

# **CH105(I)**

# **Inorganic Chemistry**

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**Can be reached via**

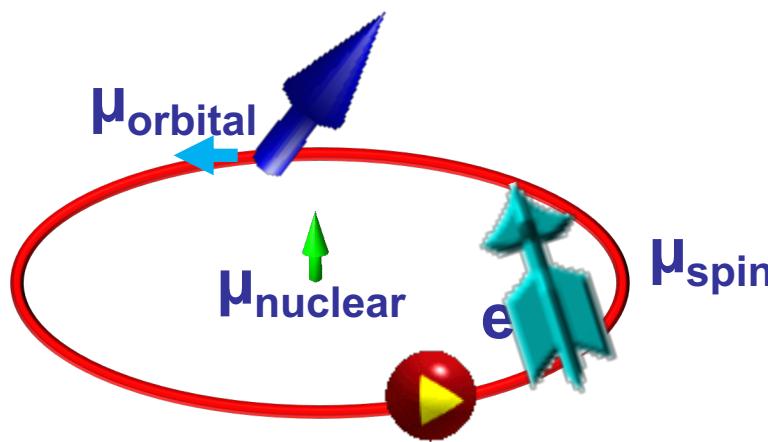
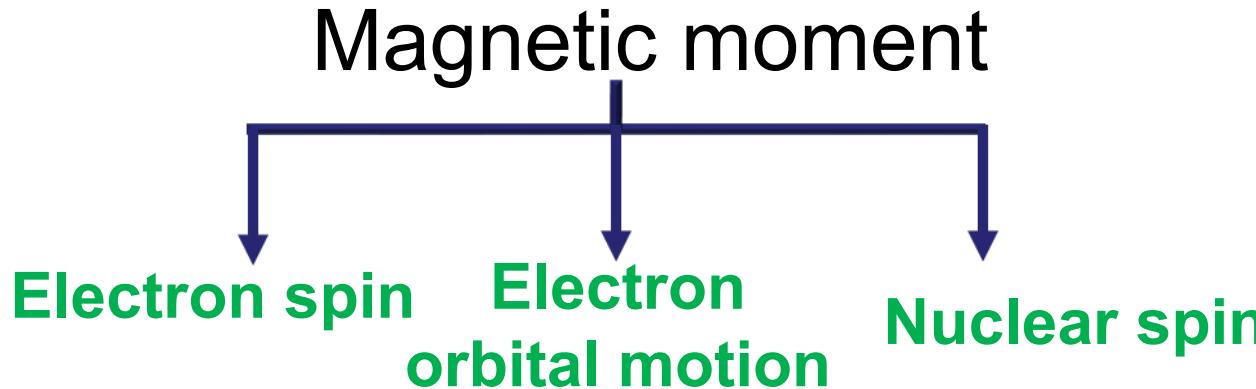
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**Or via moodle .....**

**Topic III**  
**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

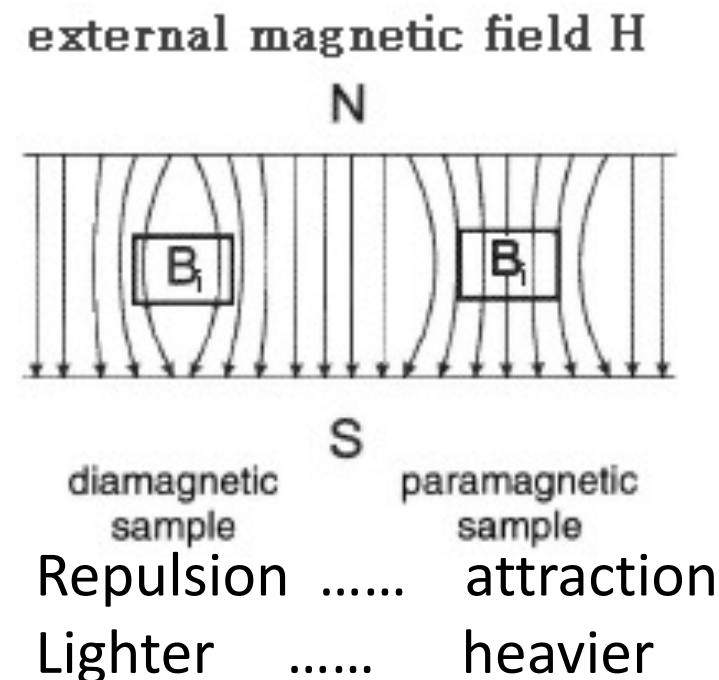
Two fundamentally different types of response:

- a) Diamagnetism - M and  $\chi$  are negative
- b) Paramagnetism - M and  $\chi$  are positive

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

Molecules with paired and unpaired e<sup>-</sup>'s = "paramagnetic"

Molecules with only paired e<sup>-</sup>'s = "diamagnetic"



# Dia and Paramagnetic compounds

*N<sub>2</sub> diamagnetic*

Pouring liquid dinitrogen



liquid dinitrogen  
does NOT stick



Dia.M. ex. H<sub>2</sub>O, KCl organic ligands,  
etc.

Bismuth metal (most diamagnetic  
of all metals)

diamagnetic

## *O<sub>2</sub> paramagnetic*

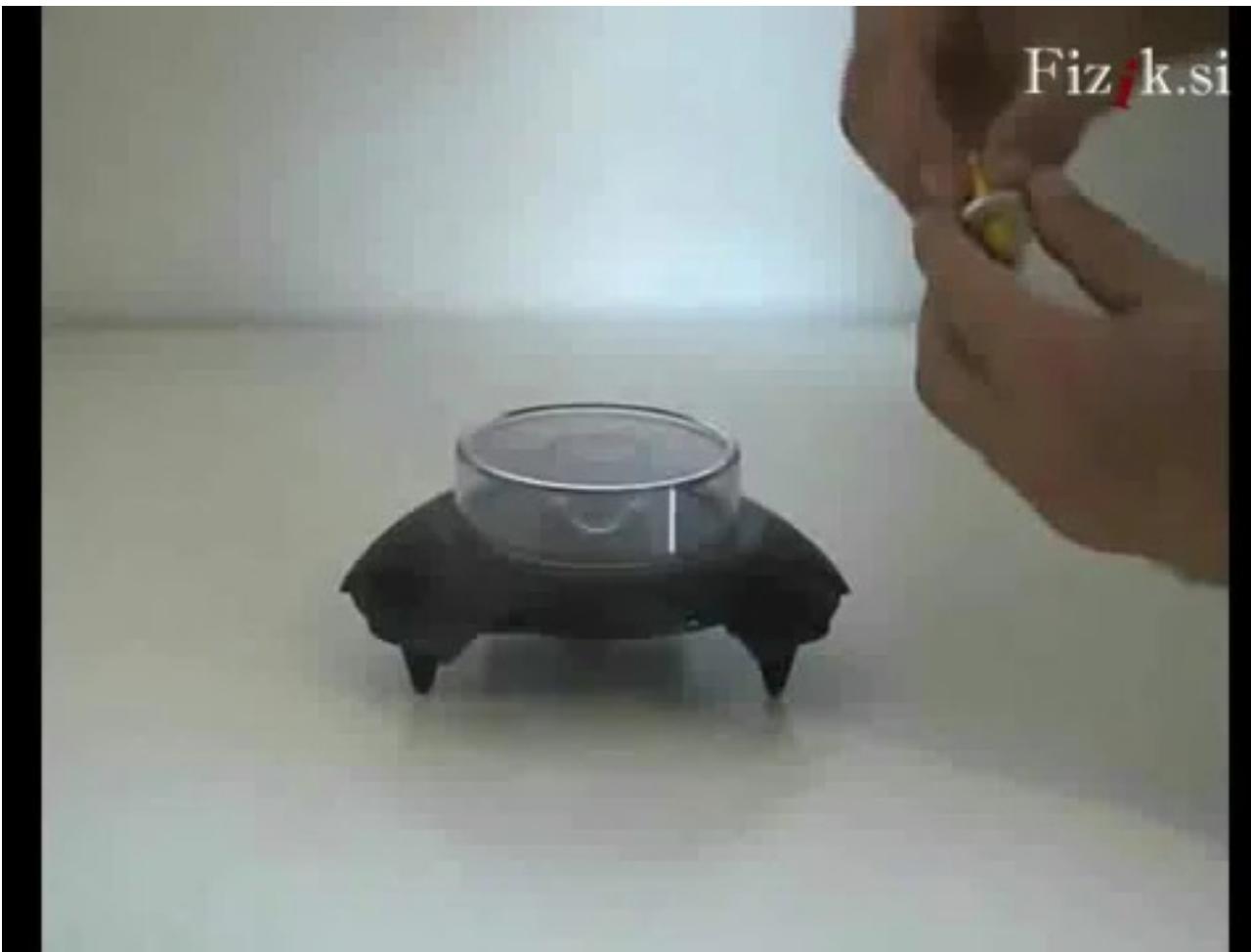
when dioxygen is in its ground state it is a triplet (spin S=1) and its reactivity is weak.



Liquid O<sub>2</sub>



## Video Magnetic Levitation: Property of diamagnetic molecules-I



Courtesy:<https://www.youtube.com/watch?v=g4lW7xydnH8>

## 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,  $\chi$ .

When the field is weak,  $\chi$  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

$\beta$  = Bohr Magneton

$N$  = Avogadro's number

Notes:

1.  $\chi$  is a fundamental property of magnetic materials

.....while  $\mu_{so}$  (B.M) is arbitrarily derived from  $\chi$ .

2. If  $\mu_{so}$  is constant with changing temperature

.....then  $\chi$  must increase as  $T$  is decreased.

3.  $\mu_{so}$  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  $\mathbf{S}$  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)

$\mu_B$  is the Bohr magneton

H = magnetic field

This is the first order Zeeman effect (ZE)

– the splitting is proportional to H

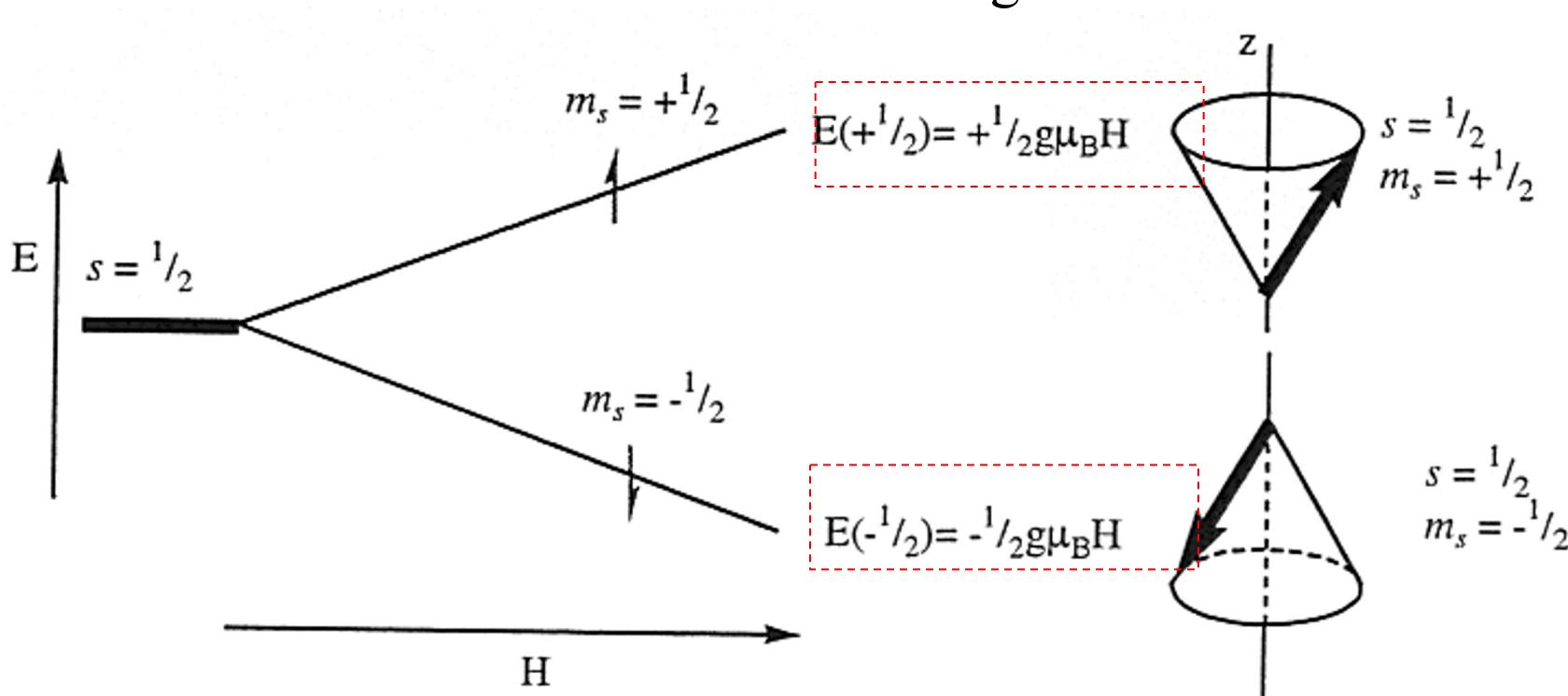
The splitting of levels by the external magnetic field is called Zeeman effect.

# The Zeeman effect: $s = \frac{1}{2}$

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

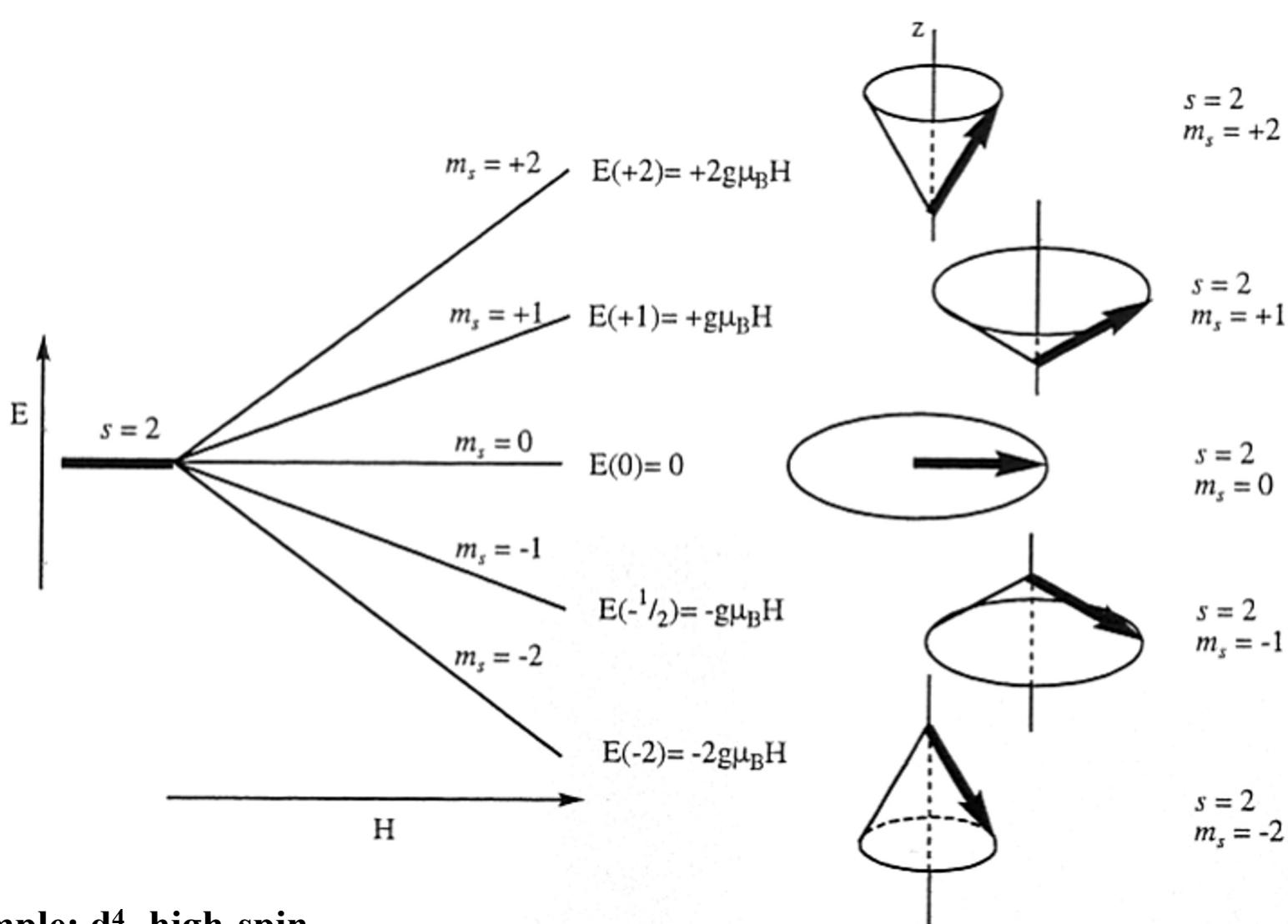
$$m_s g \mu_B H$$

$g \approx 2.0023$  (for a free electron)  
 $\mu_B$  is the Bohr magneton  
 $H$  = magnetic field

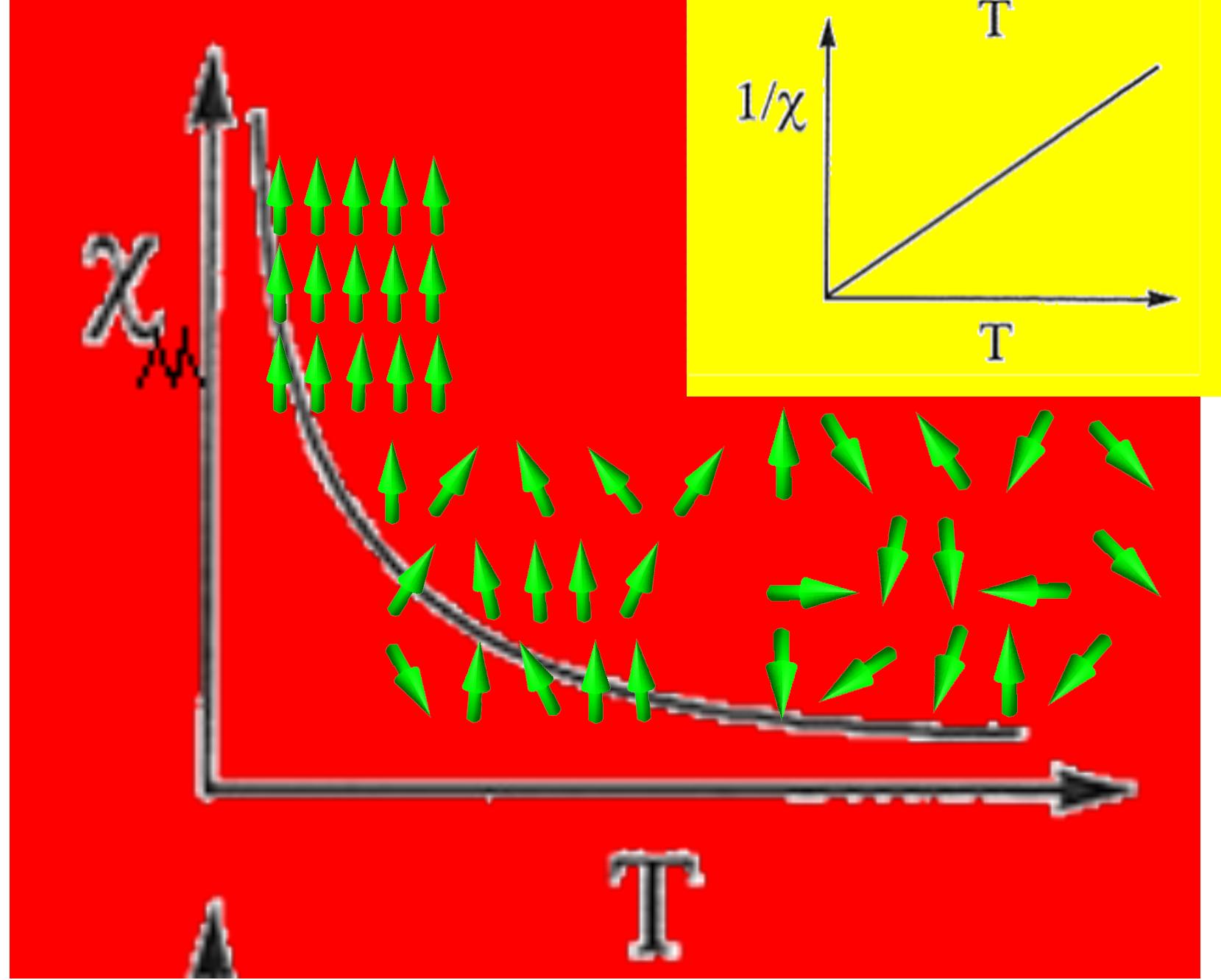


The difference in populations of  $m_s$  levels is crucial in providing the magnetization ( $M$ ) that we measure.

# 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:

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

$\theta$ = Curie-Weiss constant.

Weak, inter-molecular interactions are the usual cause of  $\theta$ .

$z$ = number of nearest neighbour interactions

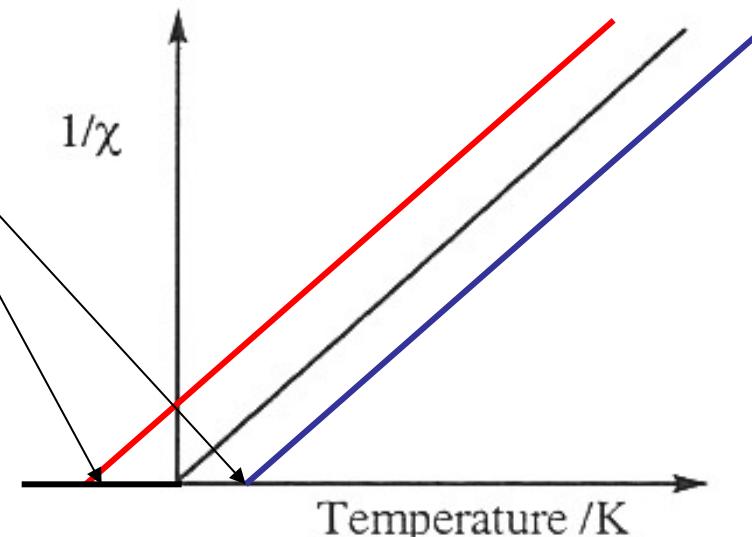
$J$ = int. between nearest neighbour

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

intercept on temperature axis =  $\theta$

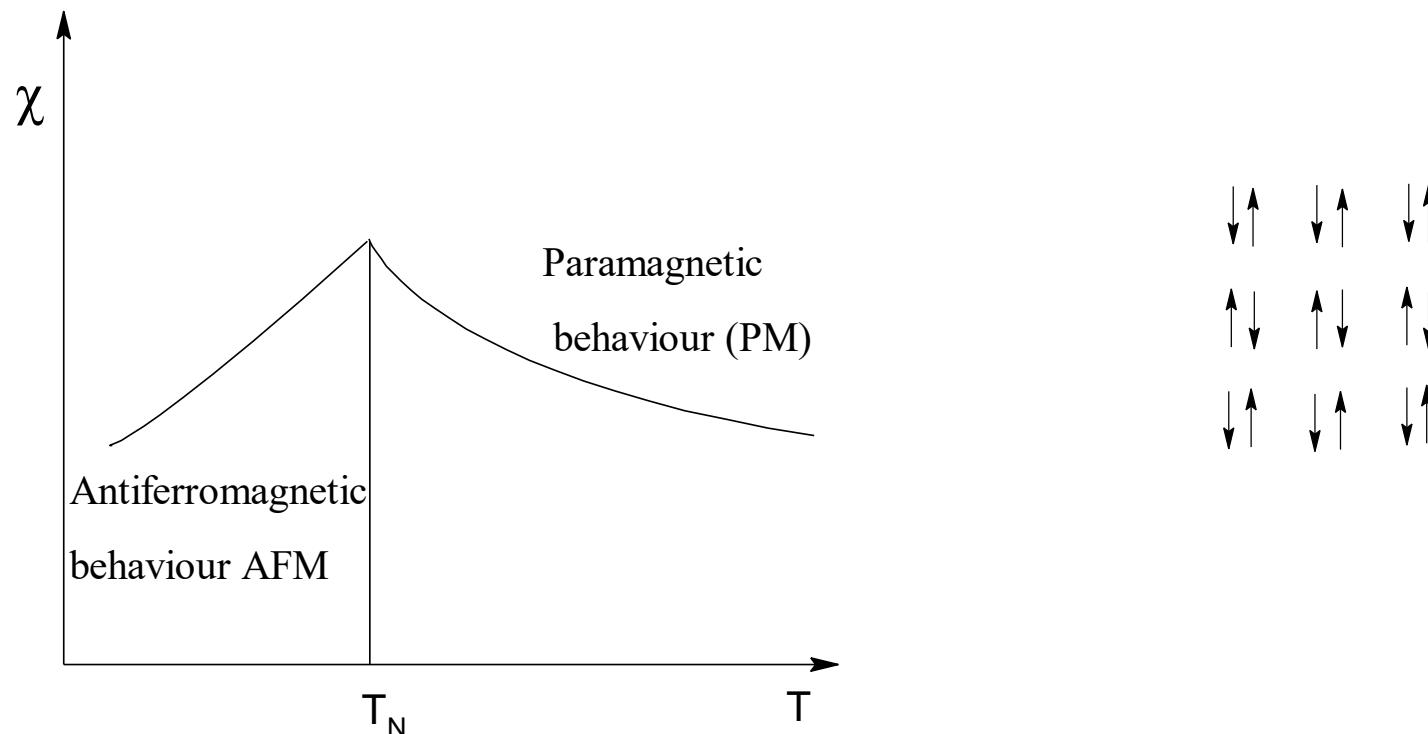
$\theta > 0$  for ferromagnets

$\theta < 0$  for antiferromagnets



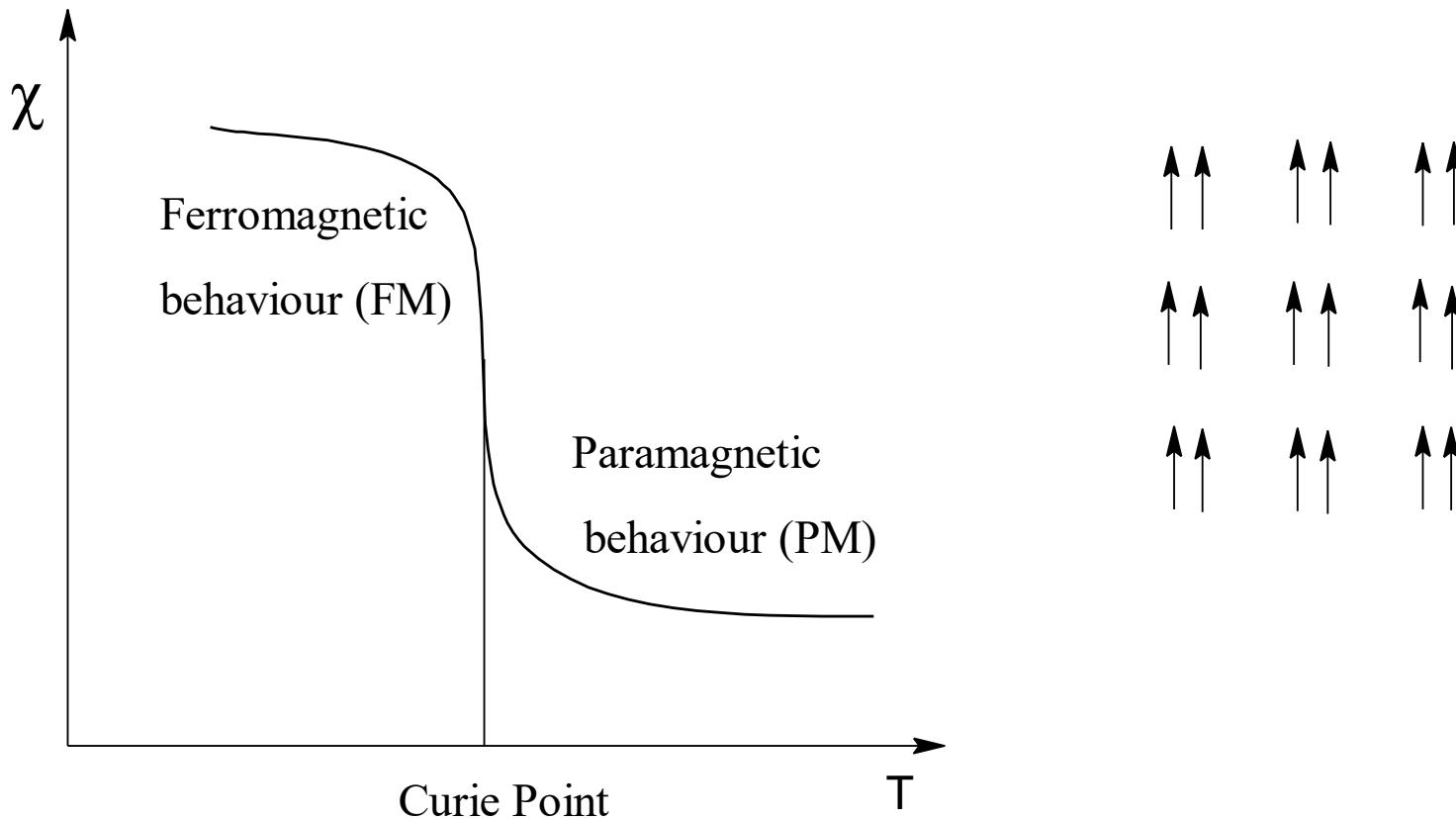
# Antiferromagnetism

- $J$  negative with spins antiparallel below  $T_N$



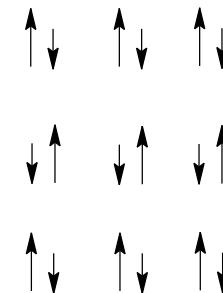
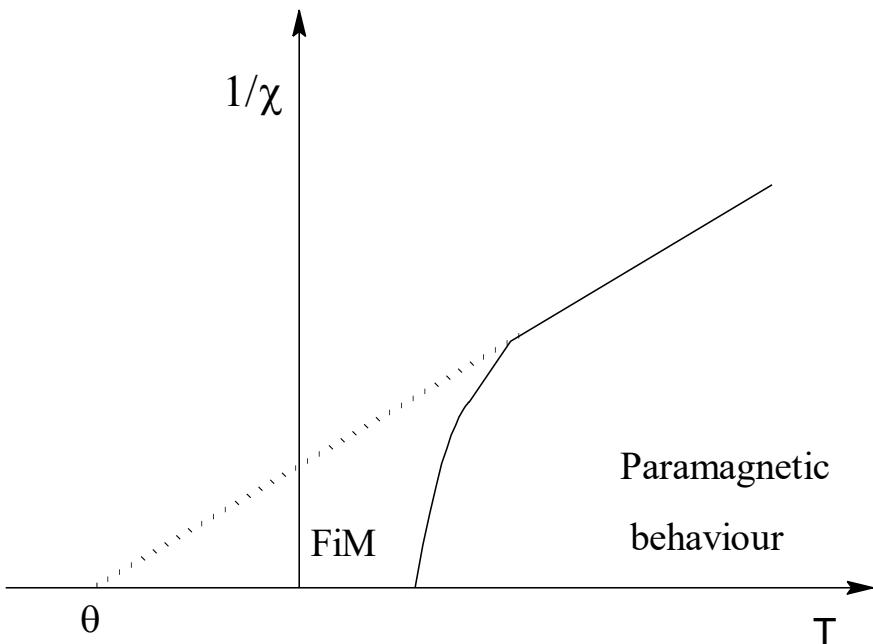
# Ferromagnetism

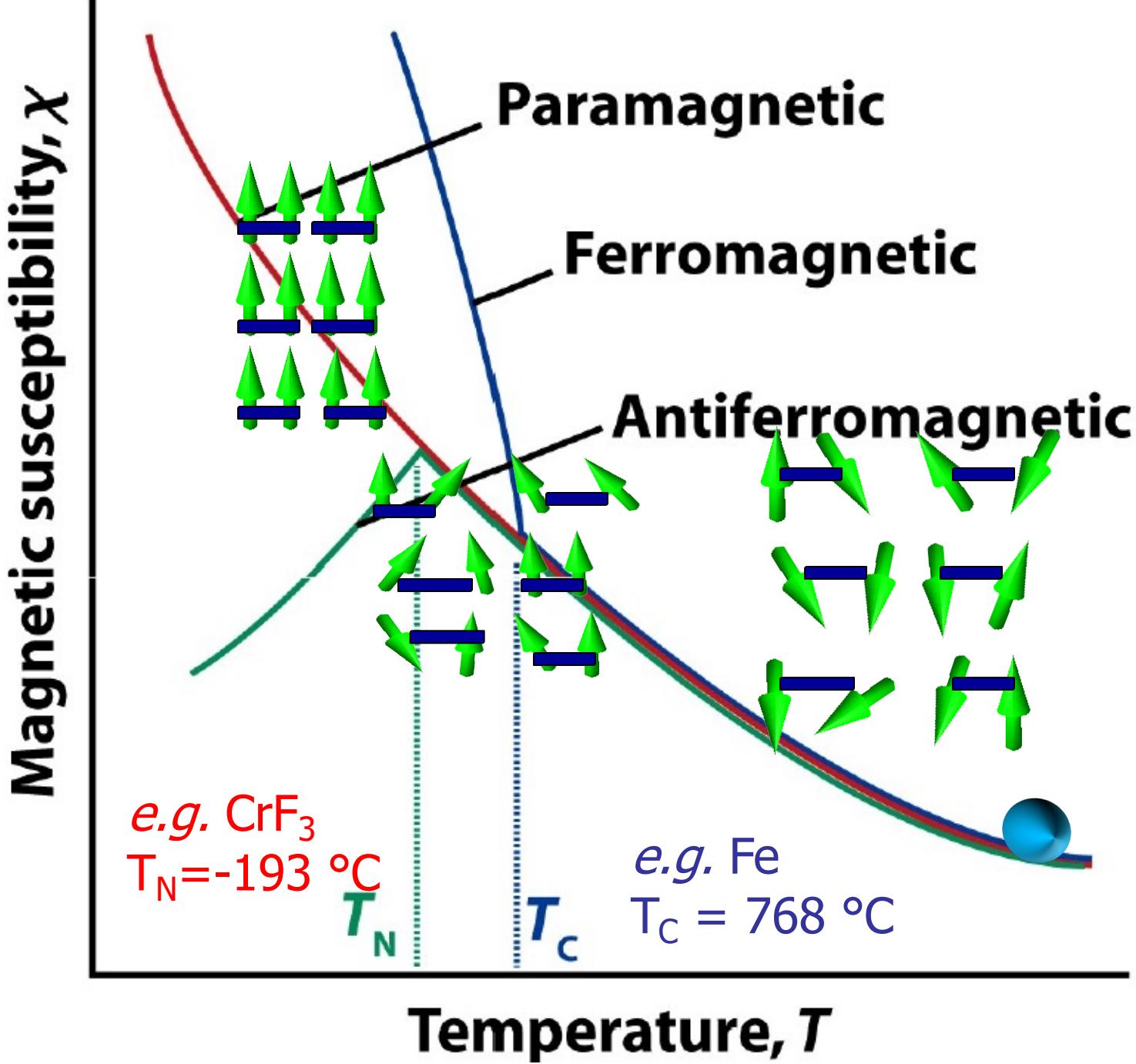
Spins parallel below  $T_c$



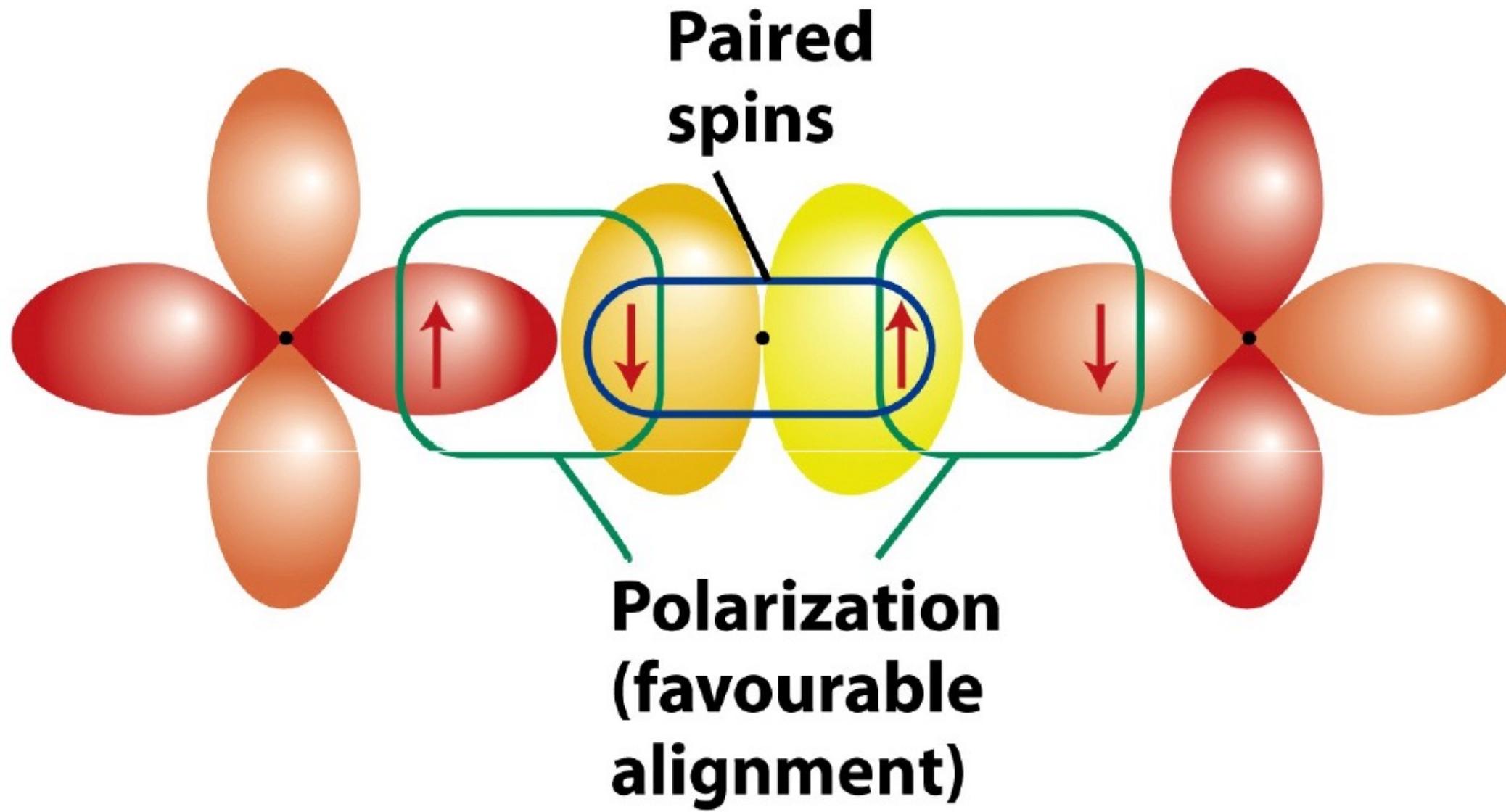
# Ferrimagnetism

- 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 ( $\mu_l$ ).

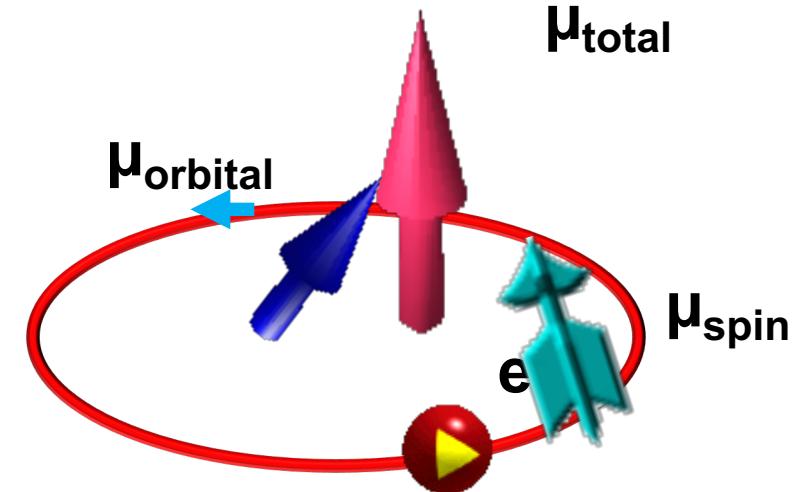
Spin motion of the electron generate spin magnetic moment ( $\mu_s$ )

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)

Different microstates exists for the same electronic configuration.

Free ions



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 ( $2S+1$ ) { $S = \text{sum of all the spins}$ } 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	$m_l$	$M_L = \sum m_l$						Ground Term	
			2	1	0	-1	-2	L	S	
$d^1$	$Ti^{3+}$		↑					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

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

Most stable term = Ground State Term

Free ions

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 $d^n$ 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	1/2	3/2	2	$^2D_{3/2}$
$d^2$	$V^{3+}$		↑	↑			3	1	2	2	$^3F_2$
$d^3$	$Cr^{3+}$		↑	↑	↑		3	3/2	3/2	3/2	$^4F_{3/2}$
$d^4$	$Mn^{3+}$		↑	↑	↑	↑	2	2	0	0	$^5D_0$
$d^5$	$Mn^{2+}$		↑	↑	↑	↑	0	5/2	-	-	$^6S$
$d^6$	$Fe^{2+}$		↑↓	↑	↑	↑	2	2	4	4	$^5D_4$
$d^7$	$Co^{2+}$		↑↓	↑↓	↑	↑	3	3/2	9/2	9/2	$^4F_{9/2}$
$d^8$	$Ni^{2+}$		↑↓	↑↓	↑↓	↑	3	1	4	4	$^3F_4$
$d^9$	$Cu^{2+}$		↑↓	↑↓	↑↓	↑↓	2	1/2	5/2	5/2	$^2D_{5/2}$

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

Where the maximum value of  $M_L$  defines  $L$

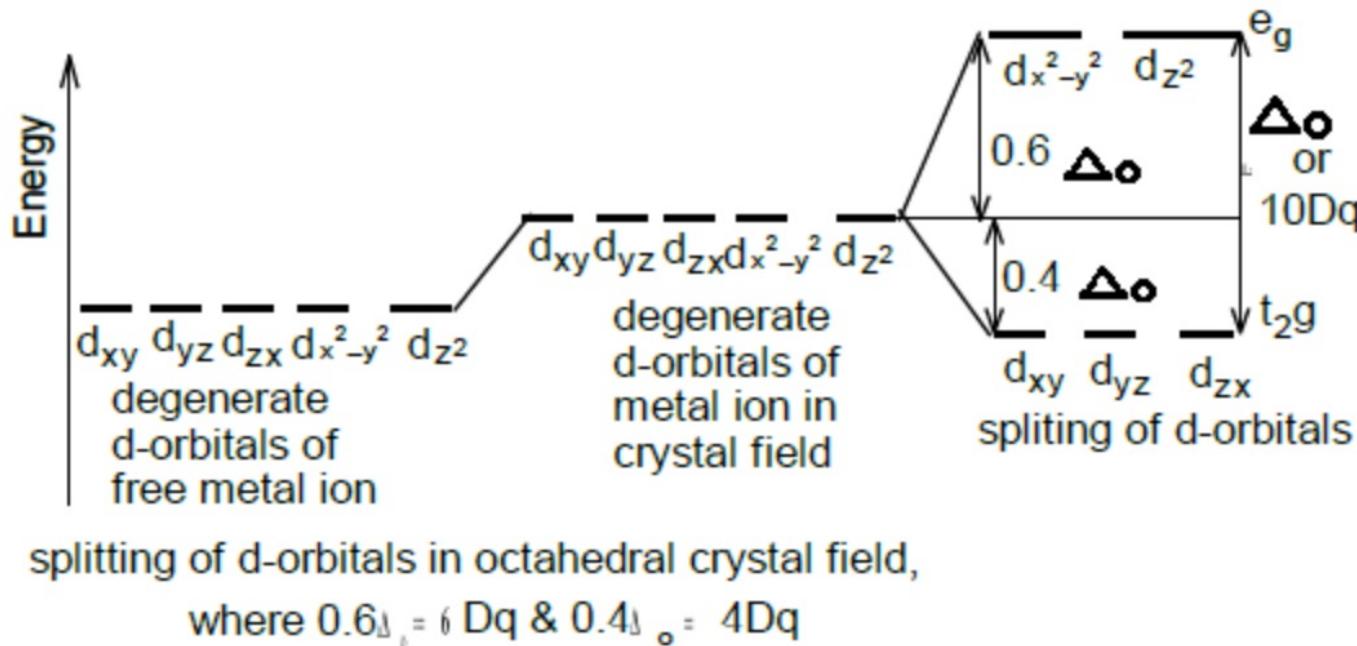
$L=0, 1, 2$  and  $3$  corresponds to  $S, P, D$  and  $F$  Terms

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



## Conditions to exhibit orbital angular momentum ( $\mu_L$ )

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  $e_g$

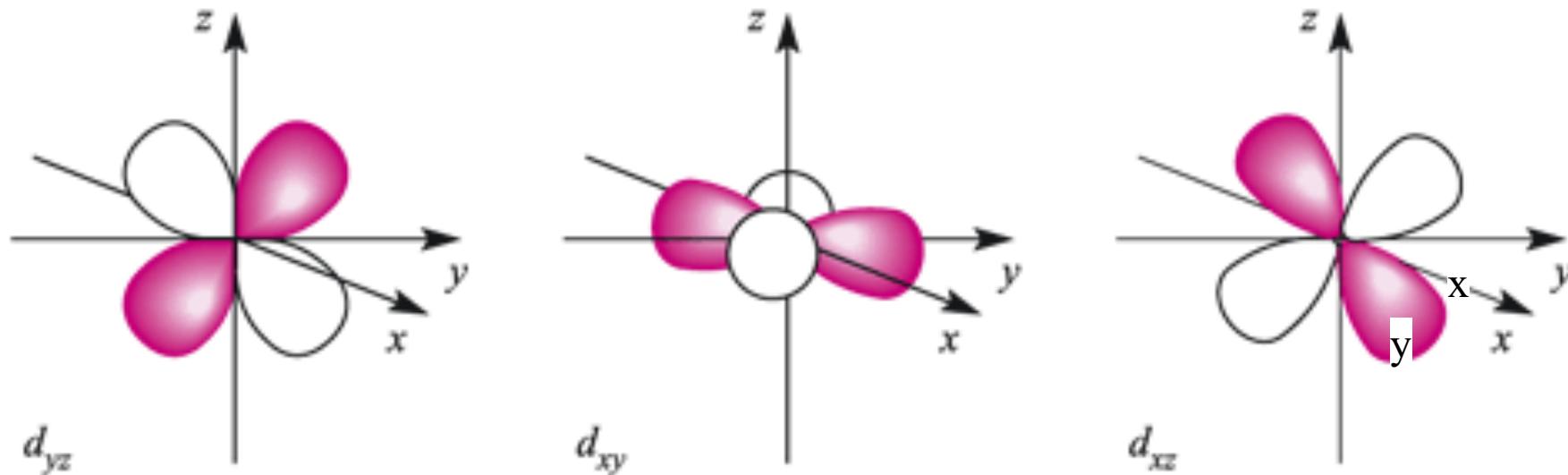
# Octahedral complexes

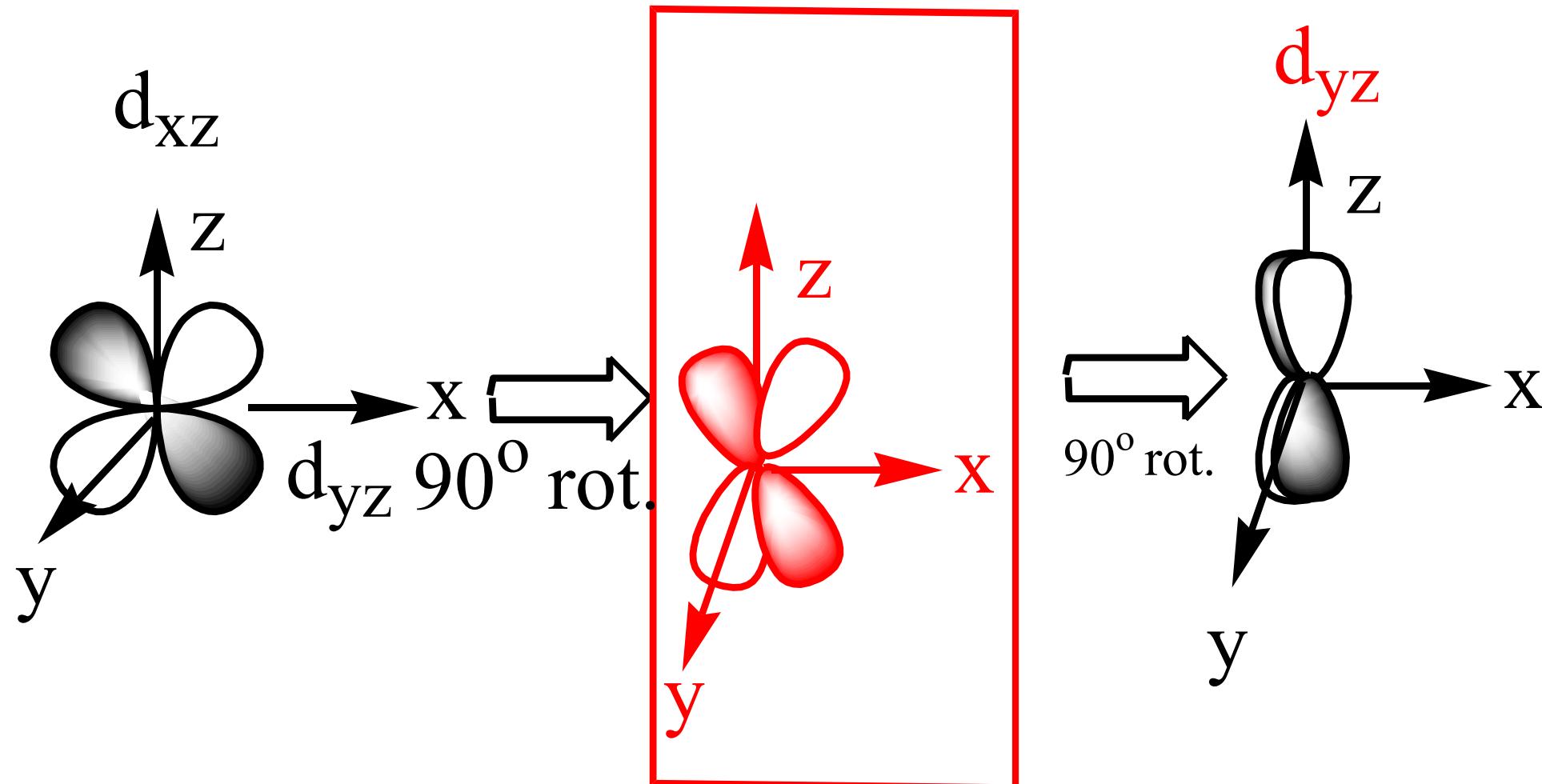
## Octahedral field

➤ 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<sub>xz</sub> / d<sub>yz</sub>

d<sub>xz</sub> / d<sub>xy</sub>

d<sub>yz</sub> / d<sub>xy</sub>

orbital motion about z axis

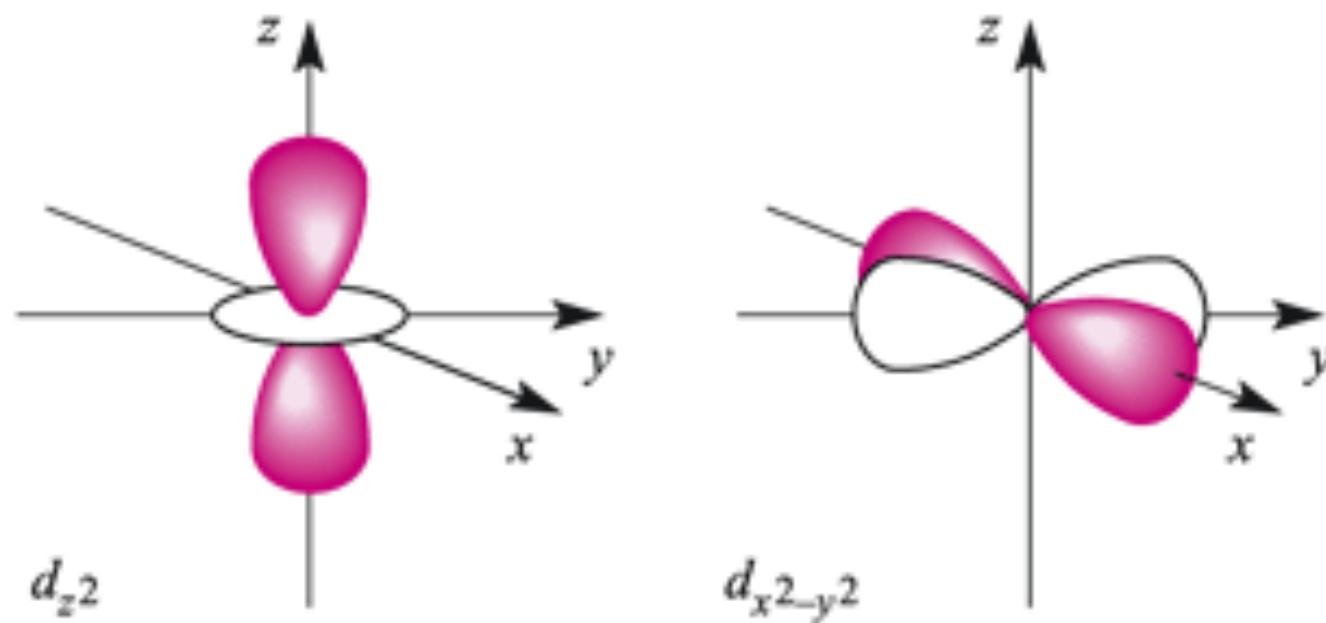
orbital motion about x axis

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

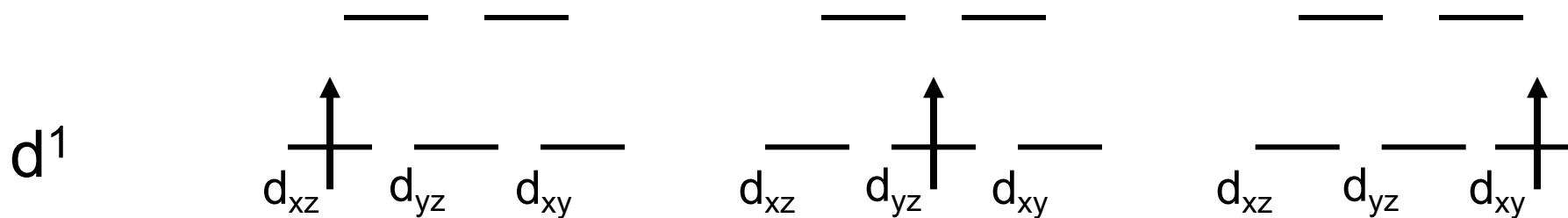
Thus an electron in an  $e_g$  orbital **can not** contribute to orbital angular momentum.



# Orbital contribution to the magnetic moment

high spin octahedral  $d^n$  ions

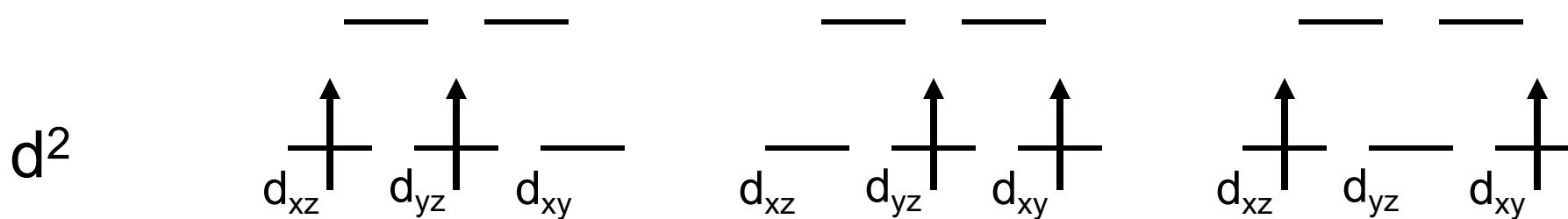
think of **possible**  $t_{2g}$  electron arrangements



Possible  $t_{2g}$  arrangements = 3

Orbital contribution = **YES**

$d^1$  e.g. Ti(III)



Possible  $t_{2g}$  arrangements = 3

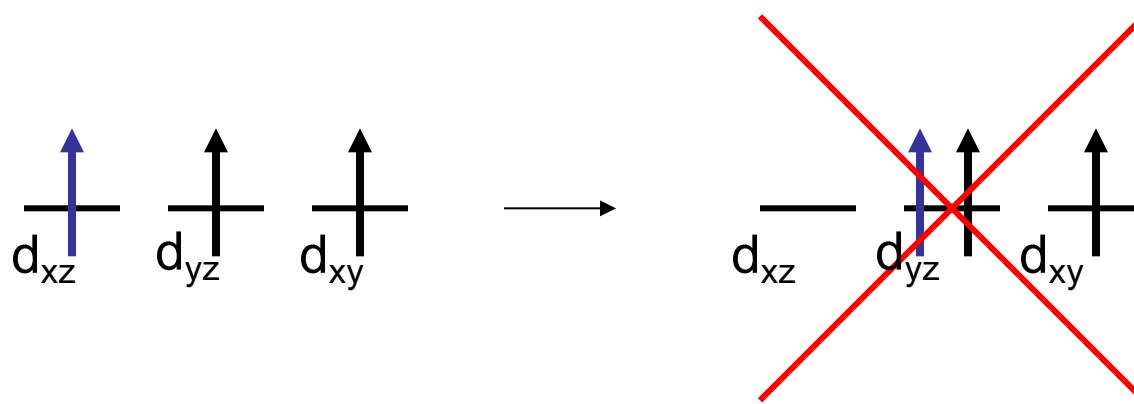
Orbital contribution = yes

$d^2$  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

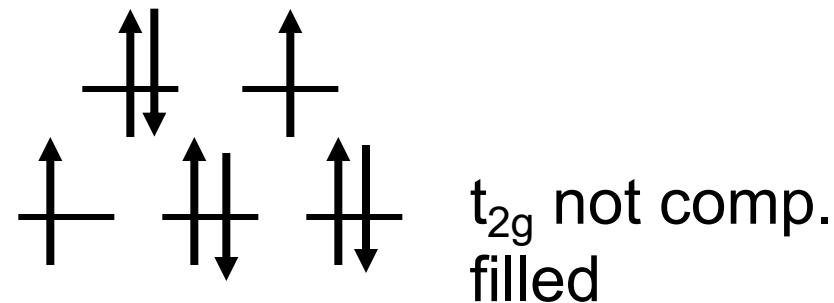
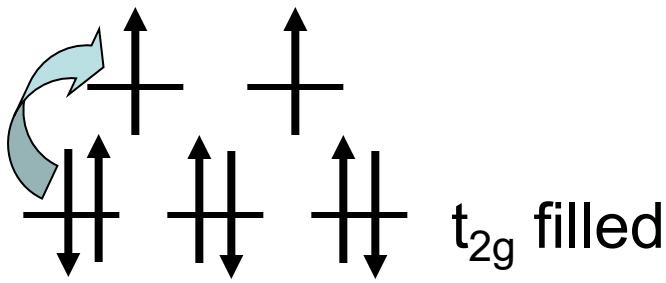
**TABLE 7.1 ORBITAL CONTRIBUTION FOR  $d^1$  TO  $d^9$  IONS IN OCTAHEDRAL AND TETRAHEDRAL STEREOCHEMISTRIES**

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

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

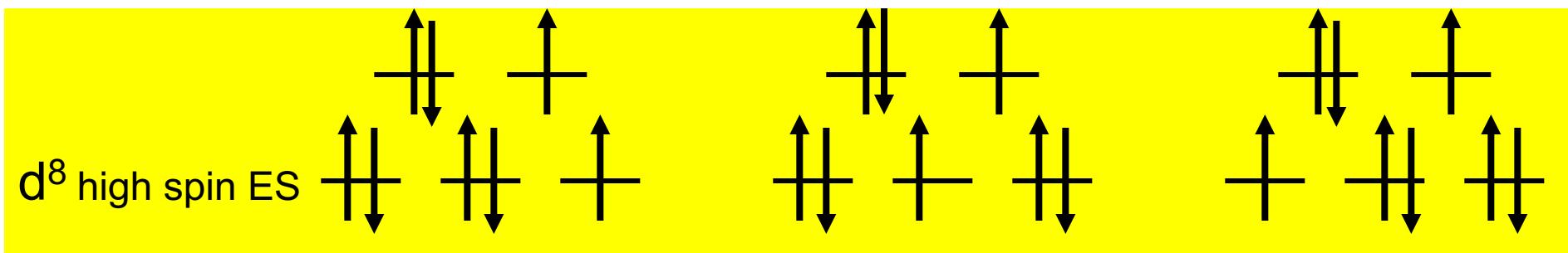
think of possible  $t_{2g}$  electron arrangements

Ni(II) d<sup>8</sup>



Excited state

Possible  $t_{2g}$  arrangements = 1  
Orbital contribution = NO



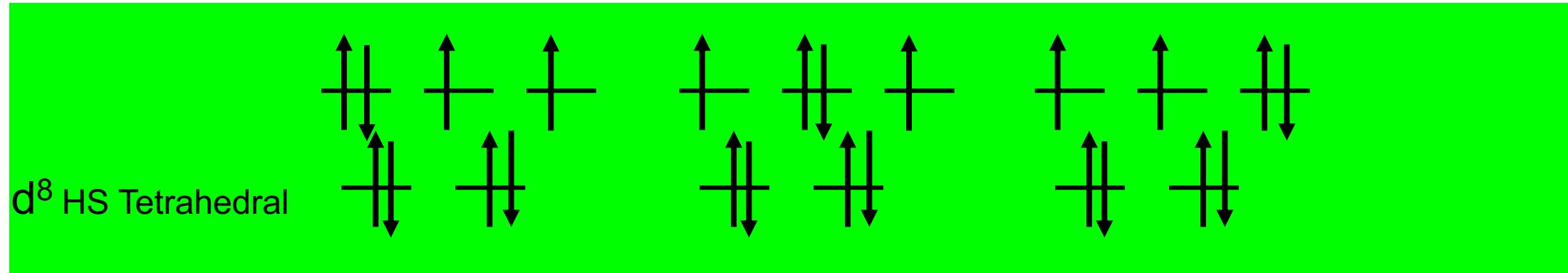
Possible  $t_{2g}$  arrangements = 3  
Orbital contribution = YES

$\mu_{\text{exp}} > \mu_s$  for Oct. Ni<sup>2+</sup>

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

Tetrahedral field

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 phosphoramide) 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  $\text{Ln}^{3+}$  ions are generally well described from the coupling of spin and orbital angular momenta  $\sim$  Russel-Saunders coupling to give J vector.
- Spin-Orbit coupling constants are large (approximately  $1000 \text{ cm}^{-1}$ ).
- Ligand field effects are very small (approximately  $100 \text{ cm}^{-1}$ ).
  - Only ground J-state is populated.
  - Spin-orbit coupling  $>>$  ligand field splitting.

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

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

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

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

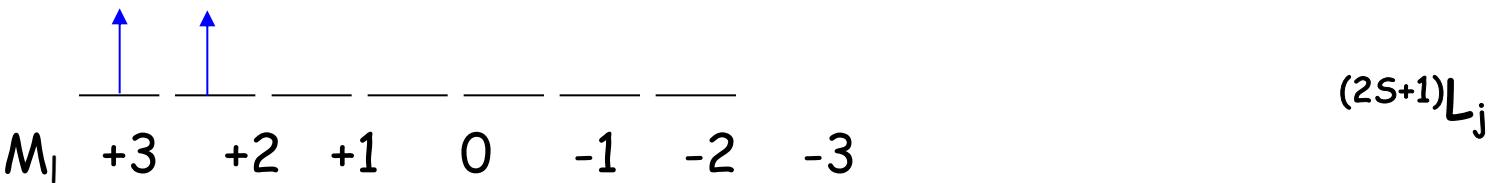
Maximum value of J for configurations for more than half-filled;

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

For  $f^0$ ,  $f^7$  and  $f^{14}$  configurations  $L=0$  hence  $\mu_J$  becomes  $\mu_S$ .

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

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



$(2S+1)L_J$

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

$$J = L+S \dots \textcolor{red}{L-S = 6, 5, 4}$$

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

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

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

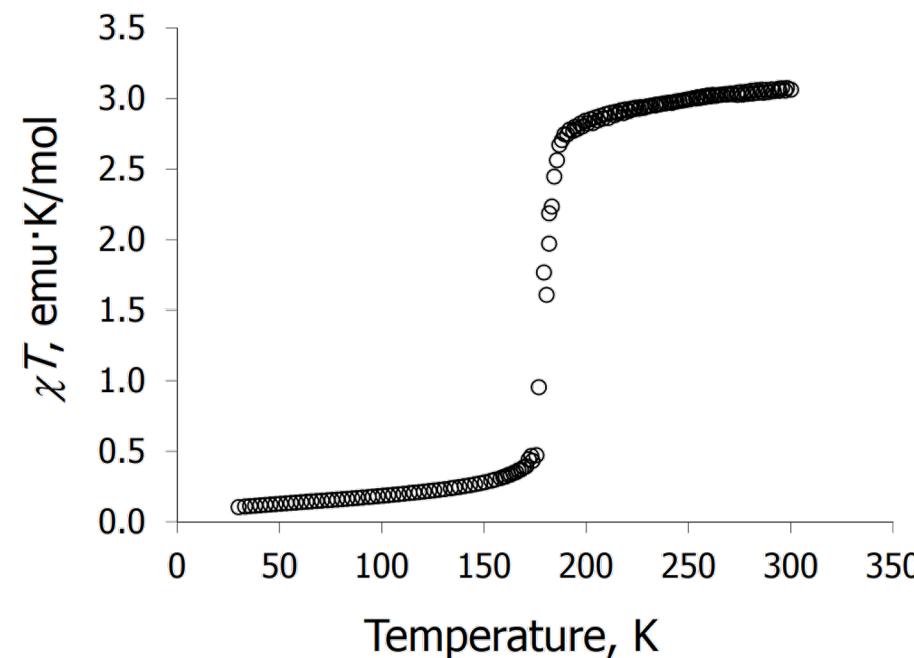
$$\mu = 4/5 \sqrt{20} = 3.6$$

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

Experiments 3.4 to 3.6 BM

- This formula fits well with experimental magnetic moments for all but  $\text{Sm}^{III}$  and  $\text{Eu}^{III}$  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 $\text{Fe}^{2+}$ octahedral complexes has sharp decrease, why?

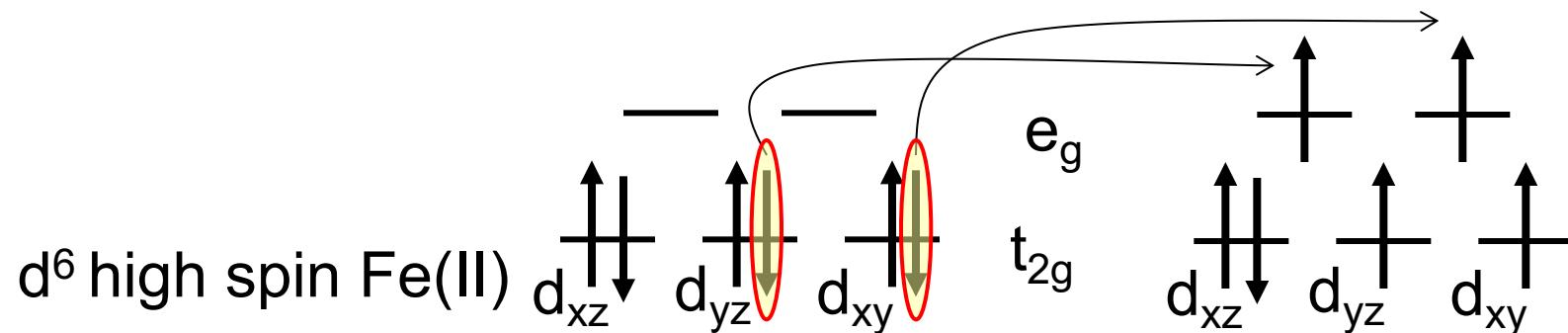


## Low-spin-High-spin transition

-Configurations  $d^4$ - $d^7$  in Octahedral has either LS or HS ground state.  
(determined by  $\Delta$  and mean spin paring 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  $|\Delta - P| \sim kT$ .

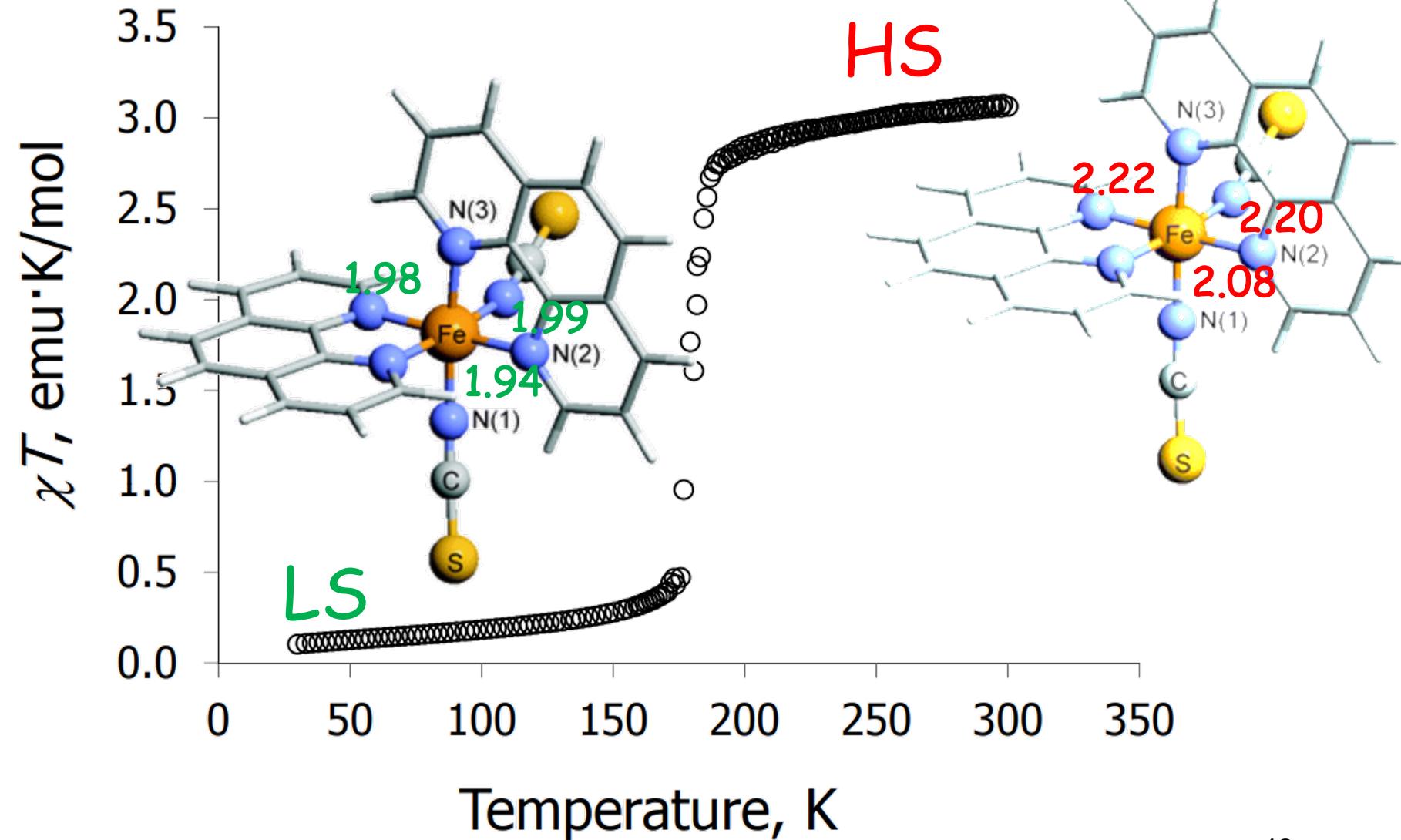
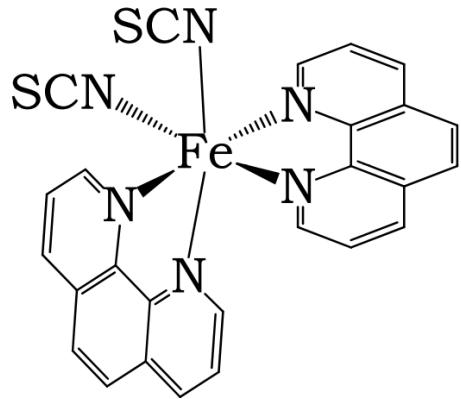


-Spin transition corresponds to an intraionic electron transfer.

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

## Spin-Crossover example Fe(II)-d<sup>6</sup> ion:

-First example of spin-crossover .



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