2022.4.27 Lecture 4

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

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Review

- Electronic states in magnetic ions

  LS coupling approach

  j-j coupling approach

- Paramagnetism by magnetic ions in insulators

  Curie law

  Breakdown of LS coupling approach in 3*d* transition metals

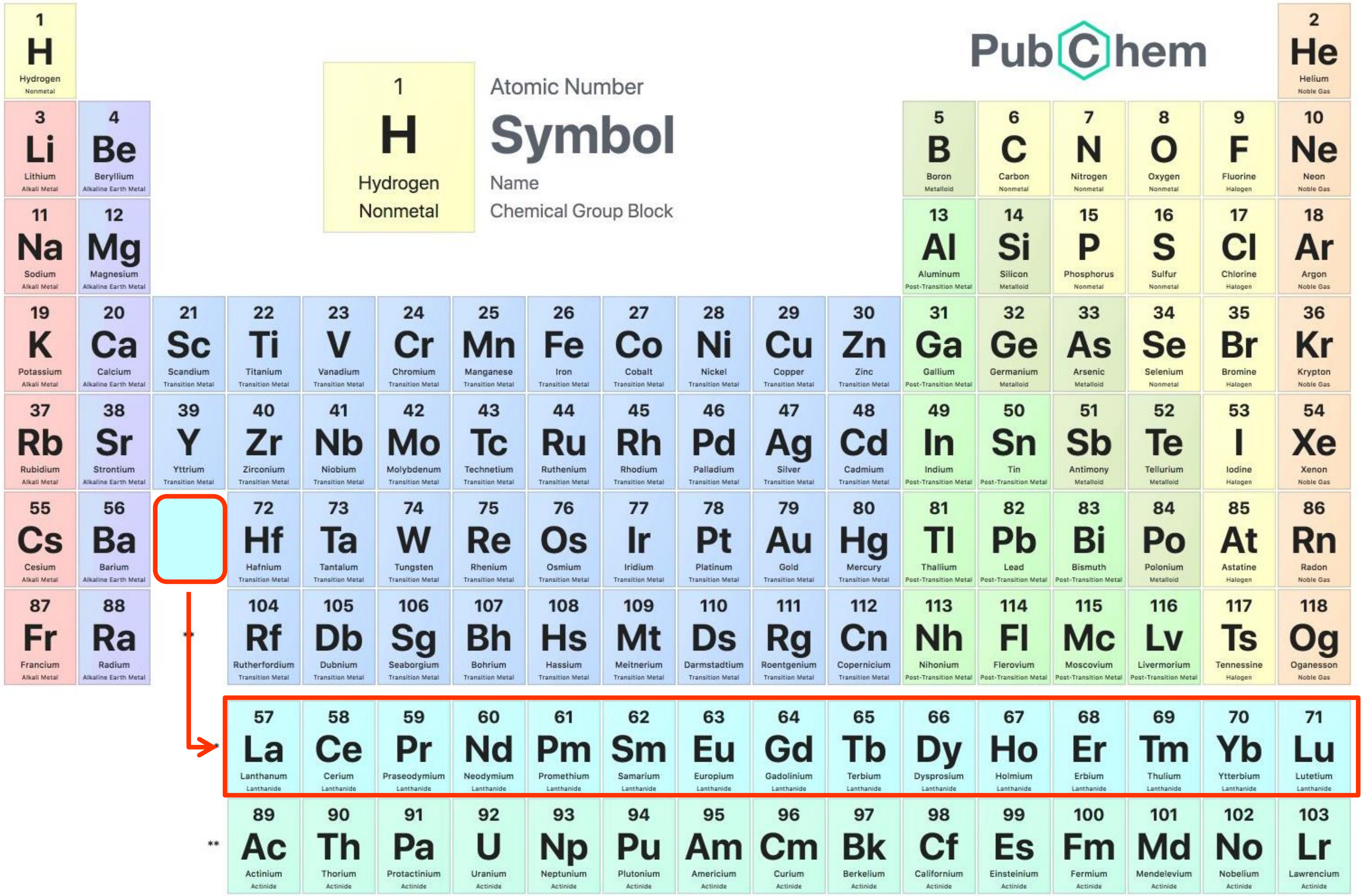
- Ligand field approach

  Octahedron potential

Agenda

- Ligand field approach to 3d orbitals in octahedral potential
- High-spin/ Low-spin state in ligand field potential
- Van Vleck (anomalous) paramagnetism
- Group theoretical approach to level splitting
- Experiments on and applications of paramagnetism

Periodic table of elements

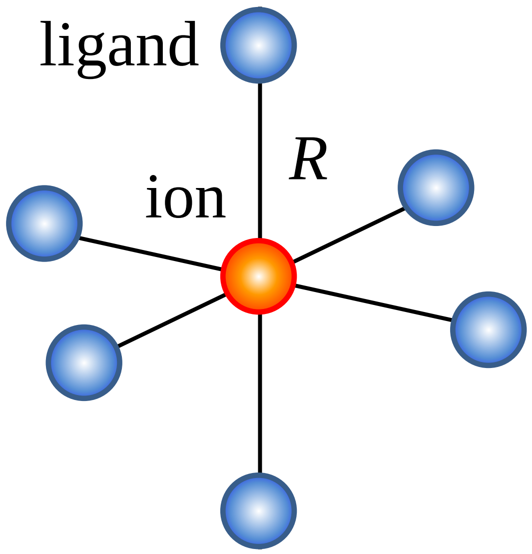


3*d* transition metals

Configuration		ion	p (exp.)	$g_J[J(J+1)]^{1/2}$	$2[S(S+1)]^{1/2}$
$3d^1$	$^2D_{3/2}$	V^{4+}	1.8	1.55	1.73
$3d^2$	$^3F_2$	V^{3+}	2.8	1.63	2.83
$3d^3$	$^4F_{3/2}$	V^{2+}	3.8	0.77	3.87
		Cr^{3+}	3.7	0.77	3.87
		Mn^{4+}	4.0	0.77	3.87
$3d^4$	$^5D_0$	Cr^{2+}	4.8	0	4.90
		Mn^{3+}	5.0	0	4.90
$3d^5$	$^6S_{5/2}$	Mn^{2+}	5.9	5.92	5.92
		Fe^{3+}	5.9	5.92	5.92
$3d^6$	$^5D_4$	Fe^{2+}	5.4	6.7	4.90
$3d^7$	$^4F_{9/2}$	Co^{2+}	4.8	6.63	3.87
$3d^8$	$^3F_4$	Ni^{2+}	3.2	5.59	2.83
$3d^9$	$^2D_{5/2}$	Cu^{2+}	1.9	3.55	1.73

The discrepancy tells that we need to take the effect of crystal field into account before going into the spin-orbit interaction.

Octahedral ligand field



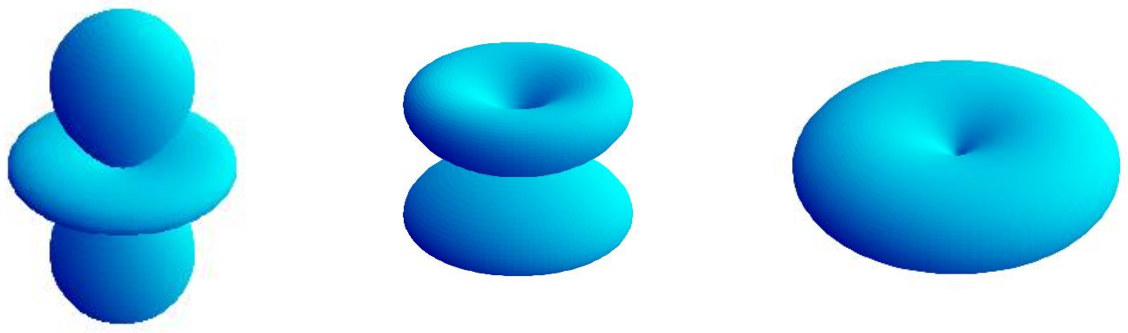
Potential generated by ligands at an octahedron vertices:

$$\frac{r}{R} \ll 1 \qquad v_{\rm cb}(\boldsymbol{r}) = eD\left(x^4 + y^4 + z^4 - \frac{3}{5}r^4\right) \qquad D = \frac{35Ze}{4R^5}$$

We are considering: Open shell 3*d* electrons

Single (3)*d* electron in $v_{\rm cb}(\boldsymbol{r})$

Diagonalization in the space of 3*d* wavefunction



$m = 0$ $\qquad$ $m = \pm 1$ $\qquad$ $m = \pm 2$

d

$$Y_{20}(\theta,\varphi) = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1),$$

$$Y_{2\pm1}(\theta,\varphi) = \mp\sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta e^{\pm i\varphi},$$

$$Y_{2\pm2}(\theta,\varphi) = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\varphi}$$

Looking for eigenfunction in tetrahedral potential

Linear combination of *d*-orbitals

Radial part → common for 5 orbitals

Angular part → second order in (x, y, z)

(1) $r^2(3\cos^2\theta - 1) = 2(x^2 + y^2) - z^2$

(2) $r^2 \cos\theta \sin\theta e^{\pm i\varphi} = z(x \pm iy)$

(3) $r^2 \sin^2\theta e^{\pm 2i\varphi} = x^2 \pm 2ixy - y^2$

Possible terms: $x^2, y^2, z^2, yz, zx, xy$

First order in x, y, z → disappearance of off-diagonal term by integration of odd-function

Candidates: $\frac{yz}{r^2}, \frac{zx}{r^2}, \frac{xy}{r^2}$ Easily obtained by adding/subtracting (2), (3)

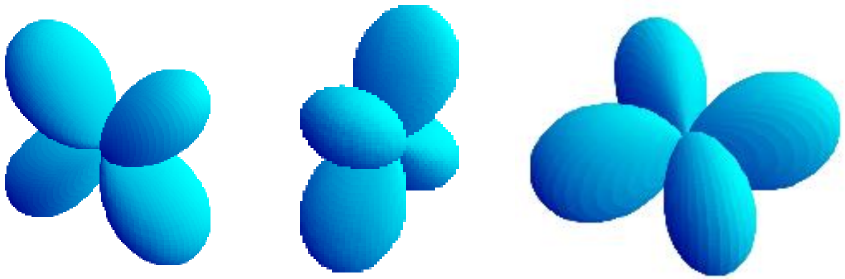
In order for vanishing off-diagonal term of $x^4 + y^4 + z^4$, we should take differences between x^2, y^2, z^2 :

$x^2 - z^2, y^2 - z^2$ orthogonalize ⟹ $3z^2 - r^2, x^2 - y^2$

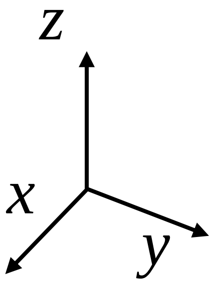
Obtained from (1) (itself), (3) (addition)

Octahedral ligand field (2)

$\phi_\xi\ (yz)$ $\phi_\eta\ (zx)$ $\phi_\zeta\ (xy)$

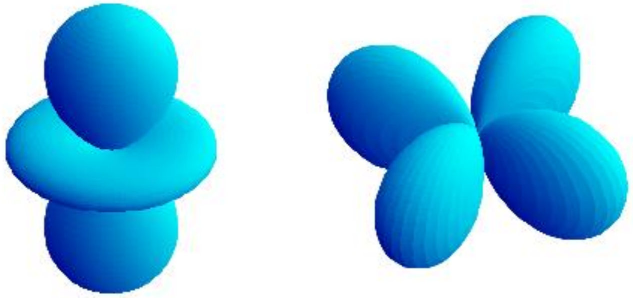


t_{2g}



$$\begin{cases} \phi_\xi = \dfrac{i}{\sqrt{2}}(\phi_{321} + \phi_{32-1}) = \sqrt{\dfrac{15}{4\pi}}\dfrac{yz}{r^2}R_{32}(r), \\ \phi_\eta = -\dfrac{1}{\sqrt{2}}(\phi_{321} - \phi_{32-1}) = \sqrt{\dfrac{15}{4\pi}}\dfrac{zx}{r^2}R_{32}(r), \\ \phi_\zeta = -\dfrac{i}{\sqrt{2}}(\phi_{322} - \phi_{32-2}) = \sqrt{\dfrac{15}{4\pi}}\dfrac{xy}{r^2}R_{32}(r) \end{cases}$$

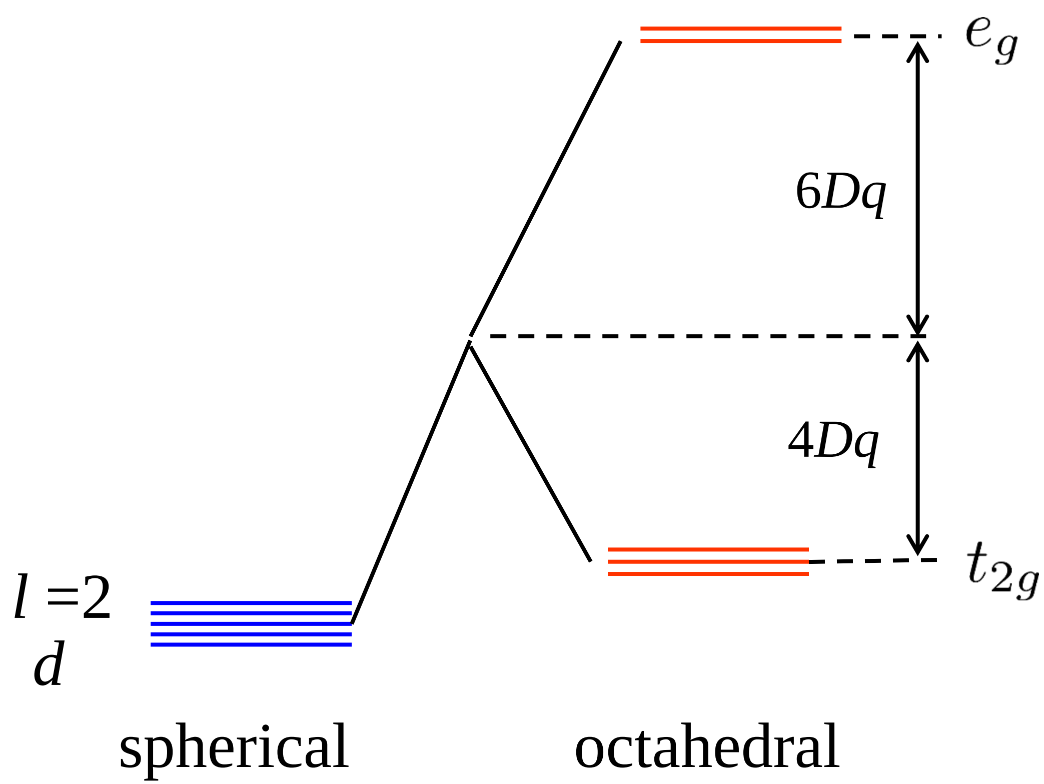
ϕ_u ϕ_v



e_g

$$\begin{cases} \phi_u = \phi_{320} = \sqrt{\dfrac{5}{16\pi}}\dfrac{3z^2 - r^2}{r^2}R_{32}(r), \\ \phi_v = -\dfrac{1}{\sqrt{2}}(\phi_{322} + \phi_{32-2}) = \sqrt{\dfrac{5}{16\pi}}\dfrac{x^2 - y^2}{r^2}R_{32}(r) \end{cases}$$

Energy level splitting and quenching of orbital magnetic moment



$$q = \frac{2e}{105}\langle r^4\rangle = \frac{2e}{105}\int |R_{32}(r)|^2 r^4 (r^2 dr)$$

Orbital angular momentum:

e.g. $$\phi_\zeta = -\frac{i}{\sqrt{2}}(\phi_{n22} - \phi_{n2-2})$$

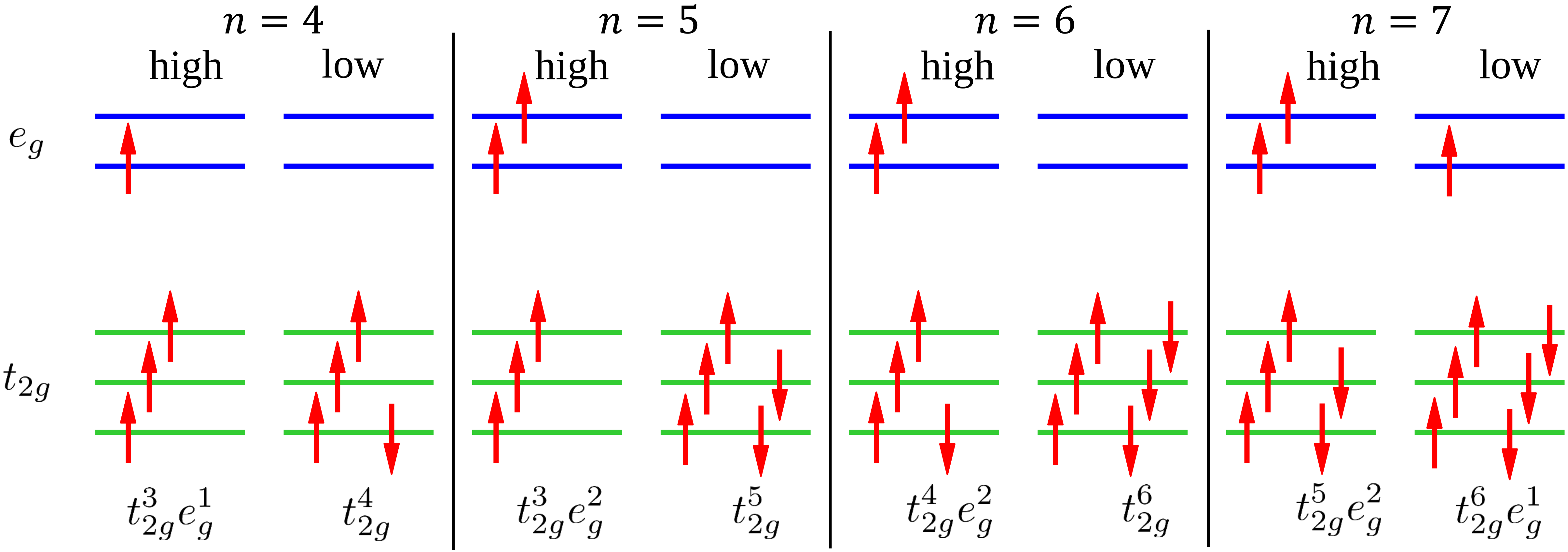
$$\langle\phi_\zeta|l_z|\phi_\zeta\rangle = 2 - 2 = 0$$

Neither t_{2g} nor e_g orbital does not have angular momentum

⇩

Explanation of quenching of orbital angular moment

High-spin and low-spin states



(Effect of crystal field) > (Coulomb repulsion)

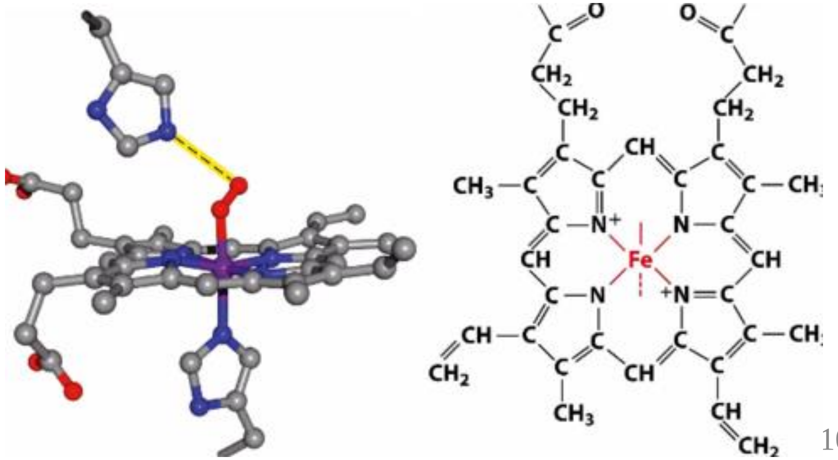
↓

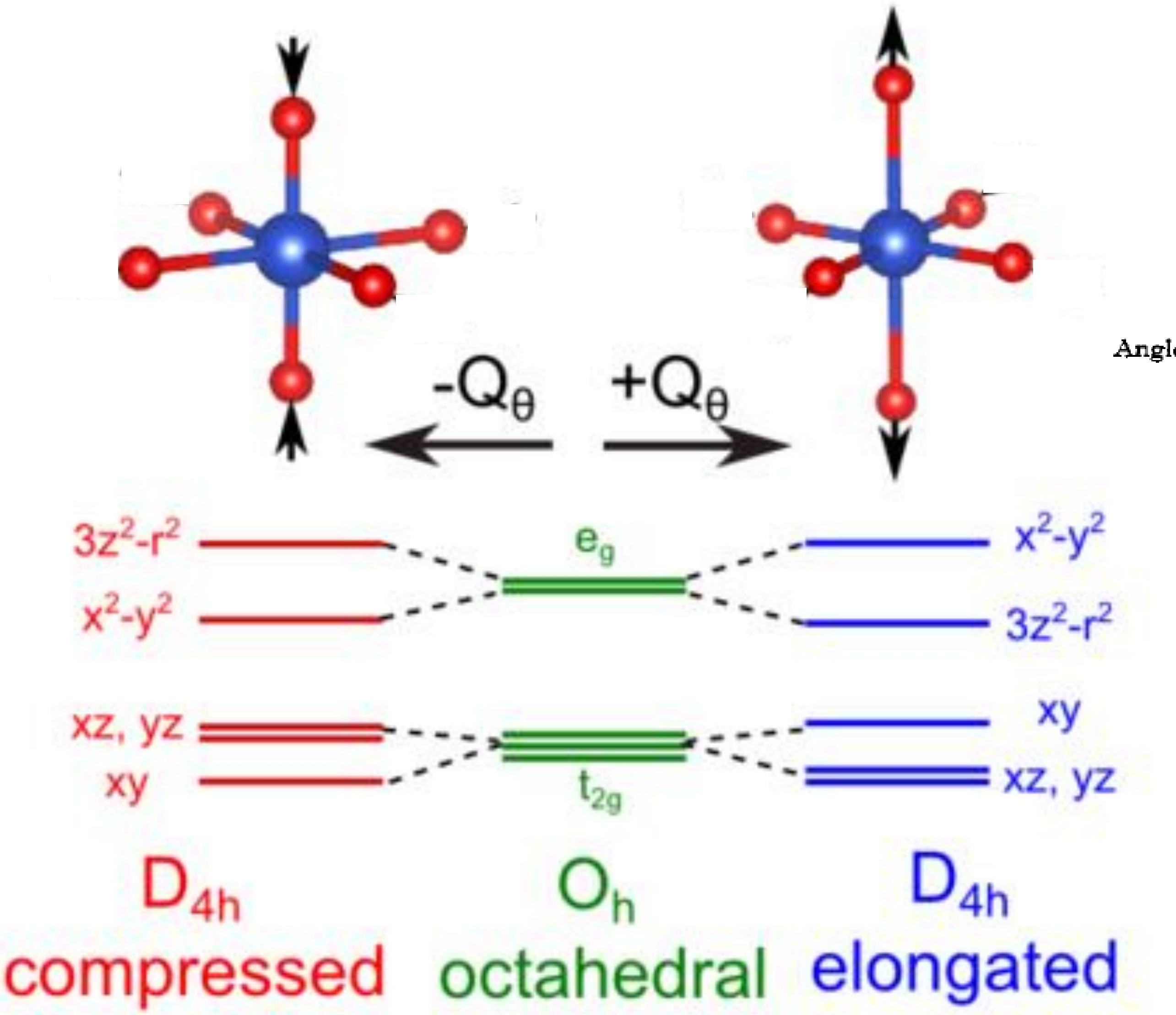
Low spin state

Ex) hemoglobin

No oxygen: $Fe^{2+}(t_{2g}^4 e_g^2)$ high spin

With oxygen: $Fe^{2+}(t_{2g}^6)$ low spin





Jahn-Teller distortion

Distortion energy = energy lowering by symmetry lowering

Plane through trigonal axis: Angle with trigonal axis (deg.)	g	Plane normal to trigonal axis: Angle with arbitrary line (deg.)	g
0	2·234	0	2·248
30	2·235	30	2·246
50	2·238	60	2·240
70	2·240	90	2·244
90	2·243		

B.Bleaney, Proc.Phys.Soc.London A63,408(1950).

$CuSiF_6 6H_2O$

Van Vleck (anomalous) paramagnetism

LS coupling approach

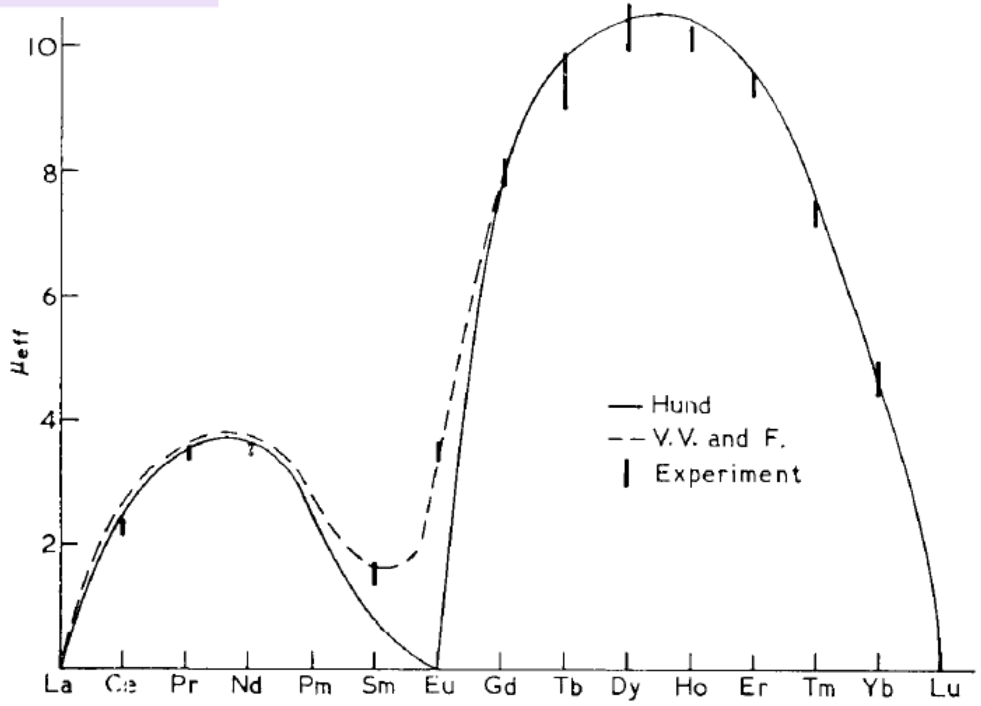
Configuration		ion	p (exp.)	$g_J[J(J+1)]^{1/2}$	$2[S(S+1)]^{1/2}$
$4f^3$	$^4I_{9/2}$	Nd^{3+}	3.8	3.62	3.68
$4f^5$	$^6H_{5/2}$	Sm^{3+}	1.5	0.84	1.53
$4f^6$	$^7F_0$	Eu^{3+}	3.6	0.00	3.40
$4f^7$	$^8S_{7/2}$	Gd^{3+}	7.9	7.94	7.94

$$\mathcal{H}_{\mathrm{SOI}} = \lambda \boldsymbol{L}\cdot\boldsymbol{S} = \frac{\lambda}{2}[J(J+1) - S(S+1) - L(L+1)]$$

In the case of Eu^{3+} (J =0)

$$\Delta E_{LS} = E_{LS}(J) - E_{LS}(J-1) = \lambda J$$

Excited state → finite moment



Very short review of point group theory

Group: Set A with operator *

1. $\forall a_1,\ a_2 \in A\ \{a_1 * a_2 \in A\}$ (closed for the operation *)
2. $\forall a_1.\ a_2,\ a_3 \in A\ \{(a_1 * a_2) * a_3 = a_1 * (a_2 * a_3)\}$ (associative law).
3. $\exists E \in A\ \{\forall a_1 \in A\ \{a_1 E = E a_1 = a_1\}\}$ (existence of unit element).
4. $\exists a_1^{-1} \in A\ \{\forall a_1 \in A\ \{a_1 a_1^{-1} = a_1^{-1} a_1 = E\}\}$ (existence of inverse element).

Element a_i → $D(a_i)$ square matrix

$a * b = c$ projection $D(a)D(b) = D(c)$

} Representation of group A

$D'(a_i) = S^{-1} D(a_i) S$ $D'(a_i),\ D(a_i)$: equivalent representation

Symmetry operation of point group

A set of symmetry operations around a point in space is called a point group

E	:	Identical operation
C_n	:	Rotation of $2\pi/n$
C_2'	:	π rotation around two-fold axis perpendicular to the principal axis. Written as C_2' or U_2 and called Umklappung.
I	:	Space inversion $(\boldsymbol{r} \to -\boldsymbol{r})$
σ	:	Mirroring
IC_n	:	Circumference. Space inversion after rotation of $2\pi/n$.
S_n	:	Improper rotation. Mirroring after rotation of $2\pi/n$.

In crystals: requirement of (discrete) translational symmetry 32 crystal point groups

Crystal point groups

system	Schönflies symbol	Hermann-Mauguin symbol: full	Hermann-Mauguin symbol: abbreviated	examples
triclinic	C_1	1	1	
	C_i, (S_2)	$\bar{1}$	$\bar{1}$	Al_2SiO_5
monoclinic	C_{1h}, (S_1)	m	m	KNO_2
	C_2	2	2	
	C_{2h}	$2/m$	$2/m$	
orthorhombic	C_{2v}	$2mm$	mm	
	D_2, (V)	222	222	
	D_{2h}, (V_h)	$2/m2/m2/m$	mmm	I, Ga
tetragonal	C_4	4	4	
	S_4	4	4	
	C_{4h}	4/m	4/m	$CaWO_4$
	D_{2d}, (V_d)	$\bar{4}2m$	$\bar{4}2m$	
	C_{4v}	$4mm$	$4mm$	
	D_4	422	42	
	D_{4h}	$4/m2/m2/m$	$4/mmm$	TiO_2, In, β-Sn
rhombohedral	C_3	3	3	AsI_3
	C_3, (S_6)	3	3	$FeTiO_3$
	C_{3v}	$3m$	$3m$	
	D_3	32	32	Se
	D_{3d}	$32/m$	$3m$	Bi, As, Sb, Al_2O_3
hexagonal	C_{3h}, (S_3)	6	6	
	C_6	6	6	
	C_{6h}	$6/m$	$6/m$	
	D_{3h}	$62m$	$62m$	
	C_{6v}	$6mm$	$6mm$	ZnO, NiAs
	D_6	622	62	CeF_3
	D_{6h}	$6/m2/m2/m$	$6/mmm$	Mg, Zn, graphite
cubic	T	23	23	$NaClO_3$
	T_h	$2/m3$	$m3$	FeS_2
	T_d	$43m$	$43m$	ZnS
	O	432	43	β-Mn
	O_h	$4/m32/m$	$m3m$	NaCl, diamond, Cu
icosahedral	C_5	5	5	
	C_{5i}, (S_{10})	10	10	
	C_{5v}	$5m$	$5m$	
	C_{5h}, S_5	5	5	
	D_5	52	52	
	D_{5d}	$52/m$	$5/m$	C_{80}
	D_{5h}	$1\bar{0}2/m$	$1\bar{0}2/m$	C_{70}
	I	532	532	
	I_h			C_{60}

Reducible/irreducible representations

R: symmetry operator Symmetry operation on functions $\varphi(\boldsymbol{r}) \to \varphi'(\boldsymbol{r}) = \varphi(R^{-1}\boldsymbol{r})$

$$\mathscr{A}_\varphi = \{\varphi_1, \varphi_2, \cdots\} \xrightarrow{R} \mathscr{A}'_\varphi = \{\varphi'_1, \varphi'_2, \cdots\}$$

If $\mathscr{A}' = \mathscr{A}$ then $\mathscr{A}$ can be a representation basis of *R*

$$D_{ij}(R) = \langle \varphi_i | R | \varphi_j \rangle$$

If block diagonalization is possible: reducible representation

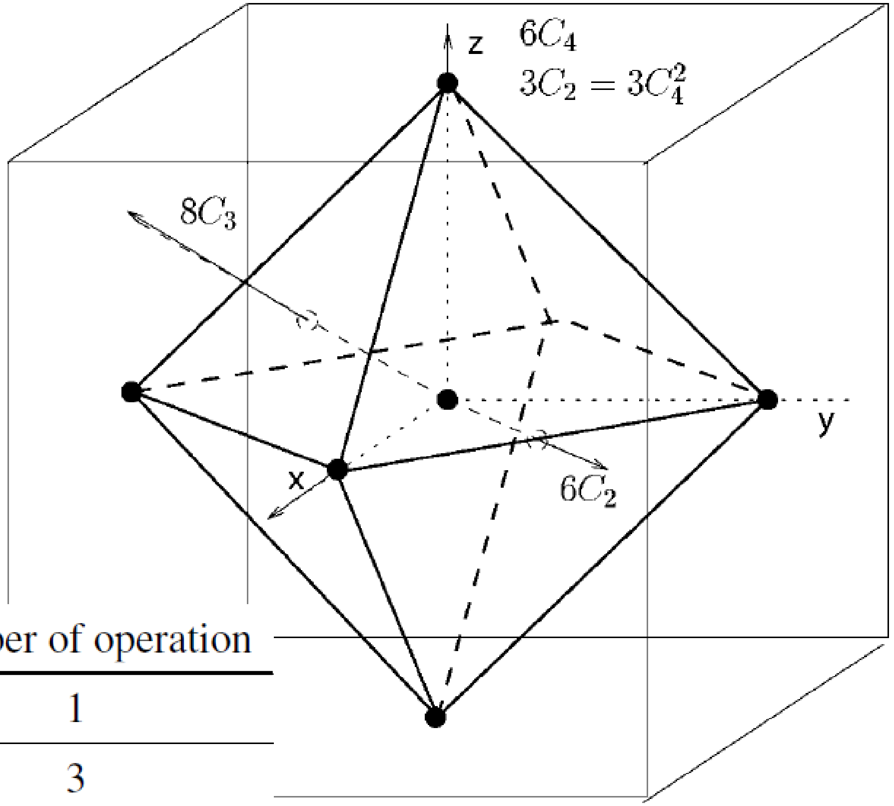
$$SD(R)S^{-1} = \begin{pmatrix} D_1(R) & & 0 \\ & D_2(R) & \\ 0 & & \ddots \end{pmatrix}$$

Direct summation: $D(R) = D_1(R) \oplus D_2(R) \oplus \cdots$

If block diagonalization is impossible: irreducible representation

$\mathrm{Tr}\left[D(R)\right]$: character of representation

Symmetry operations in group O



	Symmetry operation	Rotation axis	Number of operation
E	Identical transformation		1
C_4	$\pi/2$ rotation around 4-fold axis	x, y, z	3
$C_2 = C_4^2$	π rotation around 4-fold axis	x, y, z	3
C_4^3	$3\pi/2$ rotation around 4-fold axis	x, y, z	3
C_2	π rotation around 2-fold axis	(0,1,1), (1,0,1), (1,1,0)	6
		(0,1,−1), (−1,0,1), (1,−1,0)	
C_3	$2\pi/3$ rotation around 3-fold axis	(1,1,1), (1,1,−1), (1,−1,1), (−1,1,1)	4
C_3^2	$4\pi/3$ rotation around 3-fold axis	(1,1,1), (1,1,−1), (1,−1,1), (−1,1,1)	4

Simplification to irreducible representation by character table

O	E	$8C_3$	$3C_2 = 3C_4^2$	$6C_2'$	$6C_4$
$\Gamma_{l=0}$	1	1	1	1	1
$\Gamma_{l=1}$	3	0	-1	-1	1
$\Gamma_{l=2}$	5	-1	1	1	-1
$\Gamma_{l=3}$	7	1	-1	-1	-1
$\Gamma_{l=4}$	9	0	1	1	1
$\Gamma_{l=5}$	11	-1	-1	-1	1

Simplification of representation $\Gamma_{l=2} = E \oplus T_2$

Symmetry operation and level degeneracy

Symmetry operator *R* $\varphi' = R\varphi$

Transformation of operator: $\mathscr{O}$ $\mathscr{O} \xrightarrow{R} \mathscr{O}'$ $\mathscr{O}' R\varphi = R\mathscr{O}\varphi = R\mathscr{O}R^{-1}R\varphi$ $\mathscr{O} \xrightarrow{R} R\mathscr{O}R^{-1}$

Assume the system is invariant by operator *R*

$$R\mathscr{H}R^{-1} = \mathscr{H}, \quad \therefore [R, \mathscr{H}] = 0$$

$$\mathscr{H}\phi = E\phi$$

$$\mathscr{H}R\phi = R\mathscr{H}R^{-1}R\phi = RE\phi = ER\phi$$

$R\phi$: eigenfunction of eigenvalue E

Symmetry connected eigenfunctions

$\{\phi_i\}$: degenerated function set with eigenvalue E of $\mathscr{H}$

$$R\phi_\nu = \sum_{\mu=1}^{d} D_{\mu\nu}(R)\phi_\mu$$ must be irreducible

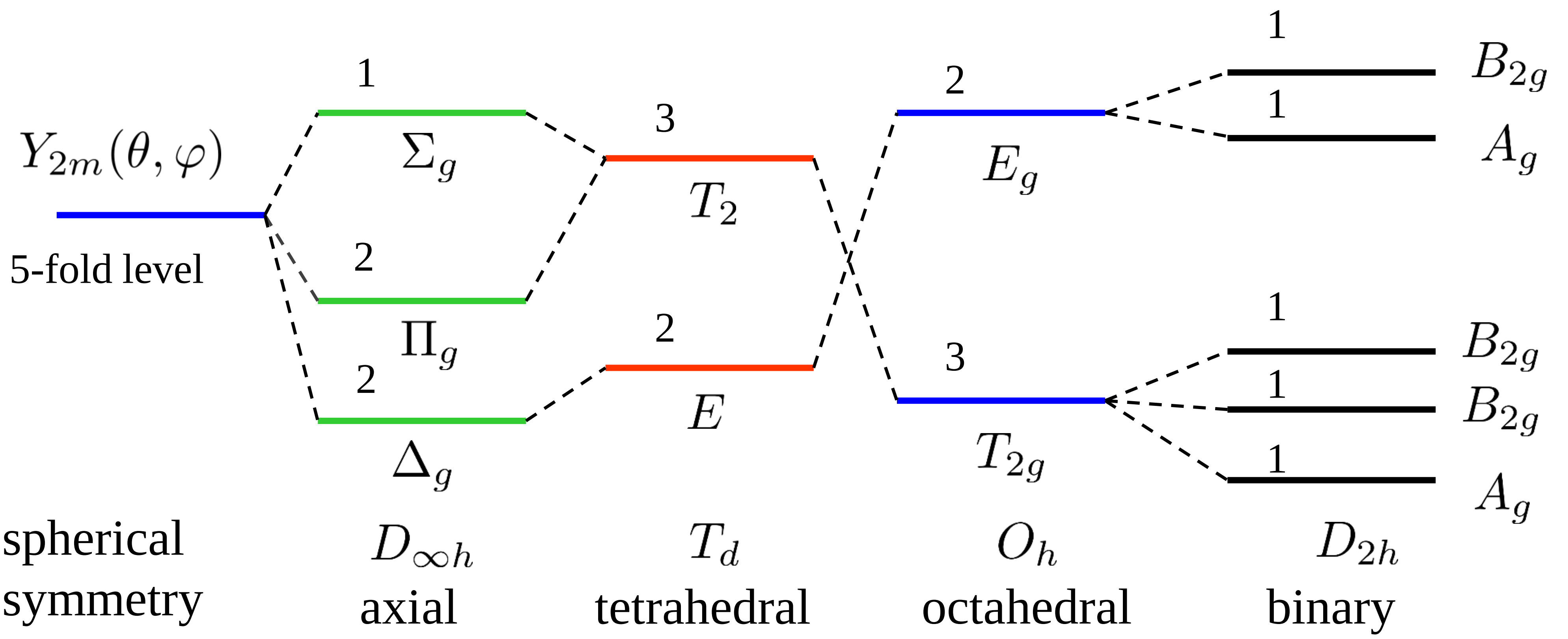
otherwise $D(R) = D_1(R) \oplus D_2(R) = \begin{pmatrix} D_1(R) & 0 \\ 0 & D_2(R) \end{pmatrix}$

not symmetry-connected

accidental degeneracy

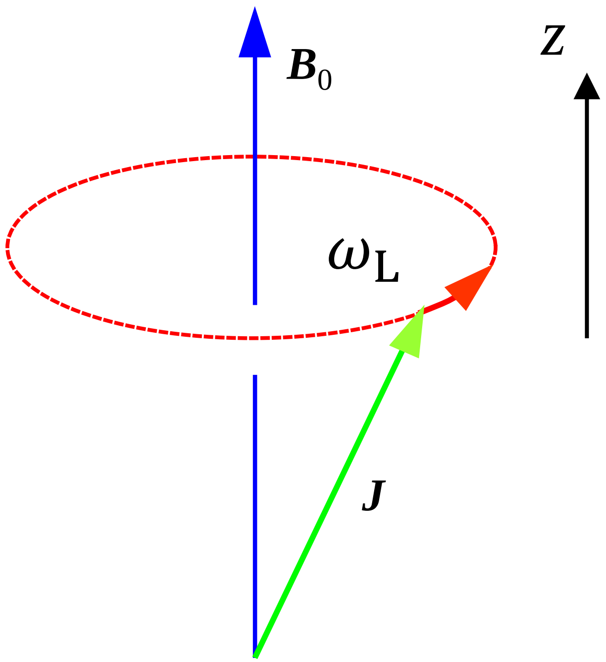
d-level splitting in various crystal fields

Simplification of representation $\Gamma_{l=2} = E \oplus T_2$



Experiments of magnetic moments on atoms/ions and applications

Magnetic resonance



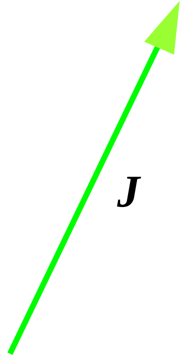
$$\mathcal{H}_1 = g_J \mu_B \boldsymbol{J} \cdot \boldsymbol{B}_0$$

$$J_y J_z - J_z J_y = i J_x, \quad J_z J_x - J_x J_z = i J_y, \quad J_x J_y - J_y J_x = i J_z$$

$$\frac{d\boldsymbol{J}}{dt} = \frac{g_J \mu_B}{\hbar} \boldsymbol{B}_0 \times \boldsymbol{J}$$

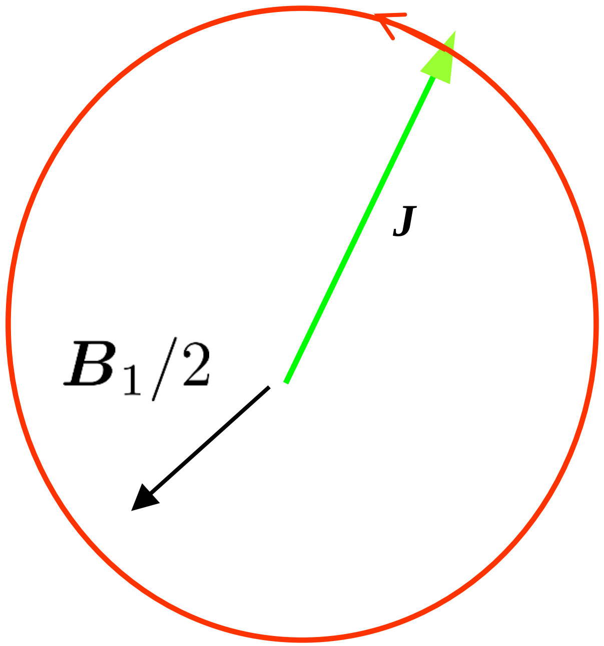
$$\omega_L = g_J \frac{e B_0}{2m}$$ Larmor precession

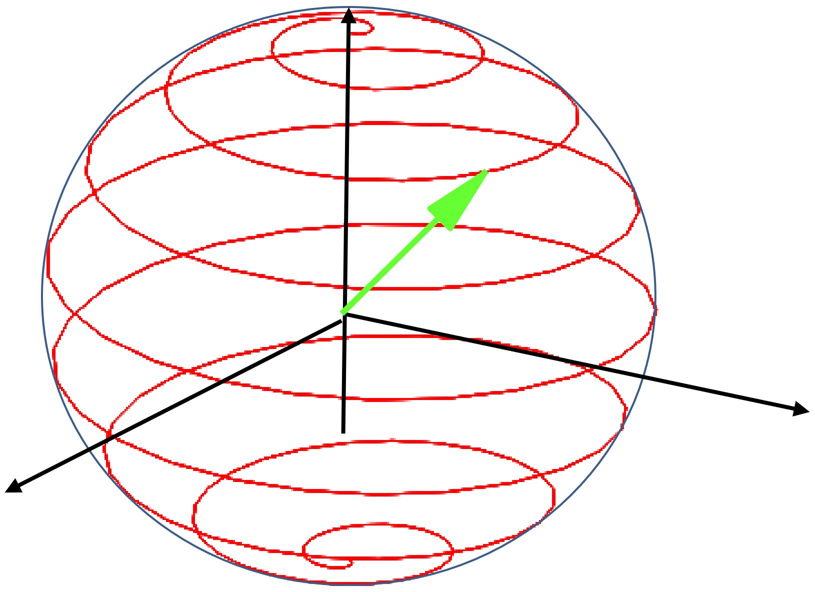
If we observe from rotational coordinate
with frequency ω_L



Precession stops: the effect of magnetic field is renormalized into the rotation

Magnetic resonance (2)





High frequency magnetic field in *xy*-plane

$$\boldsymbol{B}(t) = \boldsymbol{B}_1 \cos(\omega t) = \frac{\boldsymbol{B}_1}{2}[\exp(i\omega t) + \exp(-i\omega t)]$$

Two rotational magnetic fields

when $\omega \approx \omega_{\mathrm{L}}$

On the rotational coordinate: $\omega \approx 0, 2\omega_{\mathrm{L}}$

Ignore $2\omega_L$ component: rotational wave approximation

Precession around $\boldsymbol{B_1}$ $\omega_1 = g_j \dfrac{eB_1}{2m}$

Total motion: spiral

Summary

- Ligand field approach to 3d orbitals in octahedral potential
- High-spin/ Low-spin state in ligand field potential
- Van Vleck (anomalous) paramagnetism
- Group theoretical approach to level splitting
- Experiments on and applications of paramagnetism