

CH105(I)

Inorganic Chemistry

Prof. G. Rajaraman

Can be reached via

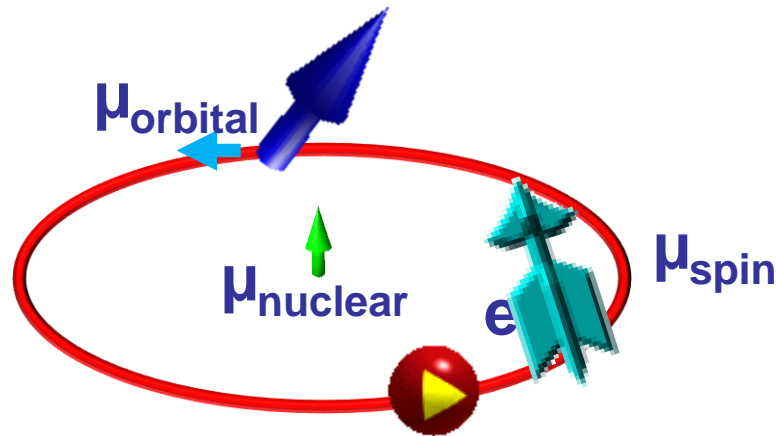
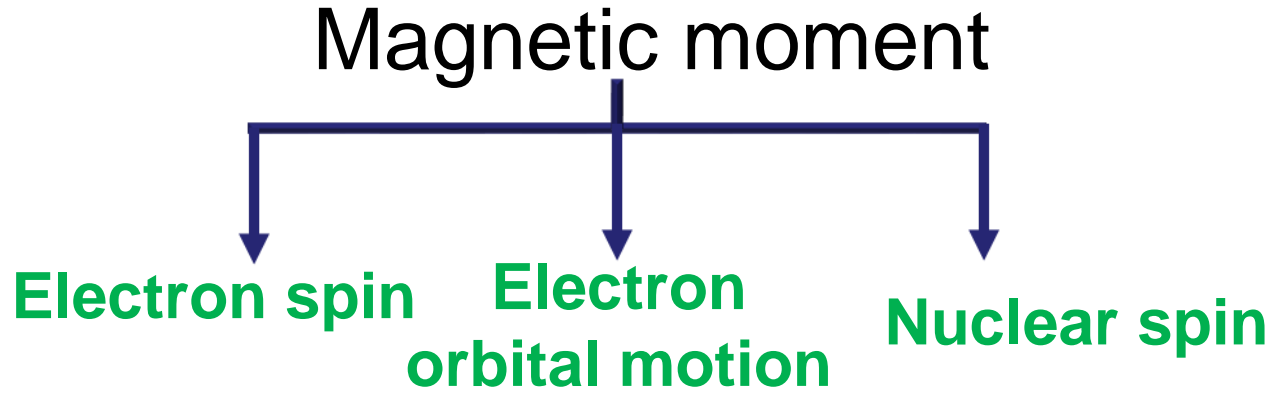
Email: rajaraman@chem.iitb.ac.in

Phone: +91-22-2576 7183

Or via moodle

Topic IV
Magnetism
Transition & Lanthanide ions
and their complexes

Various contributions to magnetic moment



- Each of these magnetic fields interact with one another and with the external magnetic fields.
- However, some of these interactions are strong, some are weak and some are negligible.

Classes of Magnetism

Two fundamentally different types of response:

- a) Diamagnetism - M and χ are negative
- b) Paramagnetism - M and χ are positive

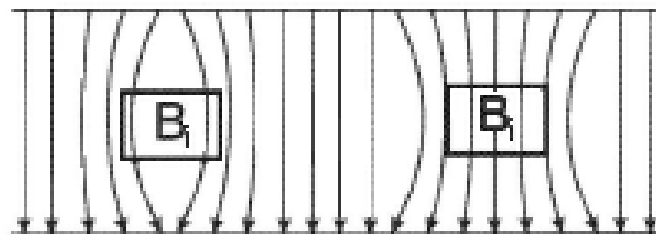
$$\chi = \chi^D + \chi^P$$

Molecules with paired and unpaired e⁻s = "paramagnetic"

Molecules with only paired e⁻s = "diamagnetic"

external magnetic field H

N



S

diamagnetic
sample

paramagnetic
sample

Repulsion attraction

Lighter heavier

Dia and Paramagnetic compounds

N₂ diamagnetic

Pouring liquid dinitrogen



liquid dinitrogen
does NOT stick



Dia.M. ex. H₂O, KCl organic ligands,
etc.

Bismuth metal (most diamagnetic
of all metals)

diamagnetic

O_2 paramagnetic

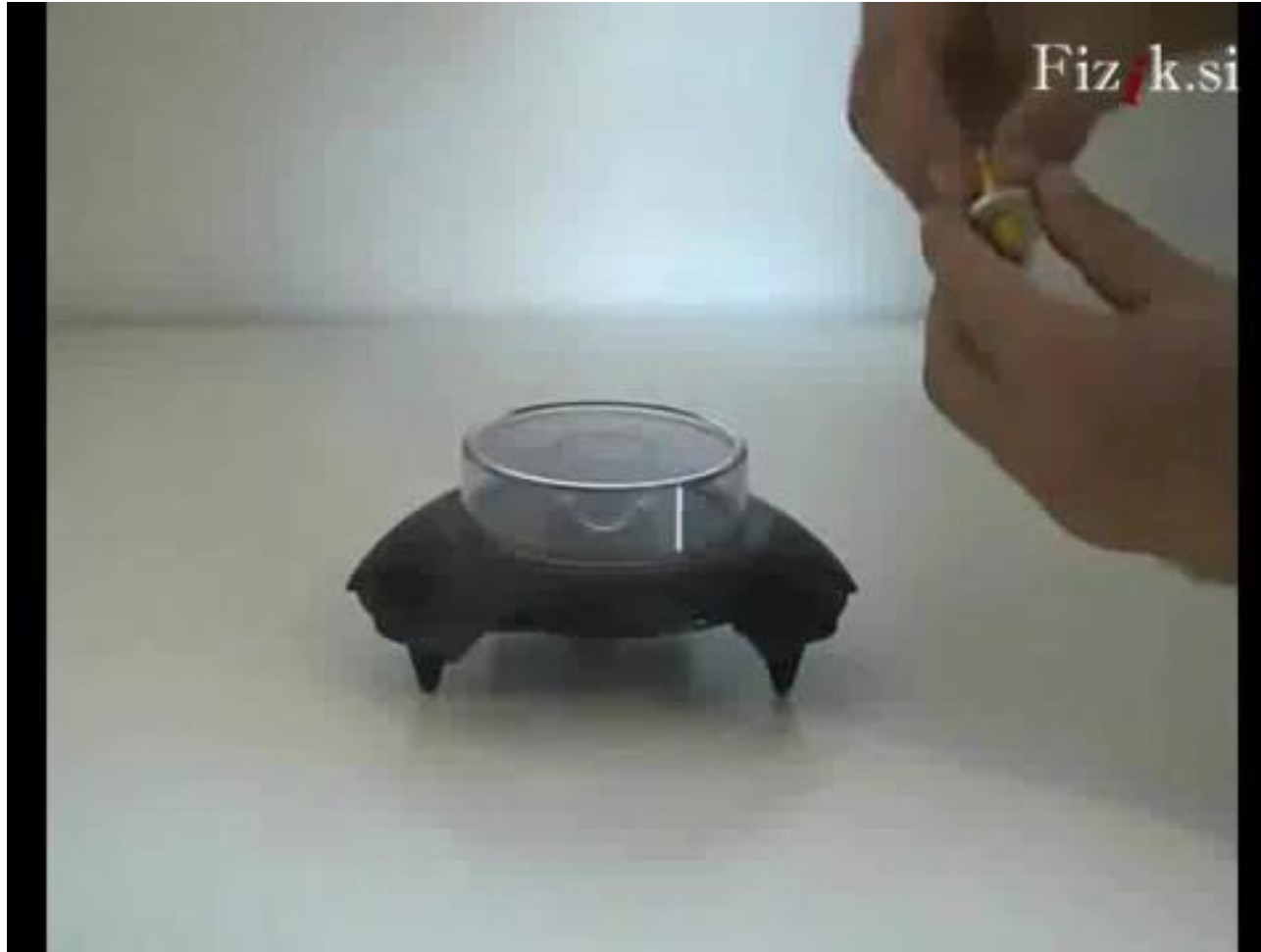
when dioxygen is in its ground state it is a triplet (spin $S=1$)
and its reactivity is weak.



Liquid O_2



Video Magnetic Levitation: Property of diamagnetic molecules-I



Courtesy:<https://www.youtube.com/watch?v=g4IW7xydnH8>

MAGNETIC SUSCEPTIBILITY

When a sample is placed in H, the field within the body differs from the free space value. The body is magnetised. The intensity of the magnetisation is the rate of change of E of the body in the field:

$$M = -\delta E / \delta H$$

The sensitivity of M to H is defined as the magnetic susceptibility, χ .

When the field is weak, χ becomes independent of H:

$$\chi = M/H$$

Molar susceptibility is given as

$$\chi_m = \chi_g \times \text{Mol. Wt.}$$

Where, M. Wt. is molecular weight of the sample

Curie's Law

$$\chi_M = \frac{C}{T}$$

where C = constant

or

$$C = \chi T = \frac{N\beta^2}{3k} g^2 S(S+1)$$

$$\mu_{so} = \sqrt{\frac{3k}{N\beta^2}} \sqrt{\chi T} = 2.828 \sqrt{\chi T}$$

$$\mu_{so} = \sqrt{g^2 S(S+1)} = \sqrt{n(n+2)}$$

Where k = Boltzmann constant

β = Bohr Magnetron

N = Avogadro's number

Notes:

1. χ is a fundamental property of magnetic materials
.....while μ_{so} (B.M) is arbitrarily derived from χ .
2. If μ_{so} is constant with changing temperature
.....then χ must increase as T is decreased.
3. μ_{so} can be easily related to the total spin S of a molecule,
.....thus linking magnetic measurements to molecular properties.

Quantum response to H

Quantum model – an electronic state with total spin angular momentum S has $2S+1$ sublevels with spin quantum numbers m_s

These levels are degenerate unless a magnetic field is applied, or they couple with other states

The application of a magnetic field leads to a **Zeeman splitting** in the $2S+1$ m_s levels, each with energy

$$m_s g \mu_B H$$

$g \approx 2.0023$ (for a free electron)

μ_B is the Bohr magneton

H = magnetic field

This is the **first order Zeeman effect** (ZE)

– the splitting is proportional to H

The splitting of levels by the external magnetic field is called Zeeman effect.

The Zeeman effect: $s = 1/2$

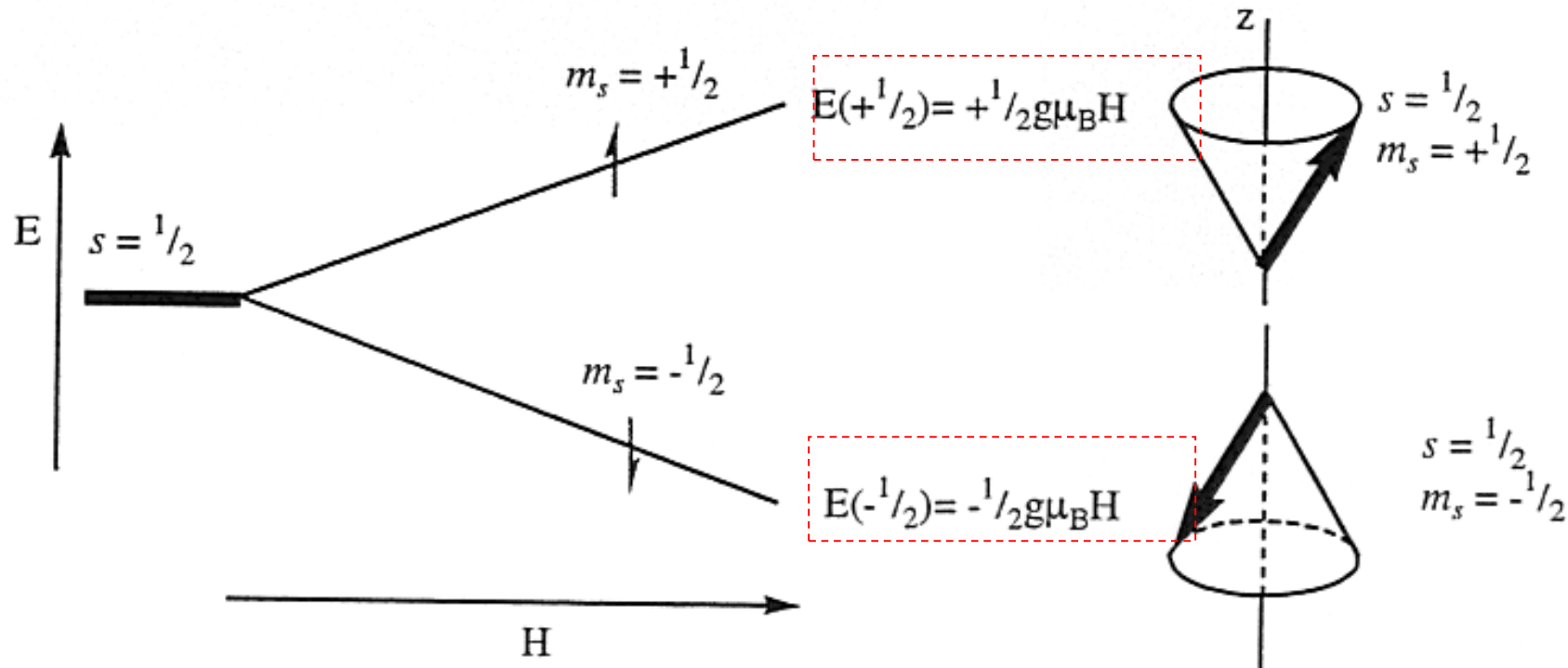
The application of a magnetic field leads to a **Zeeman splitting** in the $2S+1$ m_s levels, each with energy

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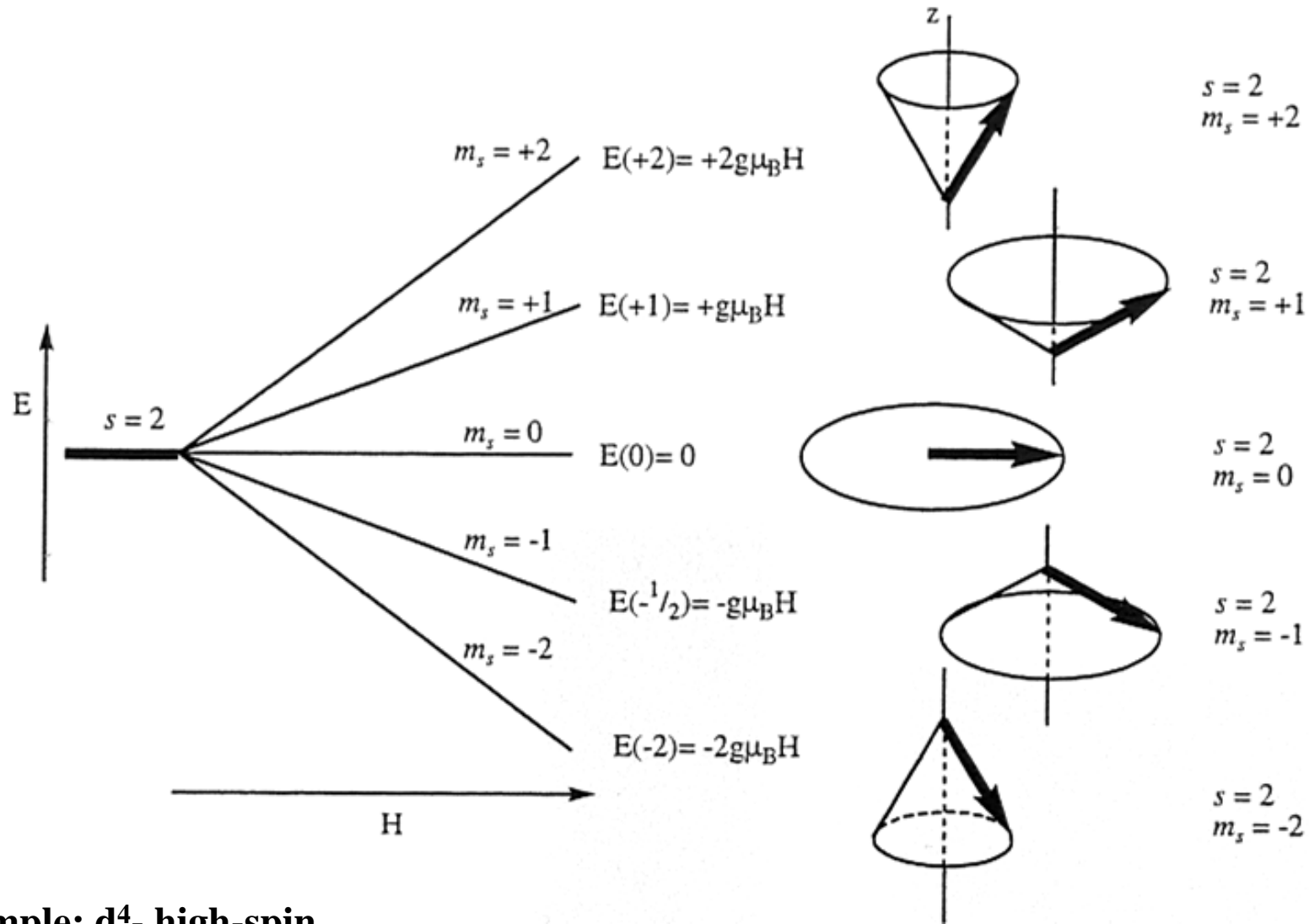
μ_B is the Bohr magneton

H = magnetic field

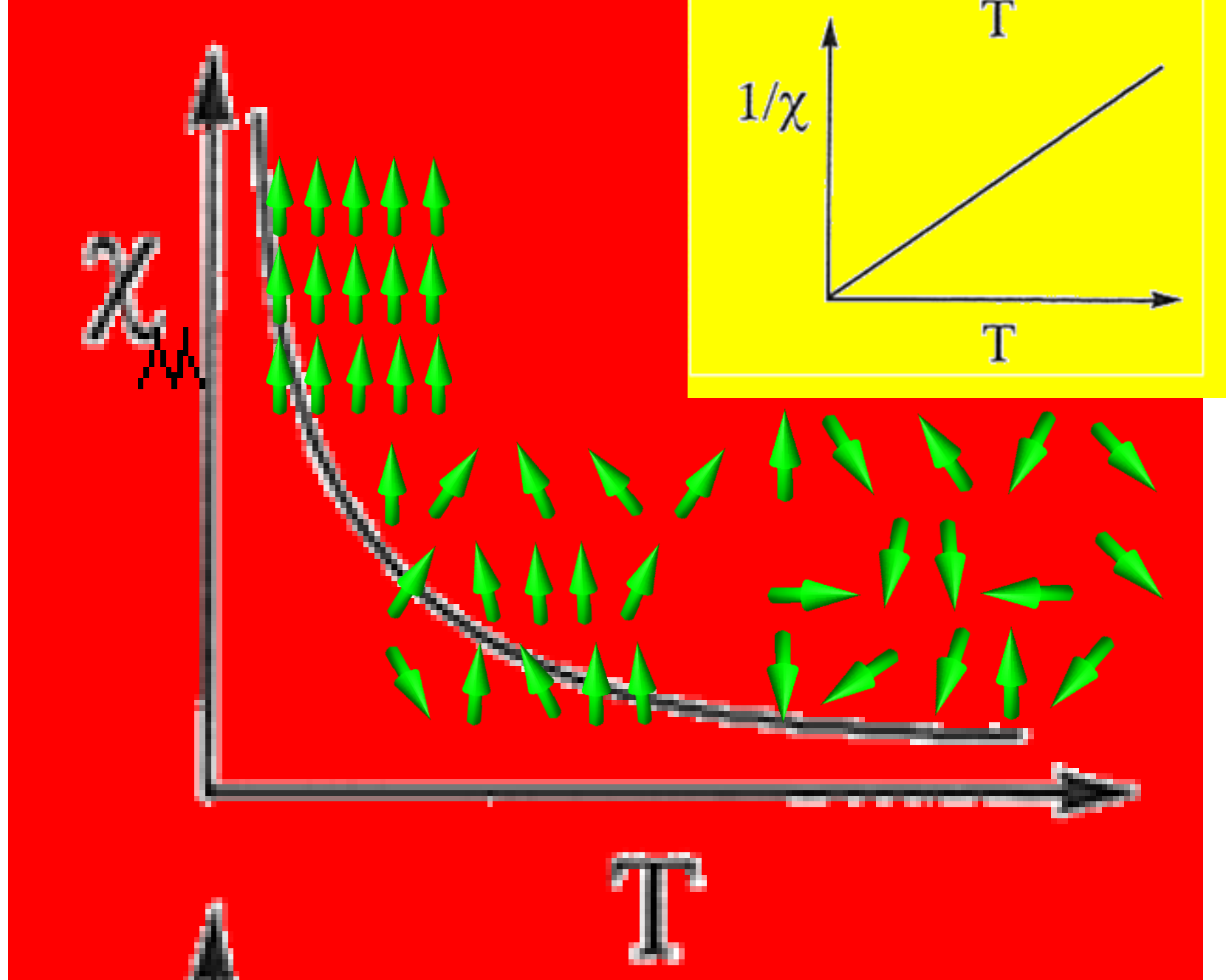


The difference in populations of m_s levels is crucial in providing the magnetization (M) that we measure.

The Zeeman effect: $S = 2$



Example: d^4 - high-spin



The Curie-Weiss Law

Later experiments showed that not all paramagnetic materials obey Curie's Law. Some materials have susceptibilities that can be fitted to the equation:

$$\chi_M = \frac{C}{(T - \theta)} \quad \theta = \frac{zJS(S+1)}{3k}$$

θ = Curie-Weiss constant.

Weak, inter-molecular interactions are the usual cause of θ .

z = number of nearest neighbour interactions

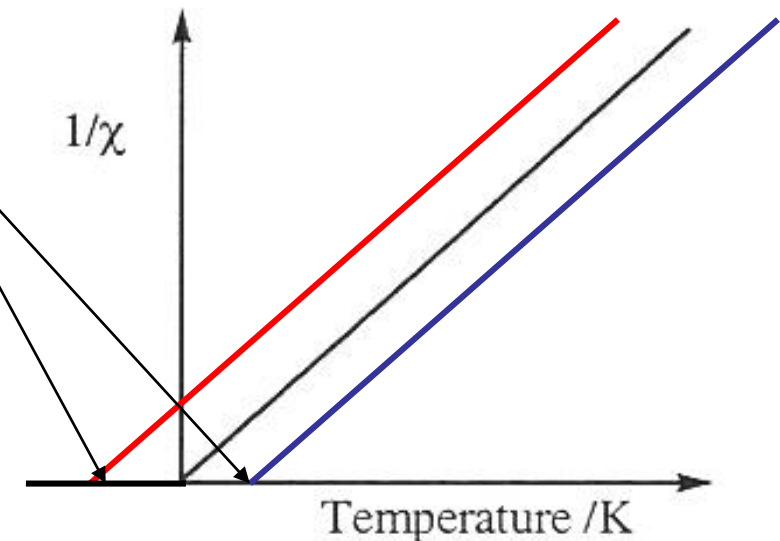
J = int. between nearest neighbour

(exchange coupling; not to confuse with J quantum number.

intercept on temperature axis = θ

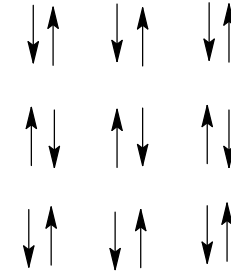
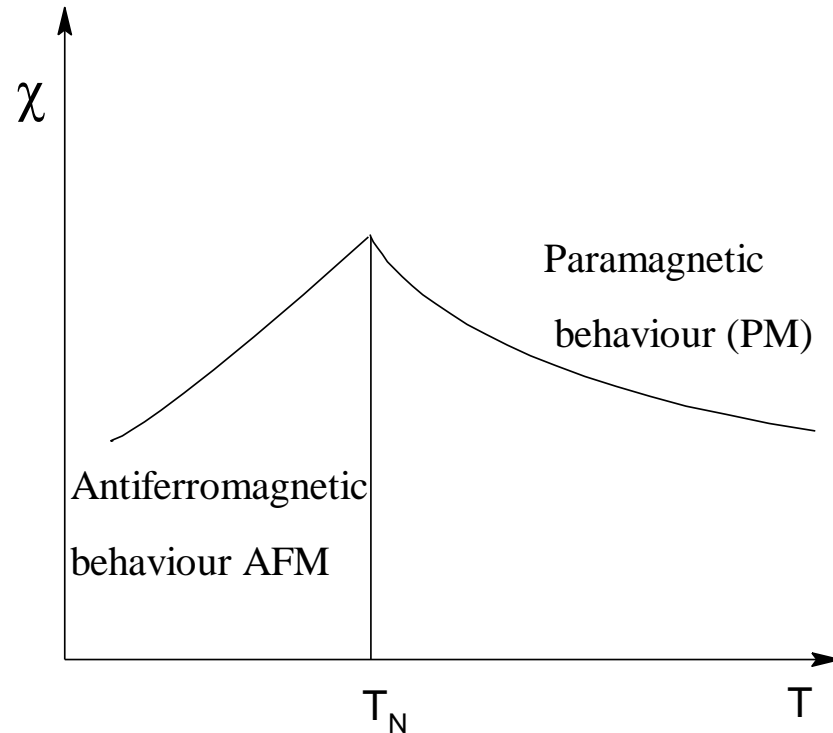
$\theta > 0$ for ferromagnets

$\theta < 0$ for antiferromagnets



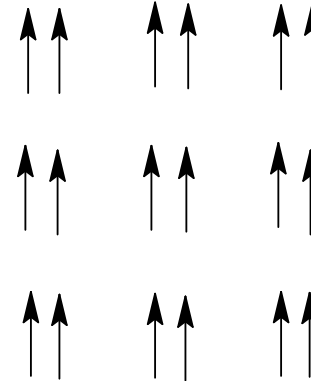
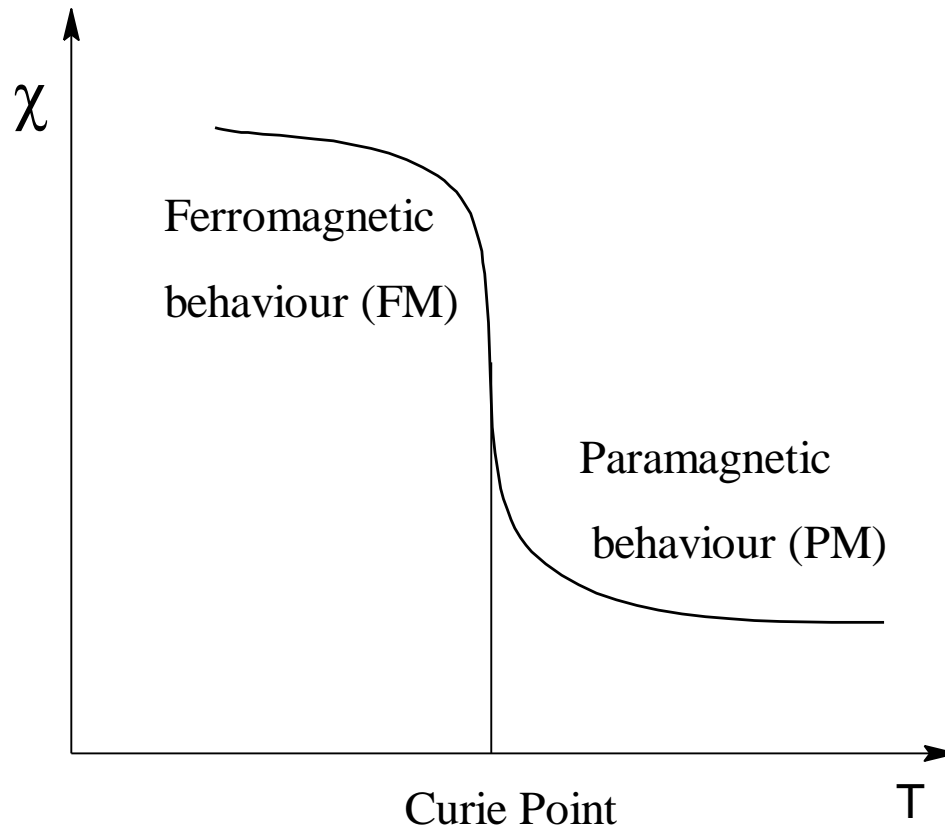
Antiferromagnetism

- J negative with spins antiparallel below T_N



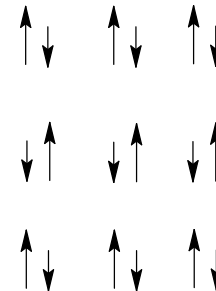
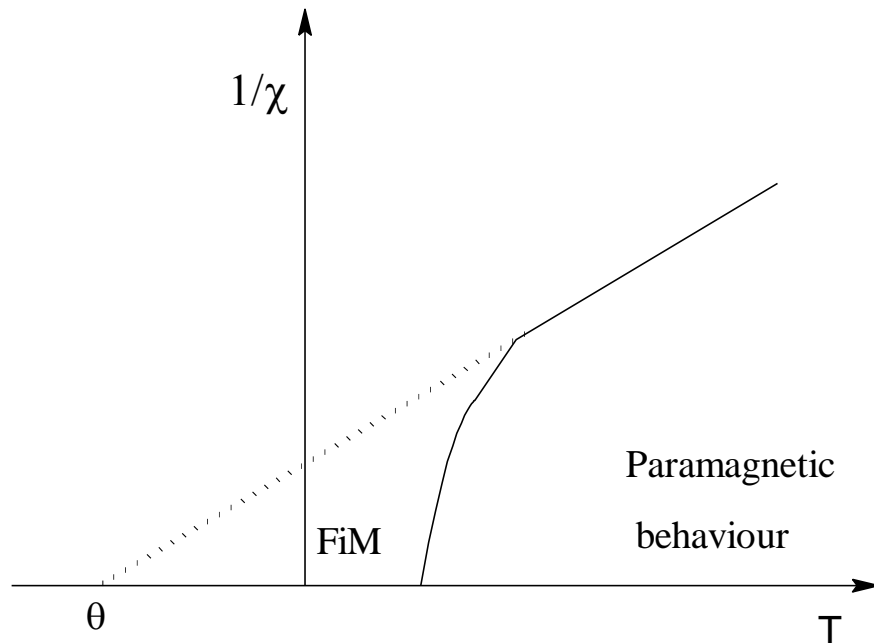
Ferromagnetism

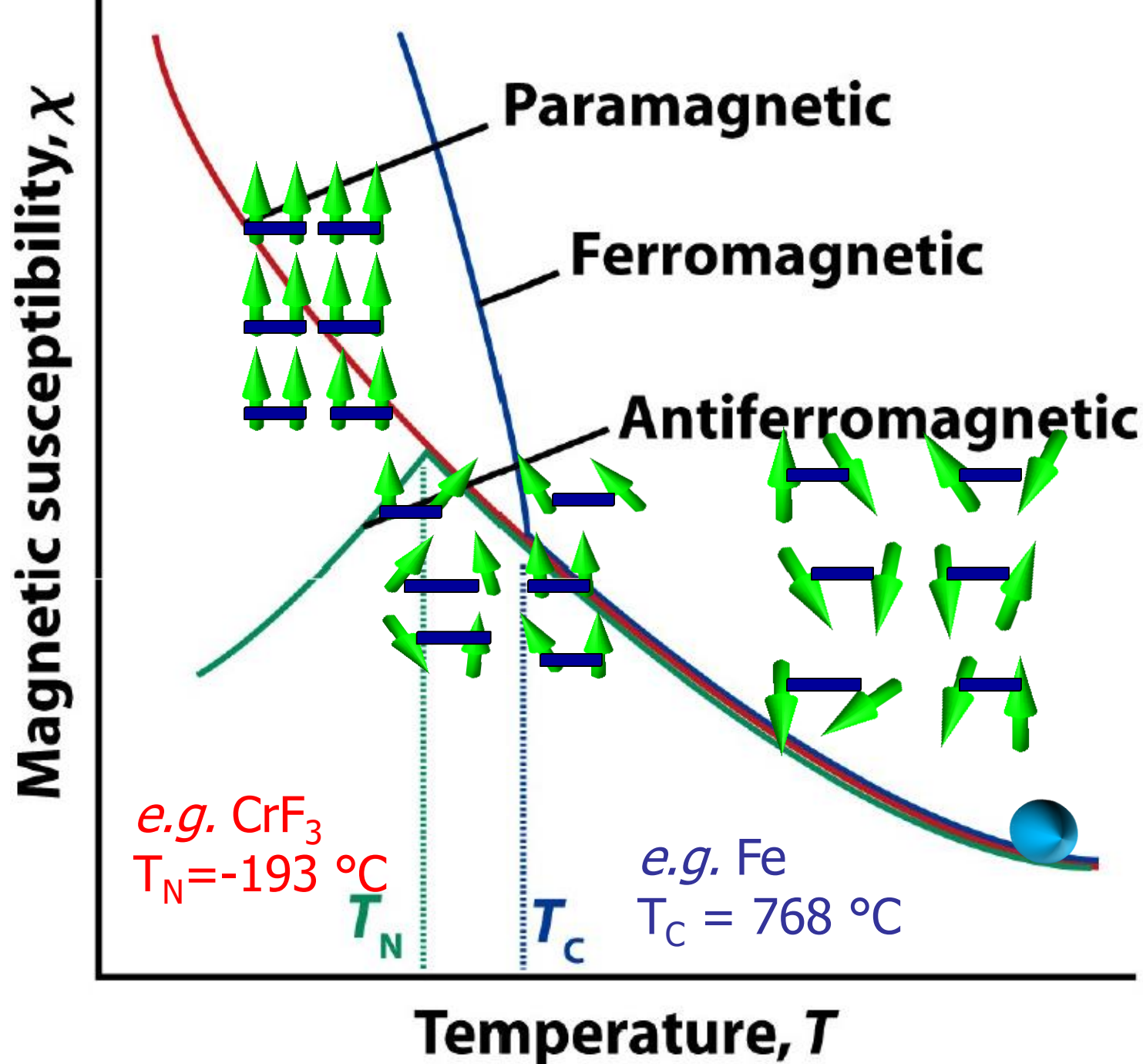
Spins parallel below T_c



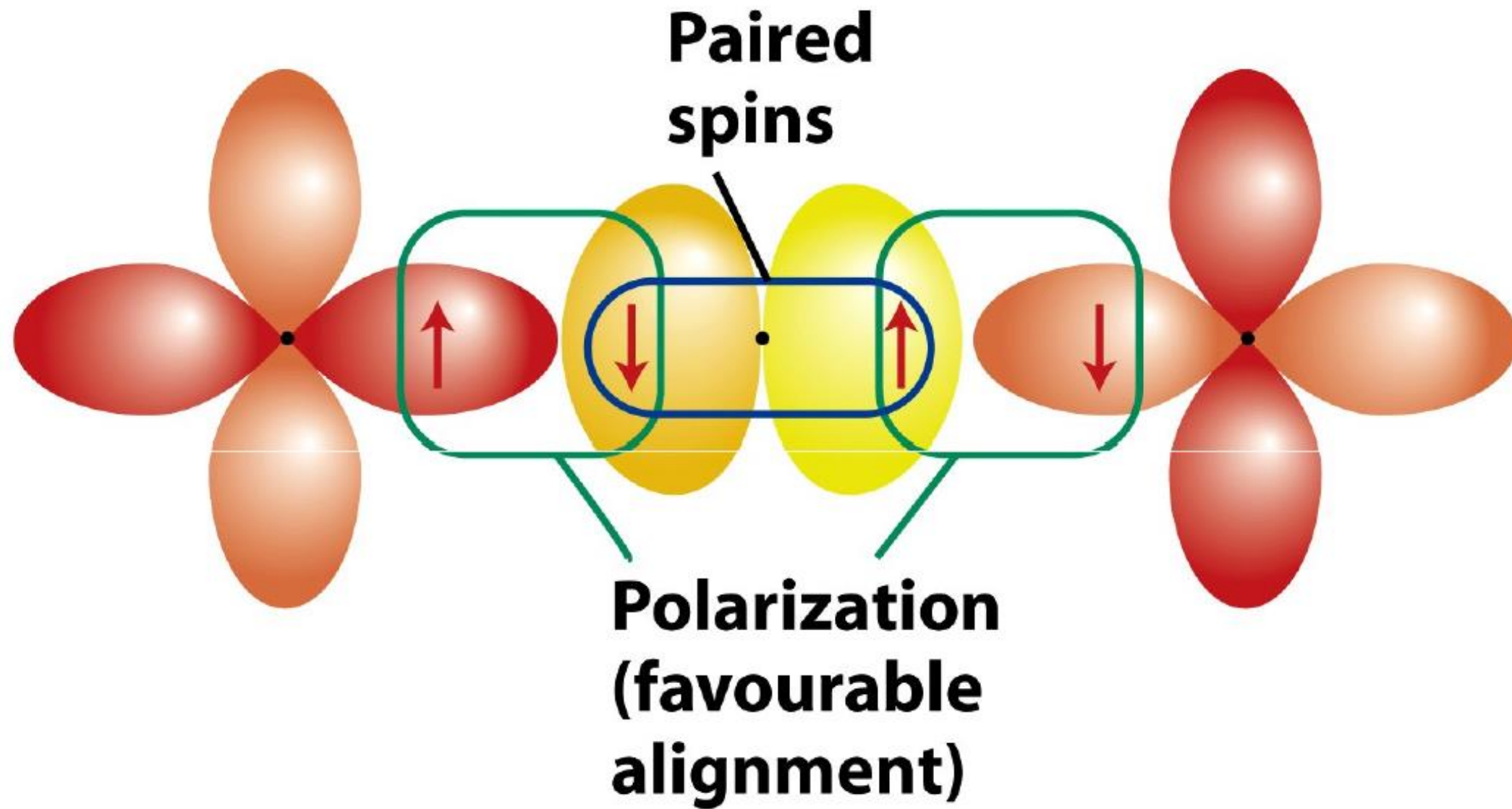
Ferrimagnetism

- Spins of unequal magnitude antiparallel below critical T





Magnetic coupling: Origin of AF interaction



Orbital contribution to magnetic moments

- $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ shows zero magnetic moment at very low temperatures, why?

Orbital Contribution to the Magnetic Moment

Orbital motion of the electron generates Orbital Magnetic Moment (μ_l).

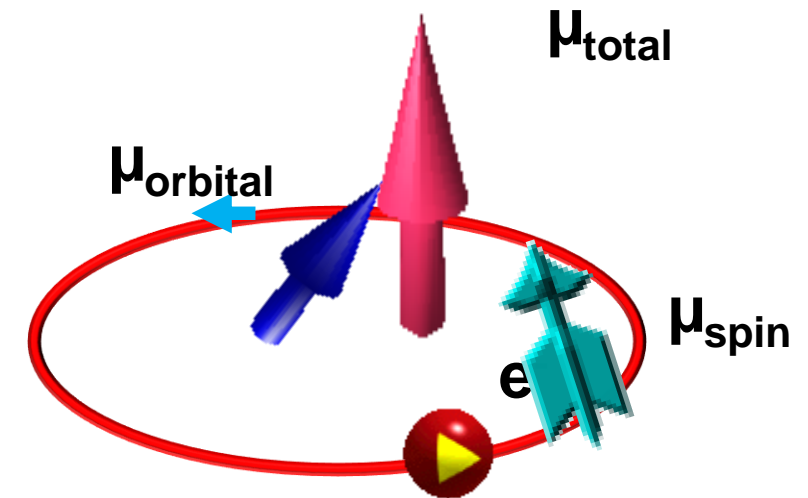
Spin motion of the electron generate spin magnetic moment (μ_s)

For multi-electron systems

$$L = l_1 + l_2 + l_3 + \dots$$

$$S = s_1 + s_2 + s_3 + \dots$$

$$\mu_{l+s} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M}$$



This equation is valid only if L and S are independent of each other.

But what if they are not independent?

How do you determine, if L and S are coupled?

Spectroscopic Terms (Term Symbols)

Free ions

Different microstates exist for the same electronic configuration.



For one unpaired electron in d orbital there are 10 possible microstates. These 10 states are degenerate and are called 2D term.

Russel-Saunders coupling is used to describe the terms. The symbol will represent the total value of azimuthal quantum numbers ($L = \sum l_i$) and it takes the letters, 'S, P, D, F, G' respectively for L values of 0, 1, 2, 3 and 4.

The degeneracy ($2S+1$) { S = sum of all the spins} is shown on the left superscript.

The term symbol is shown as $(^{2S+1})L$ {for eg., 3F corresponds to $S = 1$ and $L = 3$ }

Number of microstates for 3F is, $(2S+1) \times (2L+1) = 3 \times 7 = 21$

Ground terms for d^n configurations

Free ions

Configuration	Example	m_l					$M_L = \sum m_l$	S	Ground Term
		2	1	0	-1	-2	L		
d^1	Ti^{3+}	↑					2	1/2	2D
d^2	V^{3+}	↑	↑				3	1	3F
d^3	Cr^{3+}	↑	↑	↑			3	3/2	4F
d^4	Mn^{3+}	↑	↑	↑	↑		2	2	5D
d^5	Mn^{2+}	↑	↑	↑	↑	↑	0	5/2	6S
d^6	Fe^{2+}	↑↓	↑	↑	↑	↑	2	2	5D
d^7	Co^{2+}	↑↓	↑↓	↑	↑	↑	3	3/2	4F
d^8	Ni^{2+}	↑↓	↑↓	↑↓	↑	↑	3	1	3F
d^9	Cu^{2+}	↑↓	↑↓	↑↓	↑↓	↑	2	1/2	2D

$$\text{Ground Term} = (2S+1)L_J$$

Where the maximum value of M_L defines L

$L=0, 1, 2$ and 3 corresponds to S, P, D and F Terms

Where the maximum value of M_S defines S

Determination of ground state J

Free ions

$J = L+S, L+S-1, \dots, |L-S|$
Most stable term = Ground State Term

Determine the number of 3d electrons in the ion

Rule 1: for a given electronic configuration, the state with highest S is lowest in energy

Rule 2: for a given electronic configuration and subject to Rule 1, the state with highest L is lowest in energy

Rule 3: for a given electronic configuration and subject to Rules 1 and 2, the state with highest J is lowest in energy for ions with a greater than-half-filled 3d sub-shell; converse true for ions with a less than half-filled shell.

Ground terms for dⁿ configurations

Free ions

Configuration	Example	2	1	0	-1	-2	$M_L = \sum m_l$	L	S	J	Ground Term
d^1	Ti^{3+}	↑					2	2	1/2	3/2	$^2D_{3/2}$
d^2	V^{3+}	↑	↑				3	3	1	2	3F_2
d^3	Cr^{3+}	↑	↑	↑			3	3	3/2	3/2	$^4F_{3/2}$
d^4	Mn^{3+}	↑	↑	↑	↑		2	2	2	0	5D_0
d^5	Mn^{2+}	↑	↑	↑	↑	↑	0	0	5/2	-	6S
d^6	Fe^{2+}	↑↓	↑	↑	↑	↑	2	2	2	4	5D_4
d^7	Co^{2+}	↑↓	↑↓	↑	↑	↑	3	3	3/2	9/2	$^4F_{9/2}$
d^8	Ni^{2+}	↑↓	↑↓	↑↓	↑	↑	3	3	1	4	3F_4
d^9	Cu^{2+}	↑↓	↑↓	↑↓	↑↓	↑	2	2	1/2	5/2	$^2D_{5/2}$

$$\text{Ground Term} = (2S+1)L_J$$

Where the maximum value of M_L defines L

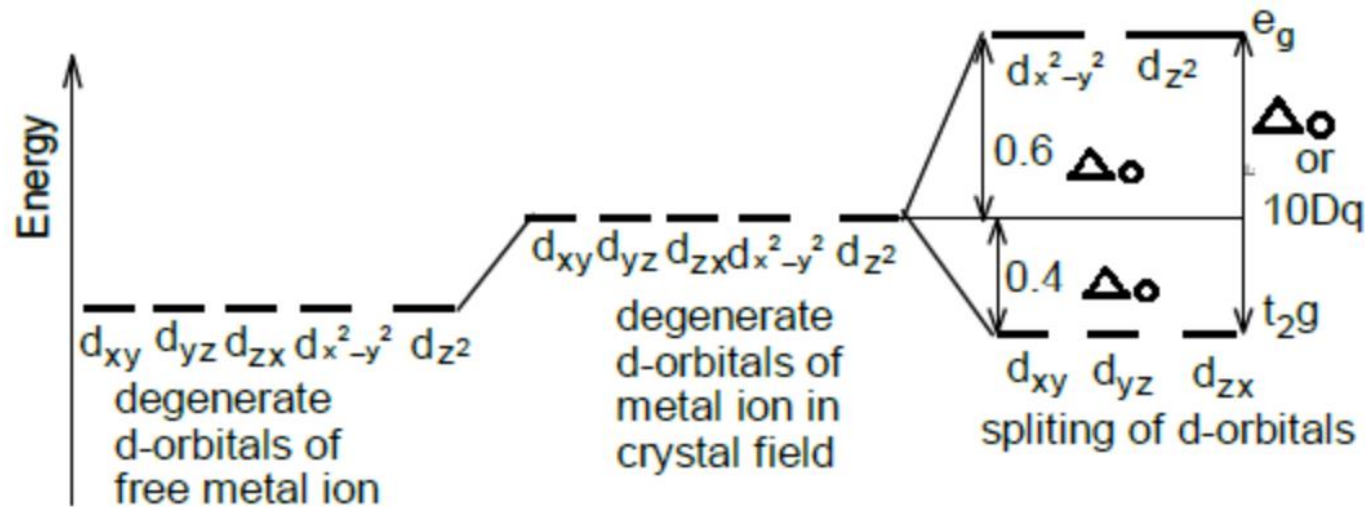
L=0, 1, 2 and 3 corresponds to S, P, D and F Terms

Where the maximum value of M_S defines S

Orbital contribution to magnetic moments in the Presence of ligand field

- First row transition metal ion in octahedral ligand field?

Recap



splitting of d-orbitals in octahedral crystal field,
where $0.6 \Delta_o = 6 Dq$ & $0.4 \Delta_o = 4 Dq$

Conditions to exhibit orbital angular momentum (μ_L)

Octahedral field

Rule #1: The orbitals should be degenerate (t_{2g} or e_g).

Rule #2 The orbitals should be similar in shape and size. Should be possible to transform an orbital into an equivalent one by rotation. This is indeed possible to transform the t_{2g} orbitals into each other by 90° rotation. Such transformation is not possible with the orbitals of e_g .

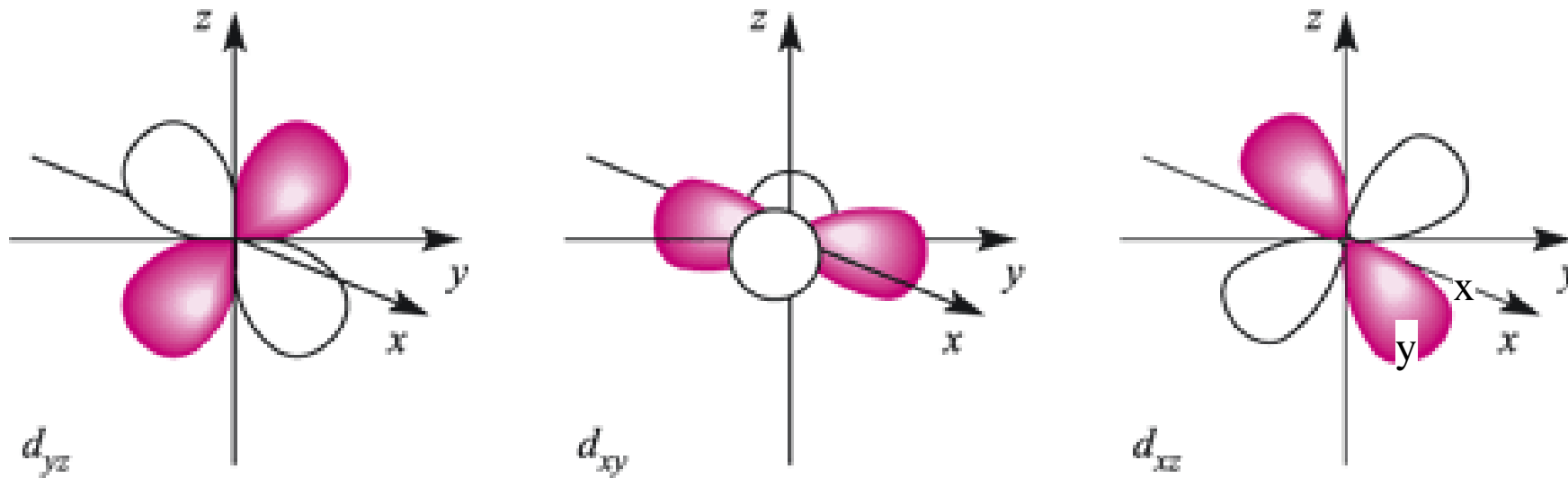
Rule #3: The orbitals must not contain electrons of identical spin during this transformation and the movement of electron

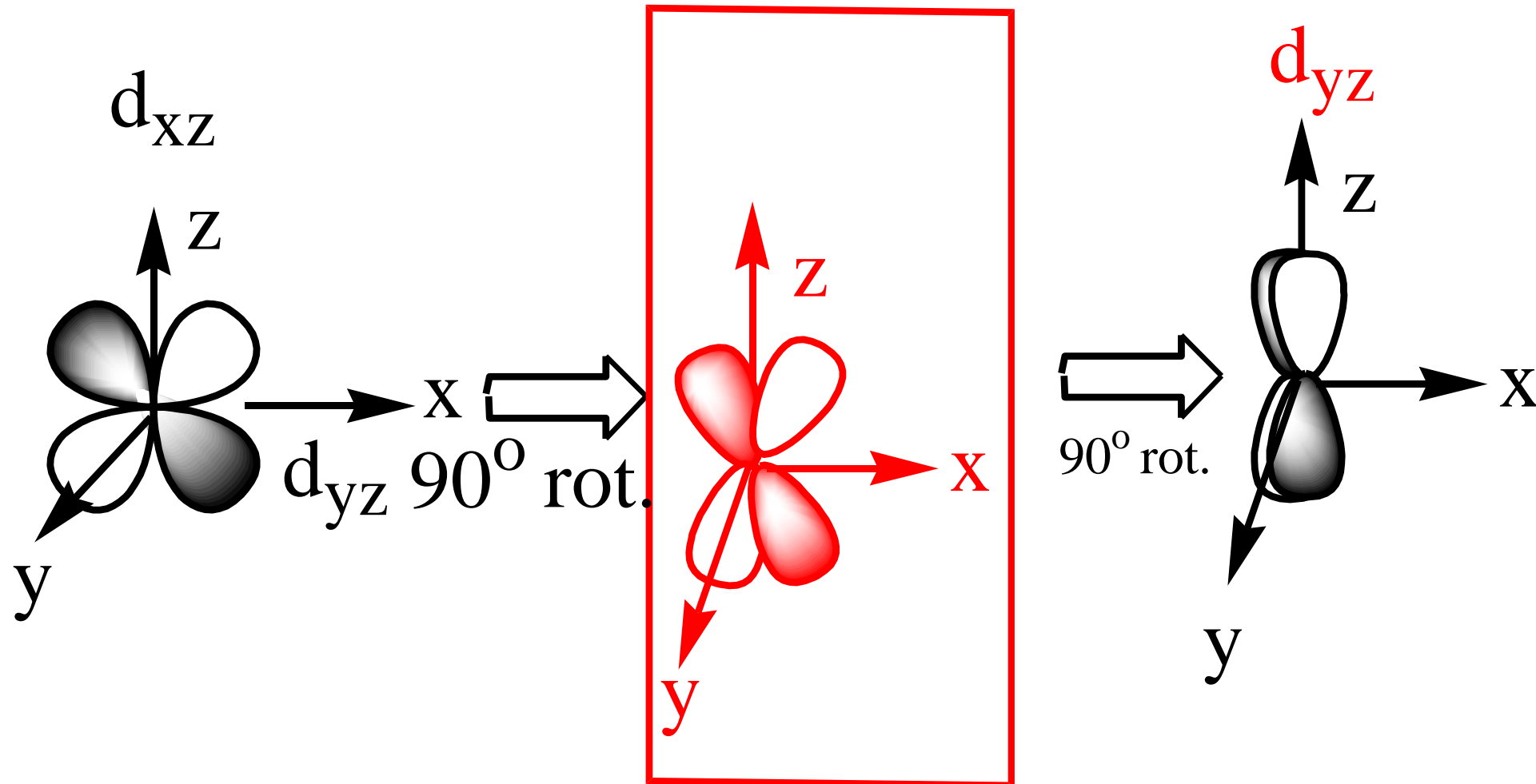
- These conditions are fulfilled only when one or two orbitals contain partially filled electrons in t_{2g} and NOT in e_g

- The degenerate t_{2g} orbitals (d_{xy} , d_{xz} , d_{yz}) can be interconverted by 90° rotations.

e.g. the d_{xz} orbital is transformed into the d_{yz} orbital by a rotation of 90° about the z -axis – during this rotation the electron is orbiting the nucleus

- Thus, an electron in a t_{2g} orbital **can** contribute to orbital angular momentum.





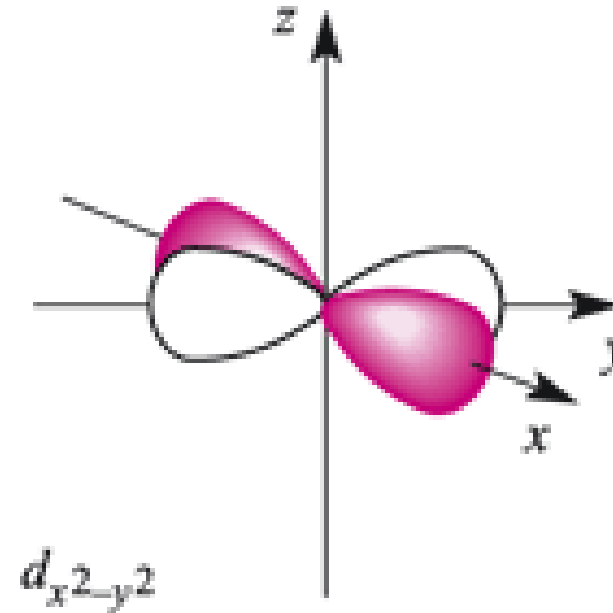
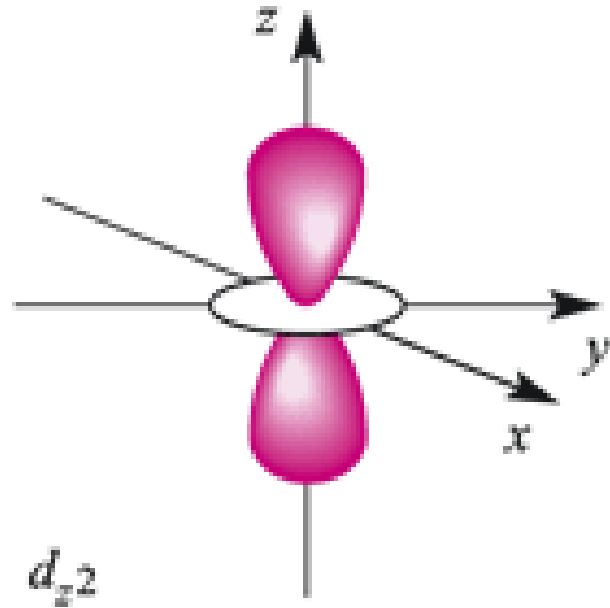
d_{xz} / d_{yz}
 d_{xz} / d_{xy}
 d_{yz} / d_{xy}

orbital motion about z axis
 orbital motion about x axis
 orbital motion about y axis

Octahedral complexes

However the e_g orbitals (d_{z^2} and $d_{x^2-y^2}$) cannot be interconverted by rotation as they are different in shapes

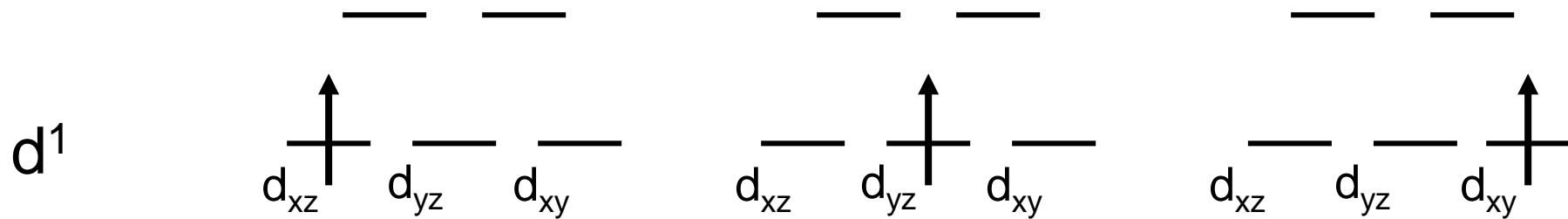
Thus an electron in an e_g orbital **can not** contribute to orbital angular momentum.



Orbital contribution to the magnetic moment

high spin octahedral d^n ions

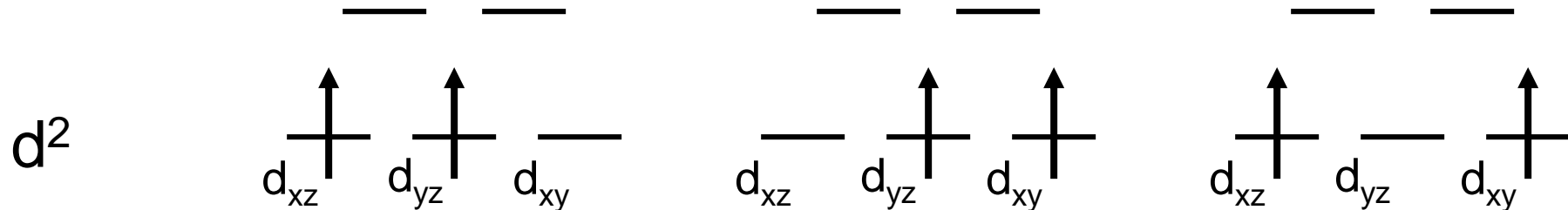
think of **possible** t_{2g} electron arrangements



Possible t_{2g} arrangements = 3

Orbital contribution = **YES**

d^1 e.g. Ti(III)



Possible t_{2g} arrangements = 3

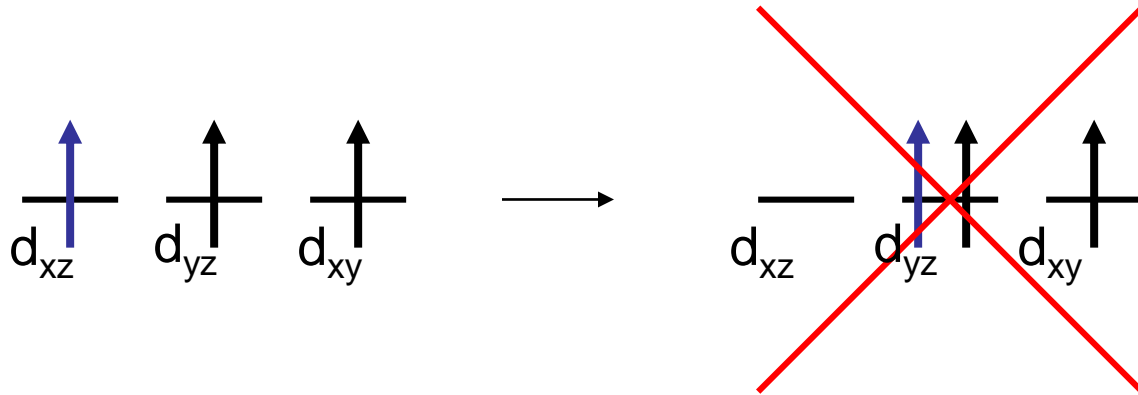
Orbital contribution = **yes**

d^2 e.g. V(III)

But, electrons in t_{2g} orbitals will not always contribute to orbital angular momentum

e.g. consider octahedral Cr(III) d^3 , t_{2g}^3

an electron in the d_{xz} orbital cannot by rotation be placed in *e.g.* the d_{yz} orbital because this orbital already contains an electron with the same spin as the incoming electron



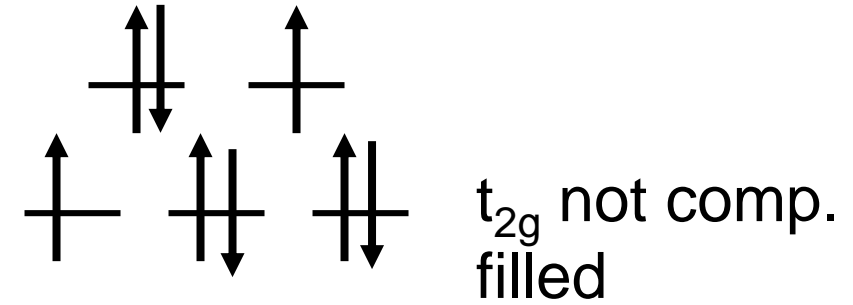
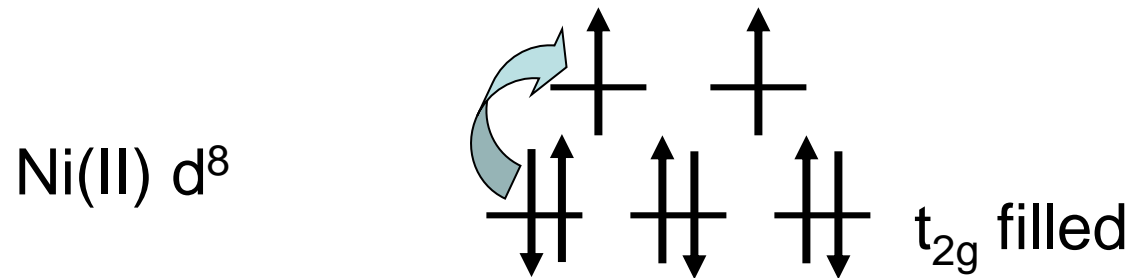
Therefore, there is only one possible t_{2g} arrangement,
and **NO** orbital angular momentum

TABLE 7.1 ORBITAL CONTRIBUTION FOR d^1 TO d^9 IONS IN OCTAHEDRAL AND TETRAHEDRAL STEREOCHEMISTRIES

	Number of d electrons	Octahedral complexes		Tetrahedral complexes		
		Configuration	Orbital contribution	Configuration	Orbital contribution	
	1	t_{2g}^1	—	e^1	no	
	2	t_{2g}^2	—	e^2	no	
HS	3	t_{2g}^3	no	$e^2 t_2^1$	—	yes
LS	4	$t_{2g}^3 e_g^1$	no	$e^2 t_2^2$	—	yes
HS	5	$t_{2g}^3 e_g^2$	—	$e^2 t_2^3$		no
LS	5	t_{2g}^5	—			
HS	6	$t_{2g}^4 e_g^2$	—	$e^3 t_2^3$		no
LS	6	t_{2g}^6	no			
HS	7	$t_{2g}^5 e_g^2$	—	$e^4 t_2^3$		no
LS	7	$t_{2g}^6 e_g^1$	no			
	8	$t_{2g}^6 e_g^2$	no	$e^4 t_2^4$	—	yes
	9	$t_{2g}^6 e_g^3$	no	$e^4 t_2^5$	—	yes

Orbital contribution to the magnetic moment: Excited state(s) contribution

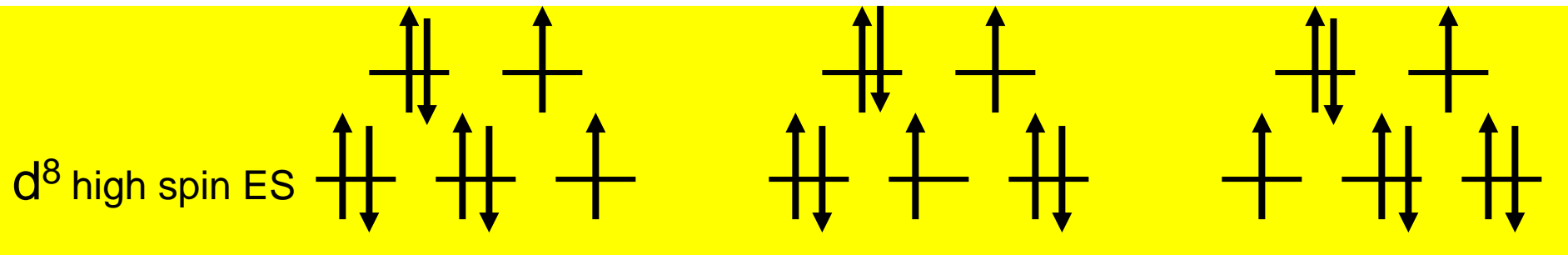
think of **possible** t_{2g} electron arrangements



Excited state

Possible t_{2g} arrangements = 1

Orbital contribution = **NO**



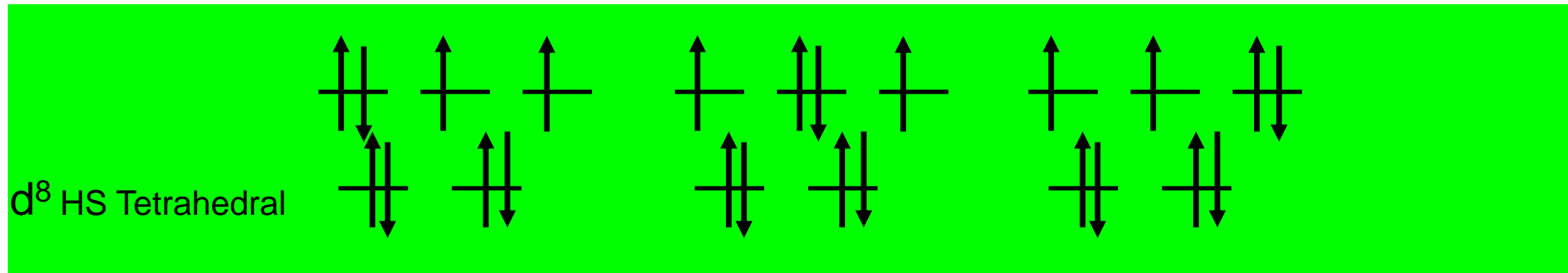
Possible t_{2g} arrangements = 3

Orbital contribution = **YES**

$\mu_{\text{exp}} > \mu_s$ for Oct. Ni^{2+}

Therefore for O_h Ni(II) the magnetic moments are larger if the GS-ES gap is small.

BUT FOR Tetrahedral Ni(II) situation is entirely different



Possible t_{2g} arrangements = 3
Orbital contribution = YES

M_{exp} O_h Ni(II) is smaller than M_{exp} T_d Ni(II)

Exp. $NiCl_4^{2-}$, $Ni(HMPA)_4^{2+}$ (HMPA=hexamethyl phosphoramidate) have mag. moment larger than 4 BM. (Larger the distortion smaller the mag.moment)

USEFUL IN DISCRIMINATING O_h vs T_d structures.

Magnetic properties of Lanthanides

- The f electrons in lanthanides are buried in the (n-2) shell.
- Thus 4f orbitals are normally unaffected by the surrounding ligands.
- Magnetic moments of Ln^{3+} ions are generally well described from the coupling of spin and orbital angular momenta ~ Russel-Saunders coupling to give J vector.
- Spin-Orbit coupling constants are large (approximately 1000 cm^{-1}).
- Ligand field effects are very small (approximately 100 cm^{-1}).
 - Only ground J-state is populated.
 - Spin-orbit coupling \gg ligand field splitting.

Magnetism is essentially independent of the environment (by approximation).

➤ Magnetic moments of a J-state is expressed by:

$$\mu_J = g_J \sqrt{J(J+1)} \mu_B \quad \text{where} \quad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

$$\text{here } J = L + S, L + S - 1, \dots, |L - S|$$

For the calculation of g_J value, we use

minimum value of J for the configurations up to half-filled

i.e. $J = L - S$ for f^0 - f^7 configurations

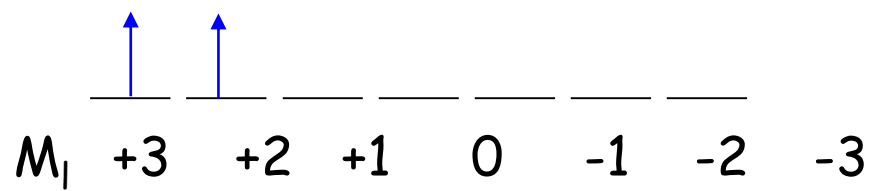
Maximum value of J for configurations for more than half-filled;

i.e. $J = L + S$ for f^8 - f^{14} configurations

For f^0 , f^7 and f^{14} configurations $L = 0$ hence μ_J becomes μ_S .

	config	g.s.	No. e-	color	calcd	obsd
La	4f ⁰	¹ S ₀	0	Colorless	0	0
Ce	4f ¹	² F _{5/2}	1	Colorless	2.54	2.3 - 2.5
Pr	4f ²	³ H ₄	2	Green	3.58	3.4 - 3.6
Nd	4f ³	⁴ I _{9/2}	3	Lilac	3.62	3.5 - 3.6
Pm	4f ⁴	⁵ I ₄	4	Pink	2.68	-
Sm	4f ⁵	⁶ H _{5/2}	5	Yellow	0.85	1.4 - 1.7
Eu	4f ⁶	⁷ F ₀	6	Pale pink	0	3.3 - 3.5
Gd	4f ⁷	⁸ S _{7/2}	7	Colorless	7.94	7.9 - 8.0
Tb	4f ⁸	⁷ F ₆	6	Pale pink	9.72	9.5 - 9.8
Dy	4f ⁹	⁶ H _{15/2}	5	Yellow	10.65	10.4 - 10.6
Ho	4f ¹⁰	⁵ I ₈	4	Yellow	10.6	10.4 - 10.7
Er	4f ¹¹	⁴ I _{15/2}	3	Rose-pink	9.58	9.4 - 9.6
Tm	4f ¹²	³ H ₆	2	pale green	7.56	7.1 - 7.6
Yb	4f ¹³	² F _{7/2}	1	Colorless	4.54	4.3 - 4.9
Lu	4f ¹⁴	¹ S ₀	0	Colorless	0	0

e.g. Pr^{3+} , $4f^2$



$(2S+1)L_J$

$$2S+1 = 3; L = 5 \longrightarrow {}^3\text{H}$$

$$J = L+S \dots \dots L-S = 6, 5, 4$$

$$\longrightarrow {}^3\text{H}_4$$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} = 0.8$$

$$\mu = g_J \sqrt{J(J+1)}$$

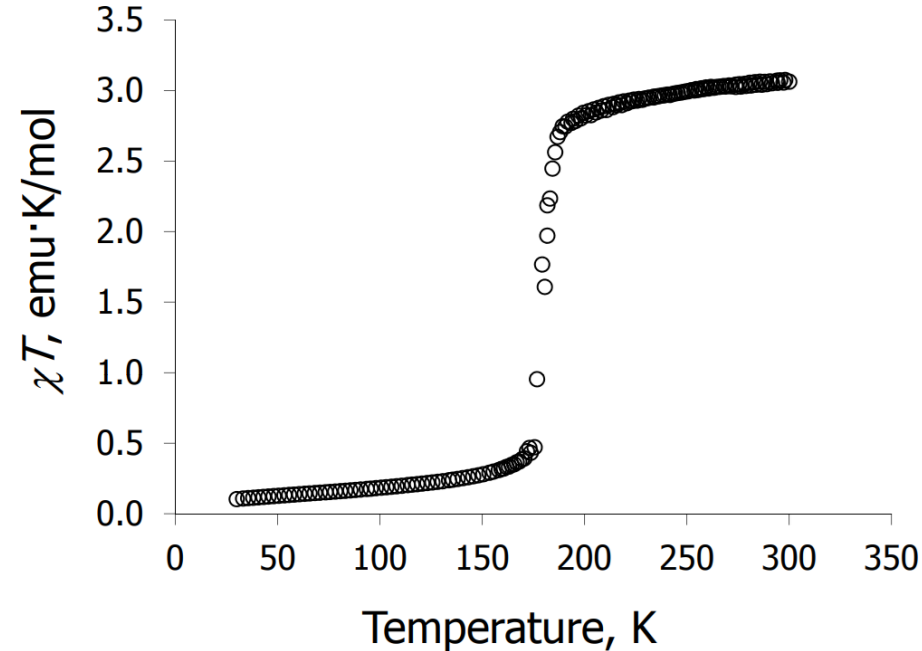
$$\mu = 4/5 \sqrt{20} = 3.6$$

$$\mu_{\text{obs}} = 3.5$$

Experiments 3.4 to 3.6 BM

- This formula fits well with experimental magnetic moments for all but Sm^{III} and Eu^{III} ions.
- Moments of these ions are altered from the formula due to temperature dependent population of low lying excited J-states

Magnetic susceptibility of some Fe²⁺ octahedral complexes has sharp decrease, why?

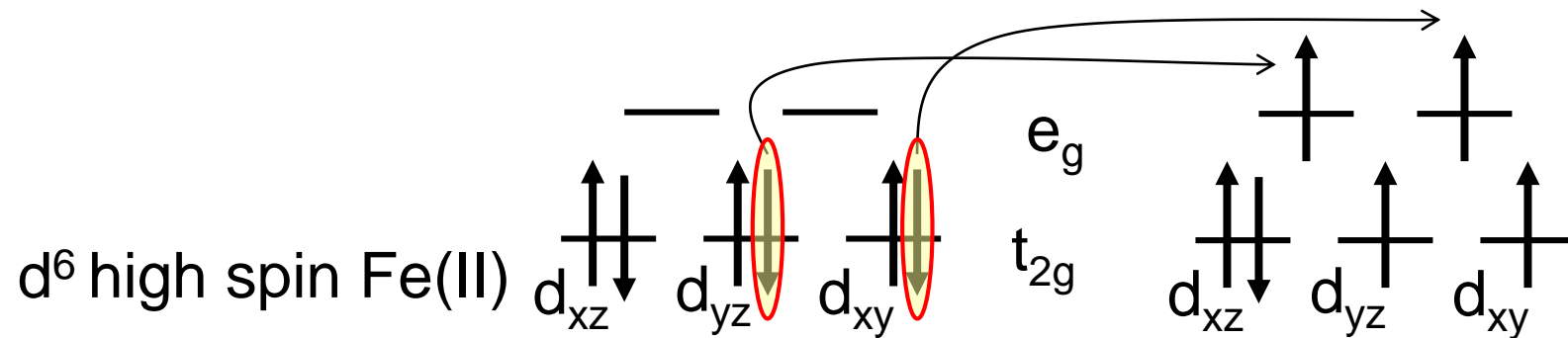


Low-spin-High-spin transition

-Configurations d^{4-7} in Octahedral has either LS or HS ground state.
(determined by Δ and mean spin pairing energy P).

- $\Delta \gg P \longrightarrow$ LS and if $\Delta \ll P \longrightarrow$ HS

-However when $\Delta \ll$ or $\gg P$ not true, a $LS \leftrightarrow HS$ transition can occur.
But often $|\Delta - P| \sim kT$.

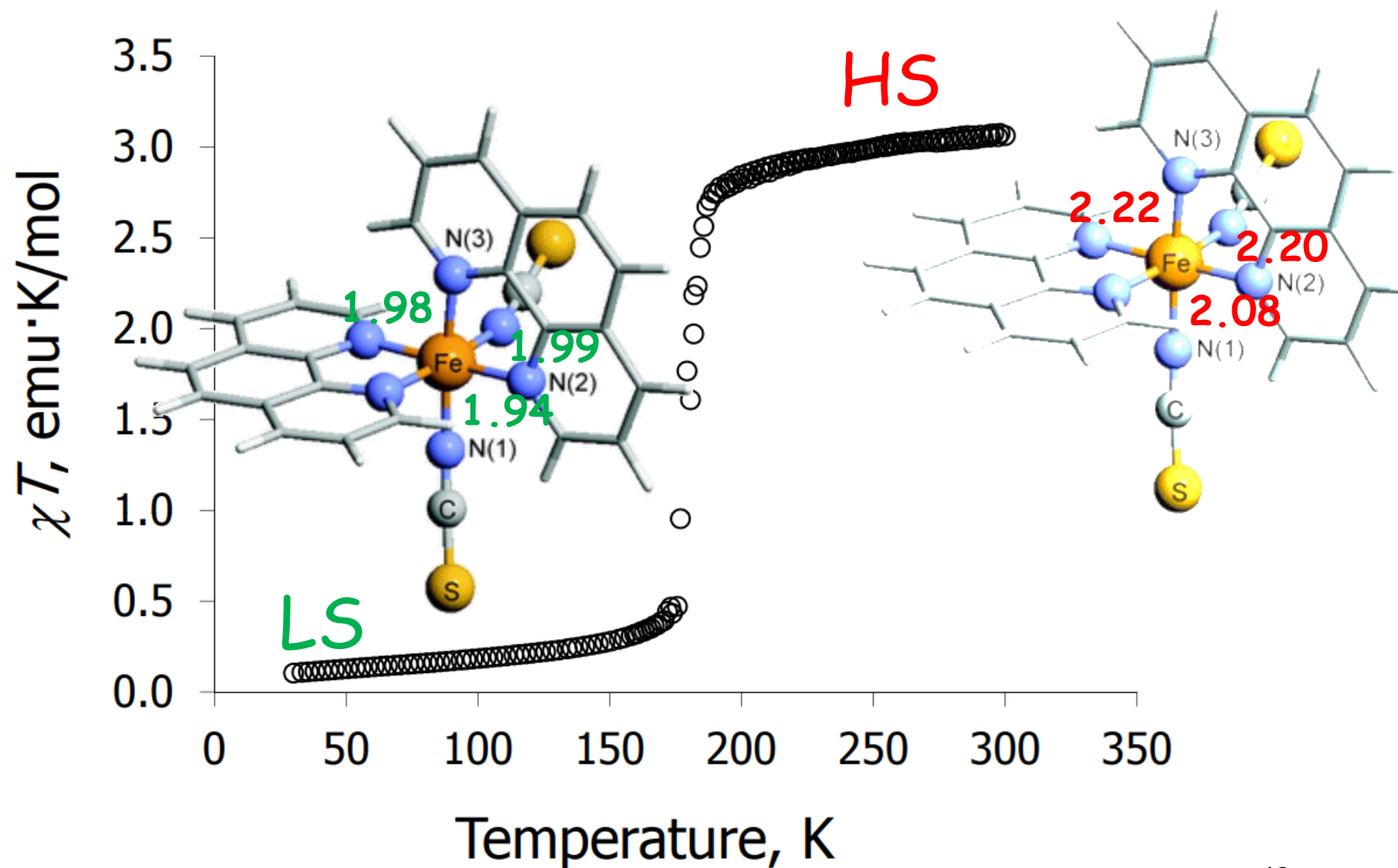
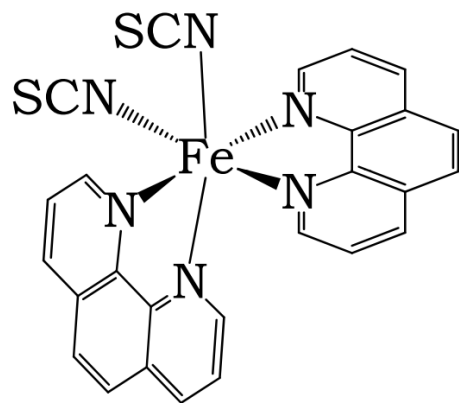


-Spin transition corresponds to an intraionic electron transfer.

- The occupancy in e_g orbitals in the HS state cause elongation of M-L bonds.

Spin-Crossover example Fe(II)-d⁶ ion:

-First example of spin-crossover .



-A abrupt change at ~176 K from $S=0$ to $S=2$.