcal{H}_0$ + $\mathcal{H}_{ee}$: + Pauli pr. e.g. 3d

$\mathcal{H}_{CF}$: t_{2g}, e_g $|d_{z^2}\rangle, \ldots$ Single el. levels

single el. levels $|l, m\rangle \simeq Y_{l,m}(\Omega)$



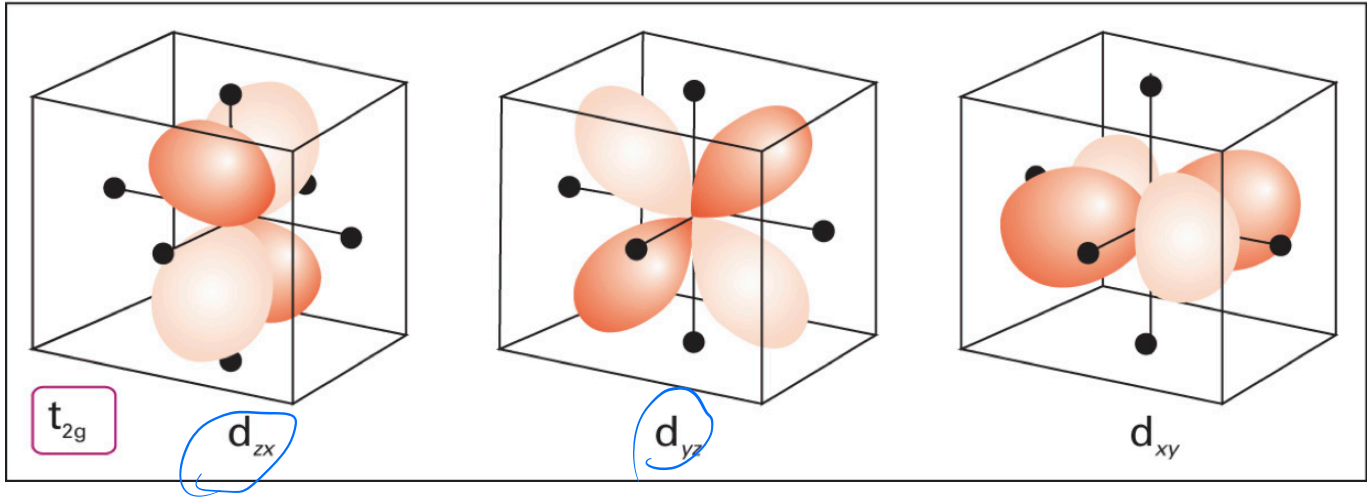
$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}\left[|2,+2\rangle + |2,-2\rangle\right]$$

$$d_{z^2} = |2,0\rangle$$

$$d_{xy} = -\frac{i}{\sqrt{2}}\left[|2,+2\rangle - |2,-2\rangle\right]$$

$$d_{xz} = -\frac{1}{\sqrt{2}}\left[|2,+1\rangle - |2,-1\rangle\right]$$

$$d_{yz} = \frac{i}{\sqrt{2}}\left[|2,+1\rangle + |2,-1\rangle\right]$$



NOMENCLATURE

	single el. level	Multi el. level
free ion	$(3d)^{ne}$	$^2P_{1/2}$ ... (Russel Saunders terms)
cf-O_h	t_{2g}, e_g	$^{2S+1}A_{...}$, ^{2S+1}E, T

Transition metals:

	A	E	T
orbital degs	1	2	3

J_{intra}

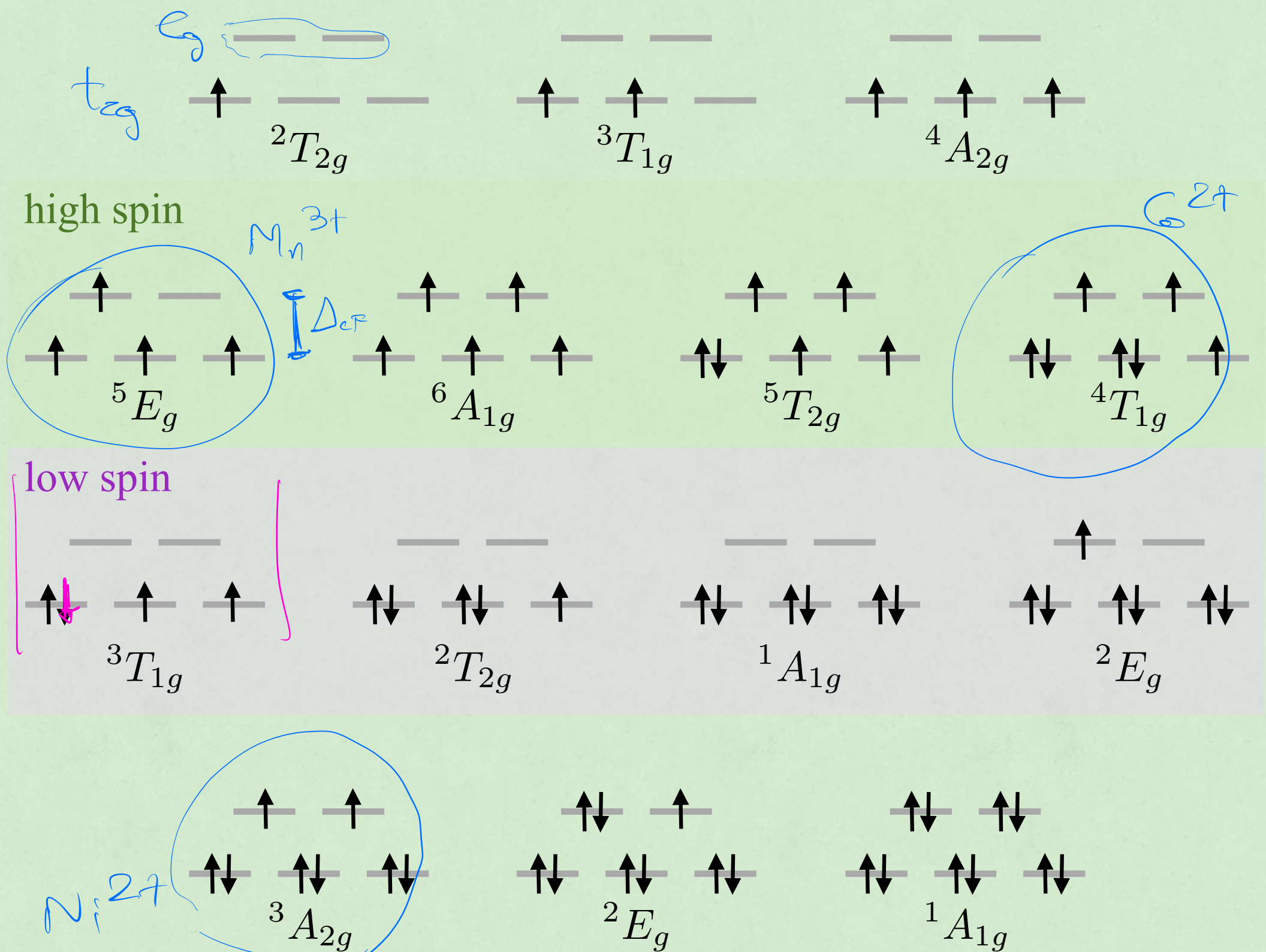
He excited states $(1S)^1 (2S)^1$

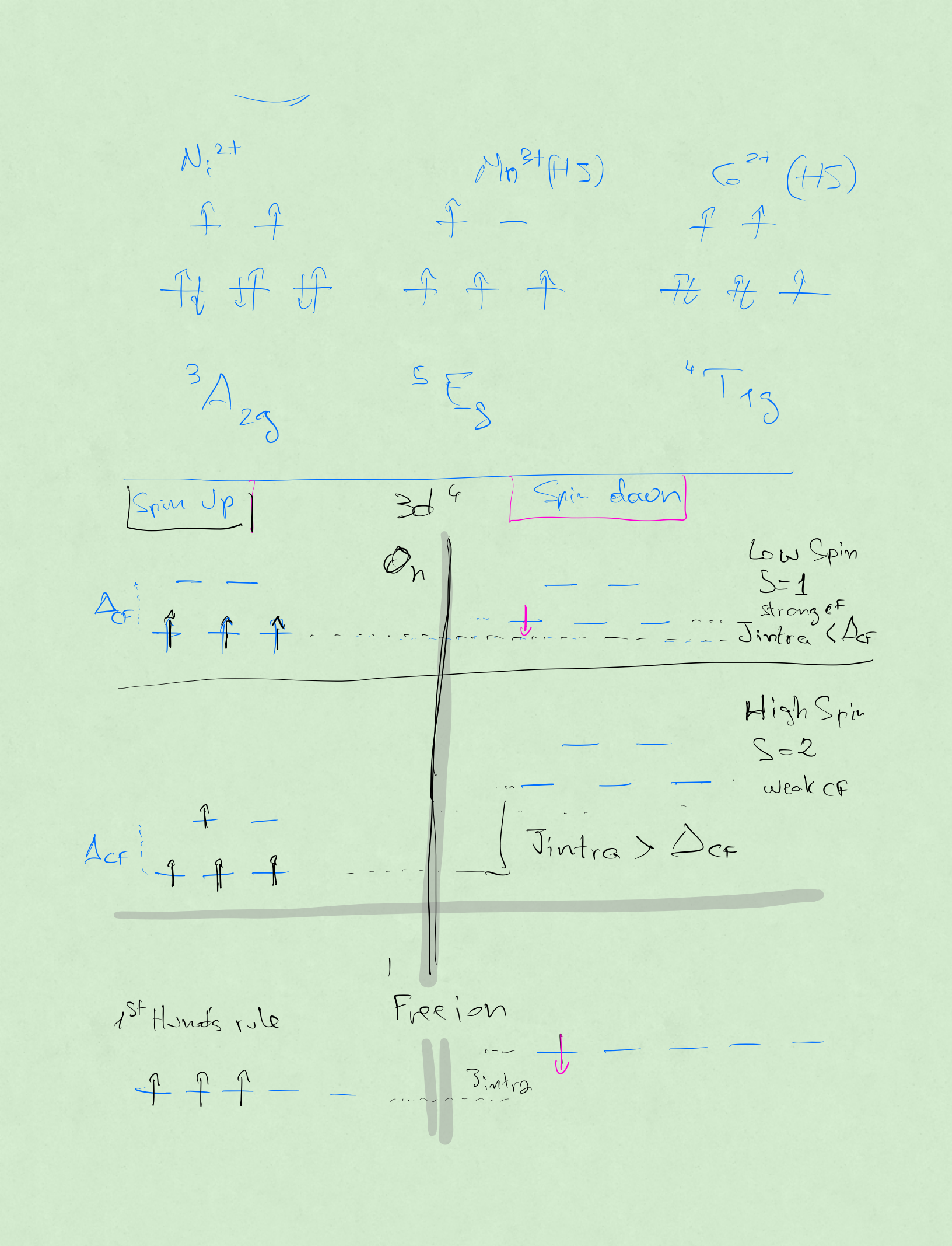
SPATIAL		Spin w.f.
$\psi^T(r_1, r_2)$	Asymm. $1 \leftrightarrow 2$	χ^T
$\psi^S(r_1, r_2)$	Symm. $2 \leftrightarrow 1$	χ^S

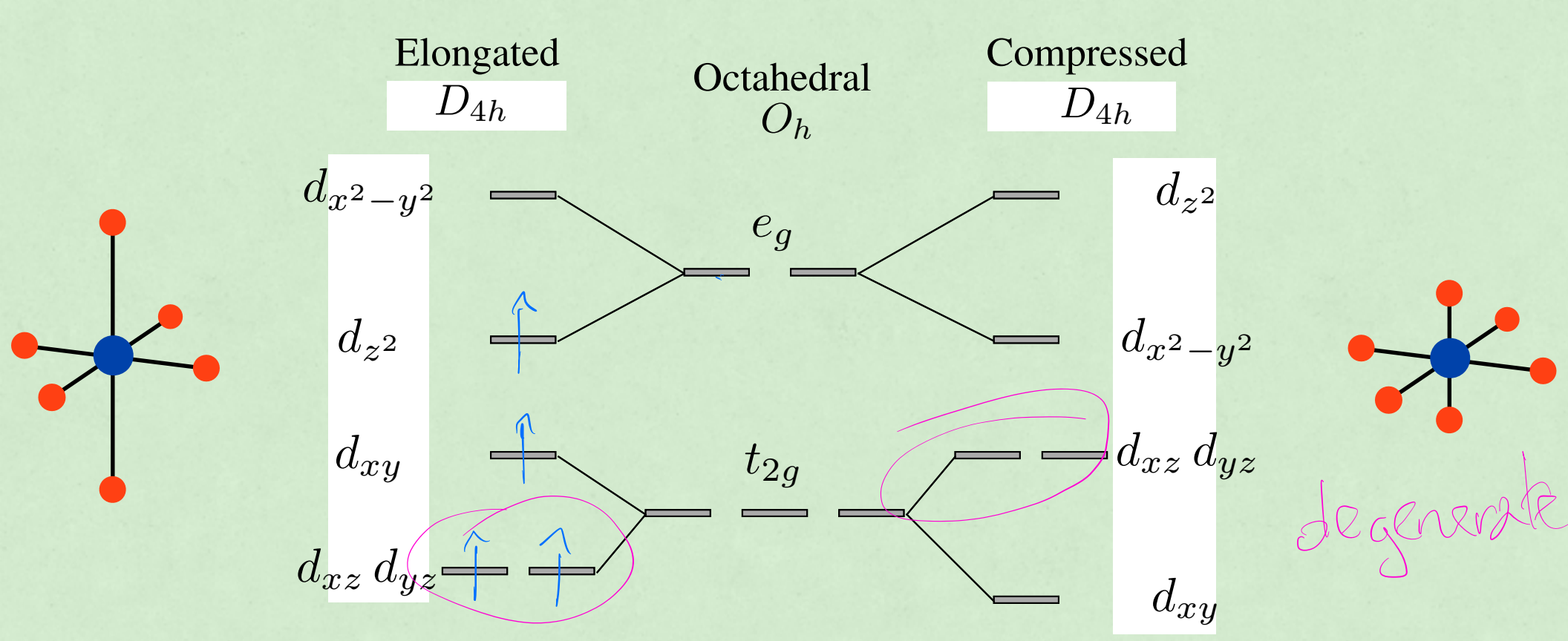
$E_S - E_T = 2J$

$\Rightarrow \quad \mathcal{H}_{exch} = -2J\, \hat{S}_1 \cdot \hat{S}_2$

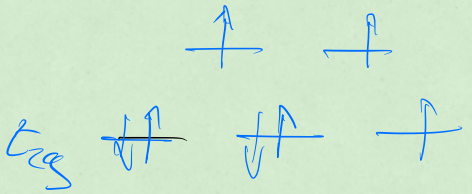
Heisenberg effective Spin Hamiltonian

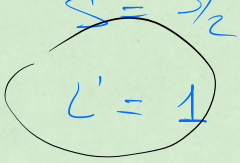

e_g
t_{2g}
$^2T_{2g}$
$^3T_{1g}$
$^4A_{2g}$
high spin
Mn^{3+}
Δ_{cr}
^5E_g
$^6A_{1g}$
$^5T_{2g}$
Co^{2+}
$^4T_{1g}$
low spin
$^3T_{1g}$
$^2T_{2g}$
$^1A_{1g}$
^2E_g
Ni^{2+}
$^3A_{2g}$
^2E_g
$^1A_{1g}$


Ni^{2+}
Mn^{3+} (HS)
Co^{2+} (HS)
$^3A_{2g}$
^5E_g
$^4T_{1g}$
Spin Up
$3d^6$
Spin down
O_h
Low Spin
S=1
strong CF
$J_{intra} < \Delta_{CF}$
Δ_{CF}
High Spin
S=2
weak CF
$J_{intra} > \Delta_{CF}$
1st Hunds rule
Free ion
J_{intra}


Elongated
D_{4h}
Octahedral
O_h
Compressed
D_{4h}
$d_{x^2-y^2}$
d_{z^2}
d_{xy}
$d_{xz}\ d_{yz}$
e_g
t_{2g}
d_{z^2}
$d_{x^2-y^2}$
$d_{xz}\ d_{yz}$
d_{xy}
degenerate

Co^{2+} $(3d)^7$ HS conf





t_{2g} { d_{xy}, d_{yz}, d_{xz}

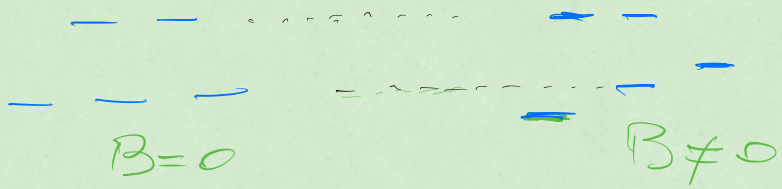
$$H_Z = \sum_i H_{Z,i} = \sum_i \mu_B B \hat{l}^z_i$$

$$\mu_B B \langle t'_{2g} | \hat{l}_z | t_{2g} \rangle =$$

	d_{xy}	d_{xz}	d_{yz}
$\langle d_{xy}$	0		
$\langle d_{xz}$		0	$-i\mu_B B$
$\langle d_{yz}$		$i\mu_B B$	0

eigv.	eigst.
0	$\lvert d_{xy} \rangle$
$\mu_B B$	$\lvert 2, +1 \rangle \propto \lvert d_{xz} \rangle + i \lvert d_{yz} \rangle$
$-\mu_B B$	$\lvert 2, -1 \rangle \propto \lvert d_{xz} \rangle - i \lvert d_{yz} \rangle$

$\Rightarrow$ t_{2g} behaves like $l' = 1$ Effectively

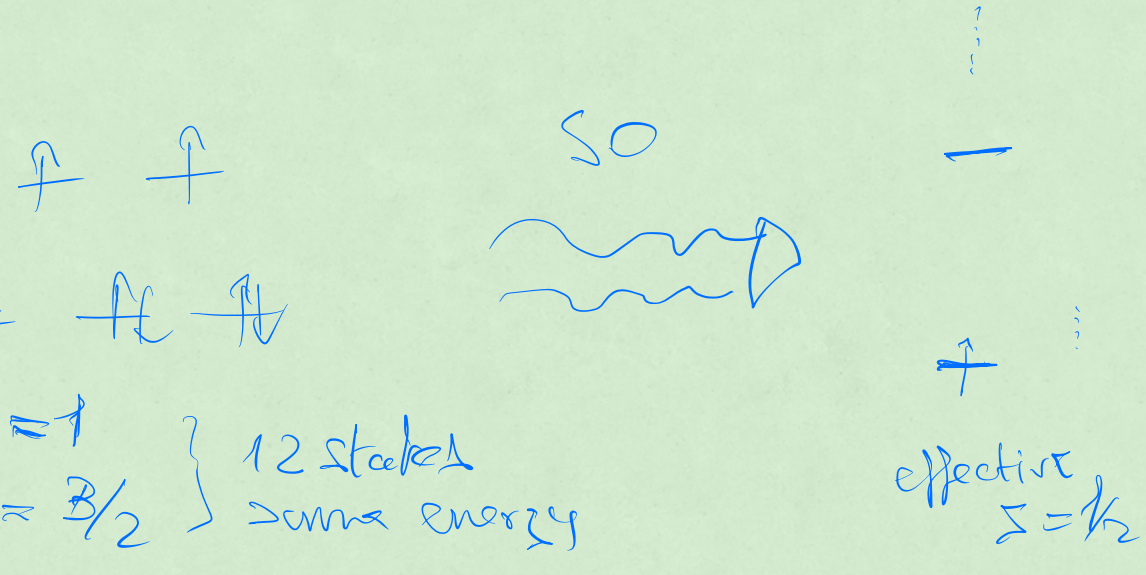


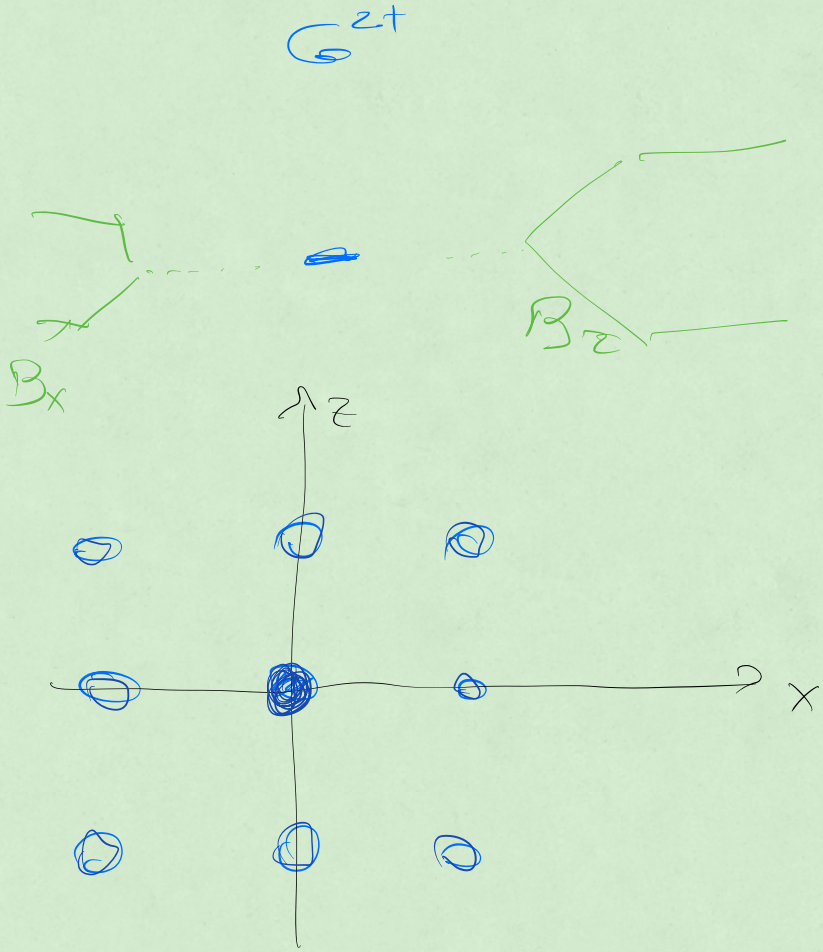
$$\langle e_g' | \hat{L}^\alpha | e_g \rangle = 0$$

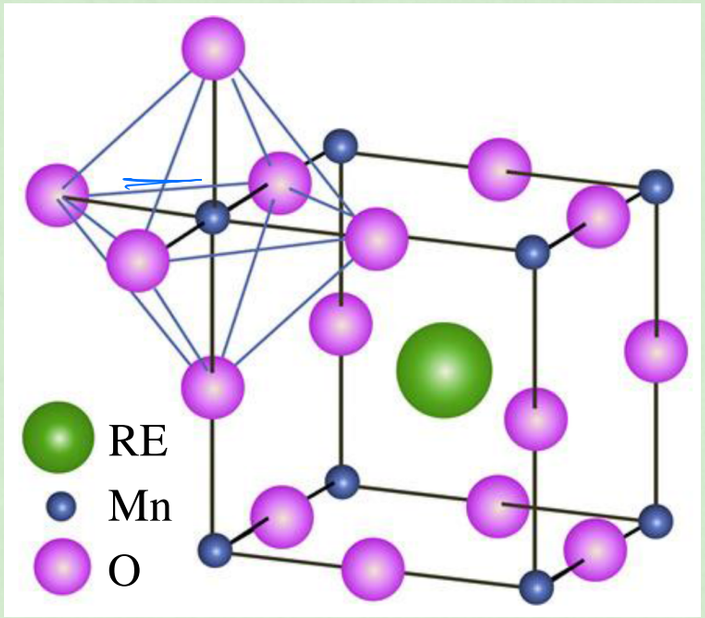
IS EFFECTIVE

1st order	$\lvert t_{2g} \rangle$	$\lvert e_g \rangle$
Zeeman Splitting	Y	N
SO coupling	Y	N

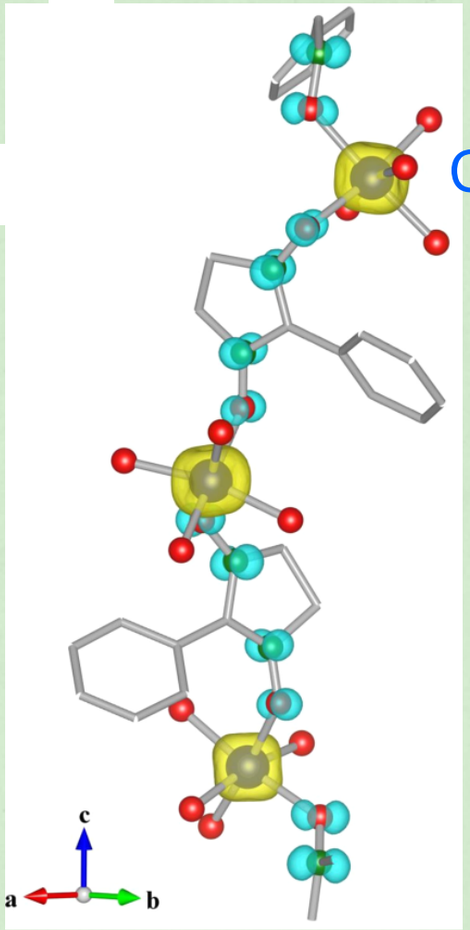
back to $\mathcal{O}^{2+} \Rightarrow$ SO is effective at 1st order



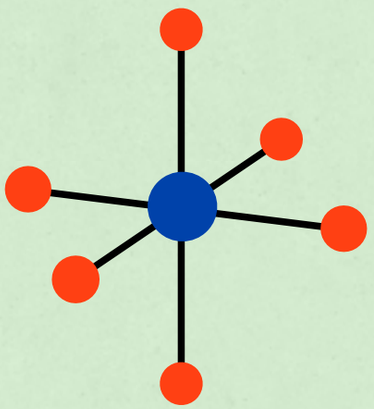

G^{zt}
B_x
B_z
z
x



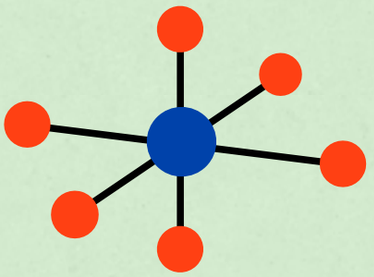
Rare-earth manganites



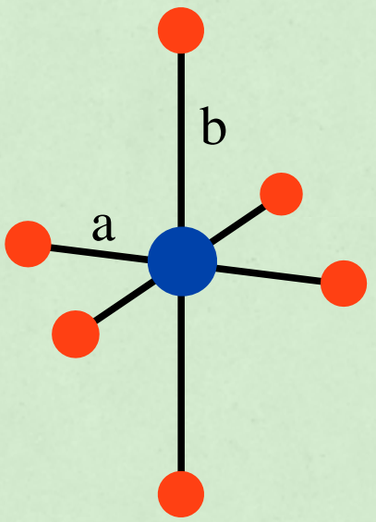
CoPhOMe spin chain



octahedral symmetry O_h



compressed octahedral symmetry D_{4h}



elongated octahedral symmetry D_{4h}