

A scenic view of a river with clear blue water, rocks, and green foliage. The water is shallow and reflects the sky and surrounding environment. A large rock is visible in the middle ground, and the banks are lined with green plants.

2022.4.27 Lecture 4

10:25 – 11:55

Lecture on **Magnetic Properties of Materials**
磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

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- 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 $3d$ transition metals

- Ligand field approach

 - Octahedron potential

- 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

Electronic states in magnetic ions (continued)

Periodic table of elements

PubChem

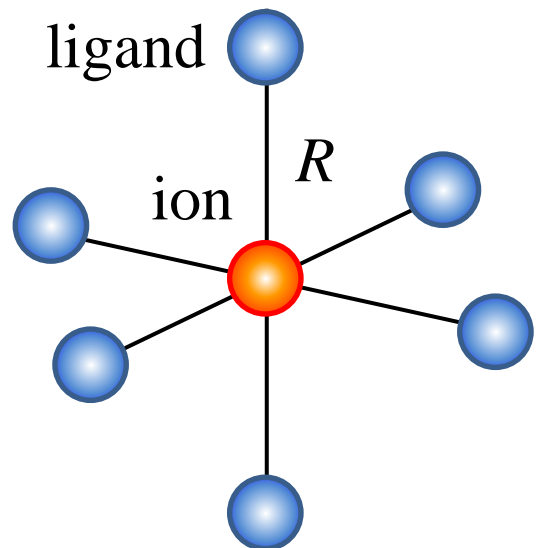
1 H Hydrogen Nonmetal																	2 He Helium Noble Gas						
3 Li Lithium Alkali Metal	4 Be Beryllium Alkaline Earth Metal																	5 B Boron Metalloid	6 C Carbon Nonmetal	7 N Nitrogen Nonmetal	8 O Oxygen Nonmetal	9 F Fluorine Halogen	10 Ne Neon Noble Gas
11 Na Sodium Alkali Metal	12 Mg Magnesium Alkaline Earth Metal																	13 Al Aluminum Post-Transition Metal	14 Si Silicon Metalloid	15 P Phosphorus Nonmetal	16 S Sulfur Nonmetal	17 Cl Chlorine Halogen	18 Ar Argon Noble Gas
19 K Potassium Alkali Metal	20 Ca Calcium Alkaline Earth Metal	21 Sc Scandium Transition Metal	22 Ti Titanium Transition Metal	23 V Vanadium Transition Metal	24 Cr Chromium Transition Metal	25 Mn Manganese Transition Metal	26 Fe Iron Transition Metal	27 Co Cobalt Transition Metal	28 Ni Nickel Transition Metal	29 Cu Copper Transition Metal	30 Zn Zinc Transition Metal	31 Ga Gallium Post-Transition Metal	32 Ge Germanium Metalloid	33 As Arsenic Metalloid	34 Se Selenium Nonmetal	35 Br Bromine Halogen	36 Kr Krypton Noble Gas						
37 Rb Rubidium Alkali Metal	38 Sr Strontium Alkaline Earth Metal	39 Y Yttrium Transition Metal	40 Zr Zirconium Transition Metal	41 Nb Niobium Transition Metal	42 Mo Molybdenum Transition Metal	43 Tc Technetium Transition Metal	44 Ru Ruthenium Transition Metal	45 Rh Rhodium Transition Metal	46 Pd Palladium Transition Metal	47 Ag Silver Transition Metal	48 Cd Cadmium Transition Metal	49 In Indium Post-Transition Metal	50 Sn Tin Post-Transition Metal	51 Sb Antimony Metalloid	52 Te Tellurium Metalloid	53 I Iodine Halogen	54 Xe Xenon Noble Gas						
55 Cs Cesium Alkali Metal	56 Ba Barium Alkaline Earth Metal	72 Hf Hafnium Transition Metal	73 Ta Tantalum Transition Metal	74 W Tungsten Transition Metal	75 Re Rhenium Transition Metal	76 Os Osmium Transition Metal	77 Ir Iridium Transition Metal	78 Pt Platinum Transition Metal	79 Au Gold Transition Metal	80 Hg Mercury Transition Metal	81 Tl Thallium Post-Transition Metal	82 Pb Lead Post-Transition Metal	83 Bi Bismuth Post-Transition Metal	84 Po Polonium Metalloid	85 At Astatine Halogen	86 Rn Radon Noble Gas							
87 Fr Francium Alkali Metal	88 Ra Radium Alkaline Earth Metal	104 Rf Rutherfordium Transition Metal	105 Db Dubnium Transition Metal	106 Sg Seaborgium Transition Metal	107 Bh Bohrium Transition Metal	108 Hs Hassium Transition Metal	109 Mt Meitnerium Transition Metal	110 Ds Darmstadtium Transition Metal	111 Rg Roentgenium Transition Metal	112 Cn Copernicium Transition Metal	113 Nh Nihonium Post-Transition Metal	114 Fl Flerovium Post-Transition Metal	115 Mc Moscovium Post-Transition Metal	116 Lv Livermorium Post-Transition Metal	117 Ts Tennessine Halogen	118 Og Oganesson Noble Gas							
		57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymium Lanthanide	60 Nd Neodymium Lanthanide	61 Pm Promethium Lanthanide	62 Sm Samarium Lanthanide	63 Eu Europium Lanthanide	64 Gd Gadolinium Lanthanide	65 Tb Terbium Lanthanide	66 Dy Dysprosium Lanthanide	67 Ho Holmium Lanthanide	68 Er Erbium Lanthanide	69 Tm Thulium Lanthanide	70 Yb Ytterbium Lanthanide	71 Lu Lutetium Lanthanide							
		89 Ac Actinium Actinide	90 Th Thorium Actinide	91 Pa Protactinium Actinide	92 U Uranium Actinide	93 Np Neptunium Actinide	94 Pu Plutonium Actinide	95 Am Americium Actinide	96 Cm Curium Actinide	97 Bk Berkelium Actinide	98 Cf Californium Actinide	99 Es Einsteinium Actinide	100 Fm Fermium Actinide	101 Md Mendelevium Actinide	102 No Nobelium Actinide	103 Lr Lawrencium Actinide							

3d 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



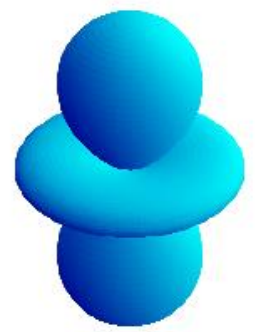
Potential generated by ligands at an octahedron vertices:

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

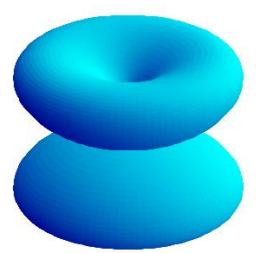
We are considering: Open shell 3d electrons

Single (3d) electron in $v_{cb}(\mathbf{r})$

Diagonalization in the space of 3d wavefunction

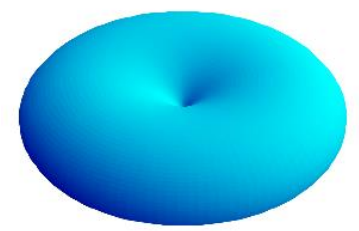


$m = 0$



$m = \pm 1$

d



$m = \pm 2$

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

$$Y_{2\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{15}{8\pi}} \cos \theta \sin \theta e^{\pm i\varphi},$$

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

Looking for eigenfunction in tetrahedral potential

Linear combination of d -orbitals

Radial part \rightarrow common for 5 orbitals

Angular part \rightarrow second order in (x, y, z)

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

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

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

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

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

Candidates: $\frac{yz}{r^2}, \frac{zx}{r^2}, \frac{xy}{r^2}$

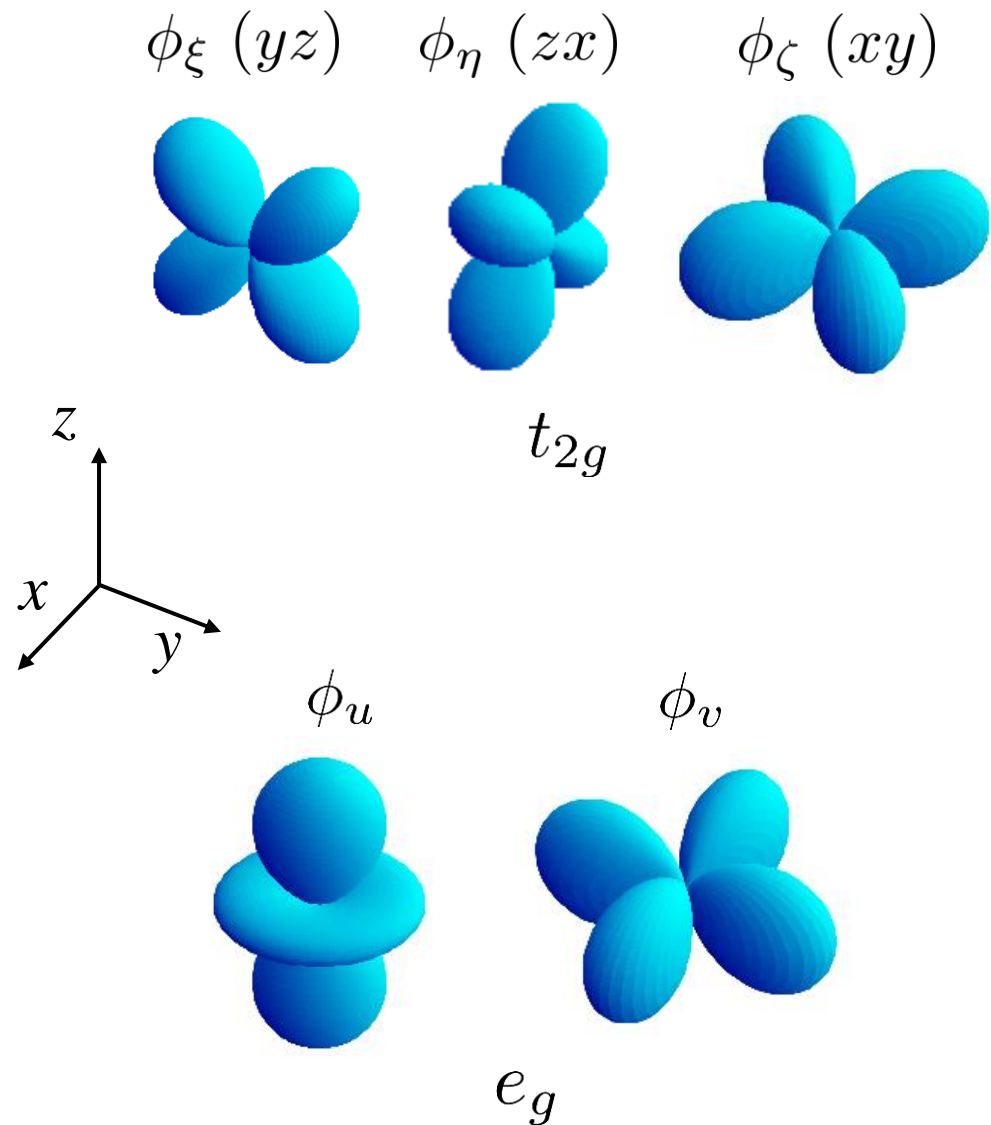
Easily obtained by adding/subtracting (2), (3)

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 :

$$x^2 - z^2, y^2 - z^2 \text{ orthogonalize } \longrightarrow 3z^2 - r^2, x^2 - y^2$$

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

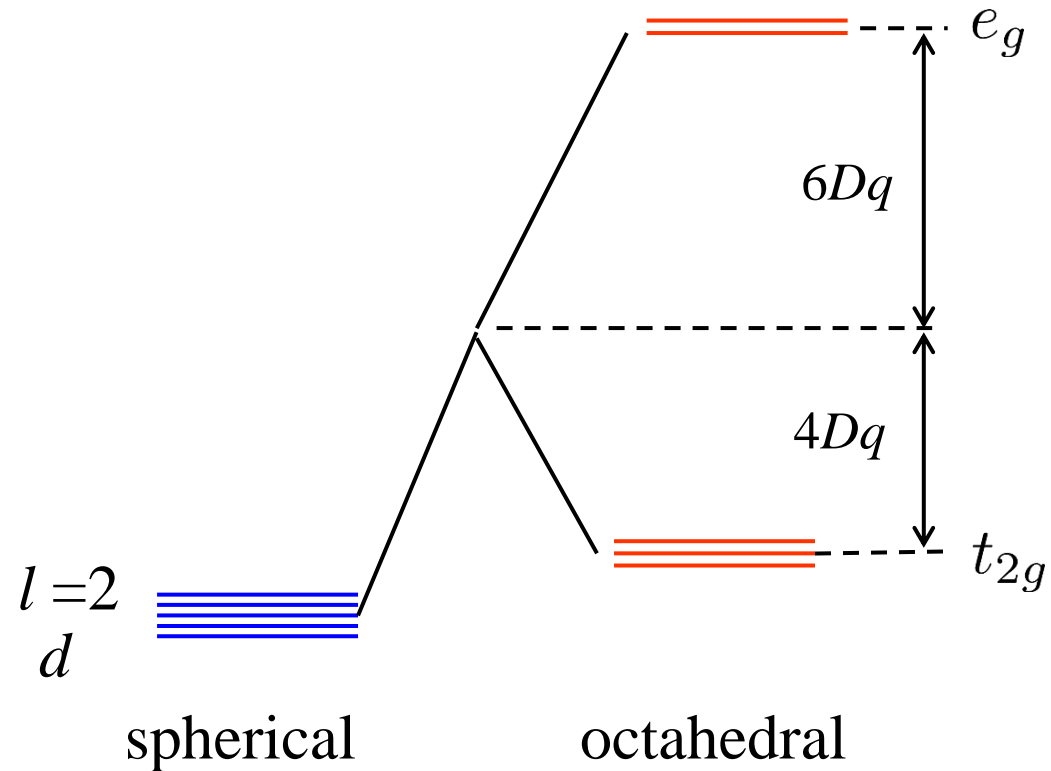
Octahedral ligand field (2)



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

$$\left\{ \begin{aligned}
 \phi_u &= \phi_{320} = \sqrt{\frac{5}{16\pi}} \frac{3z^2 - r^2}{r^2} R_{32}(r), \\
 \phi_v &= -\frac{1}{\sqrt{2}} (\phi_{322} + \phi_{32-2}) = \sqrt{\frac{5}{16\pi}} \frac{x^2 - y^2}{r^2} R_{32}(r)
 \end{aligned} \right.$$

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

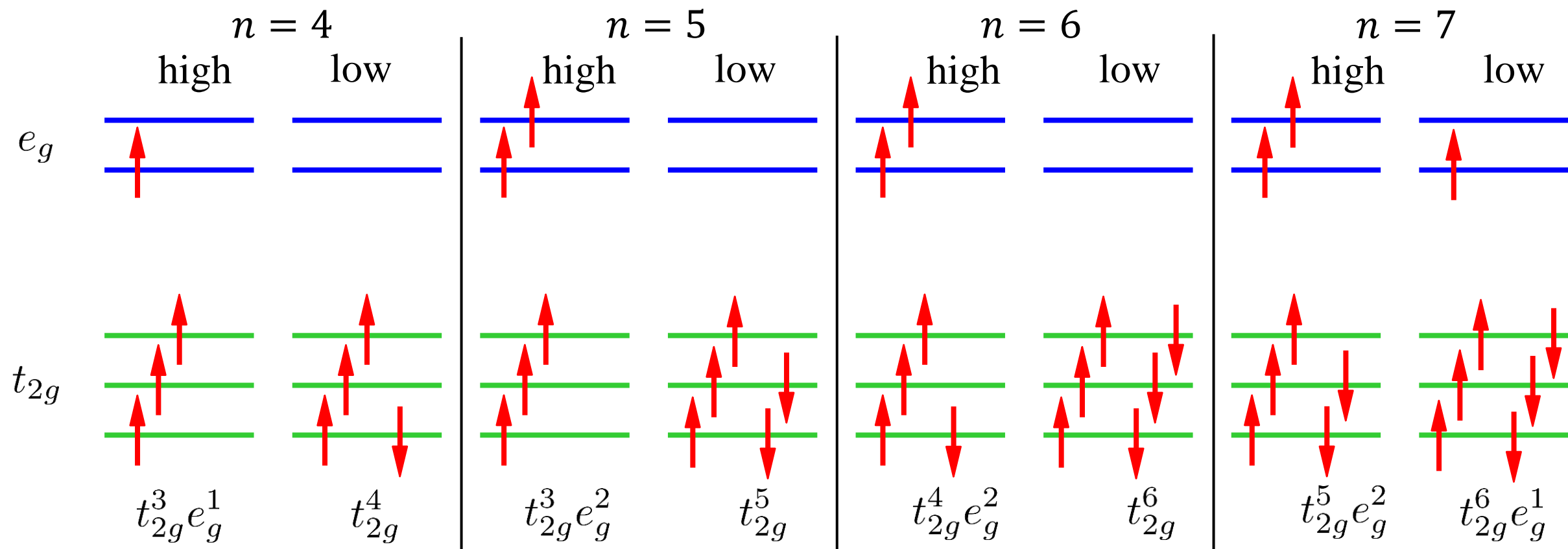
$$\langle \phi_\zeta | l_z | \phi_\zeta \rangle = 2 - 2 = 0$$

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



Explanation of quenching of orbital angular momentum

High-spin and low-spin states



(Effect of crystal field) > (Coulomb repulsion)

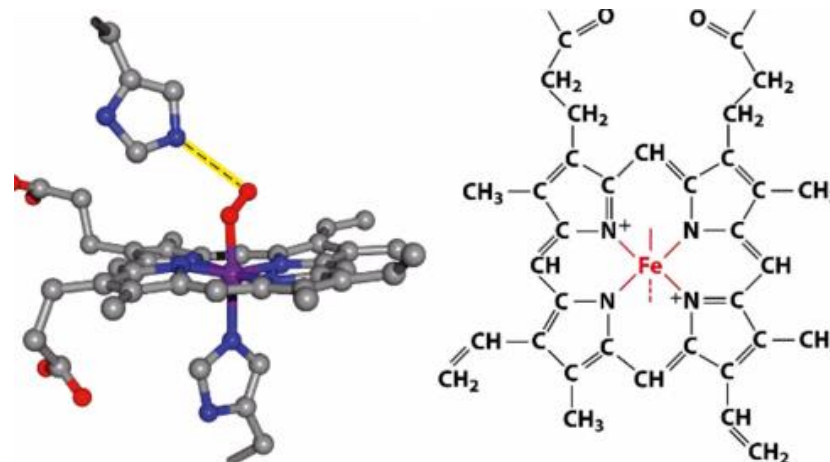


Low spin state

Ex) hemoglobin

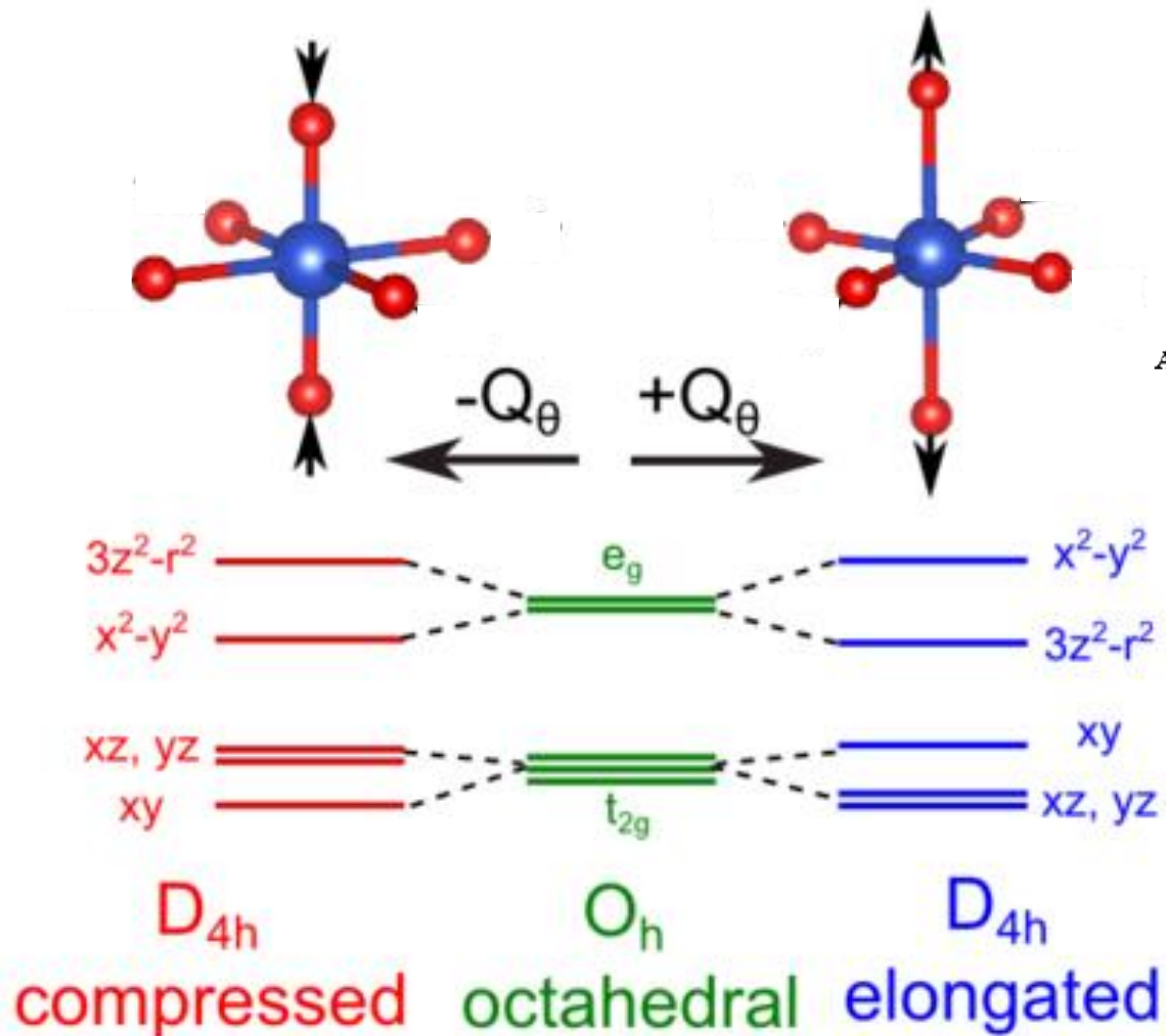
No oxygen: $\text{Fe}^{2+} (t_{2g}^4 e_g^2)$ high spin

With oxygen: $\text{Fe}^{2+} (t_{2g}^6)$ 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).



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
$4f^5$	${}^6H_{5/2}$	Sm^{3+}	1.5	0.84
$4f^6$	7F_0	Eu^{3+}	3.6	0.00
$4f^7$	${}^8S_{7/2}$	Gd^{3+}	7.9	7.94

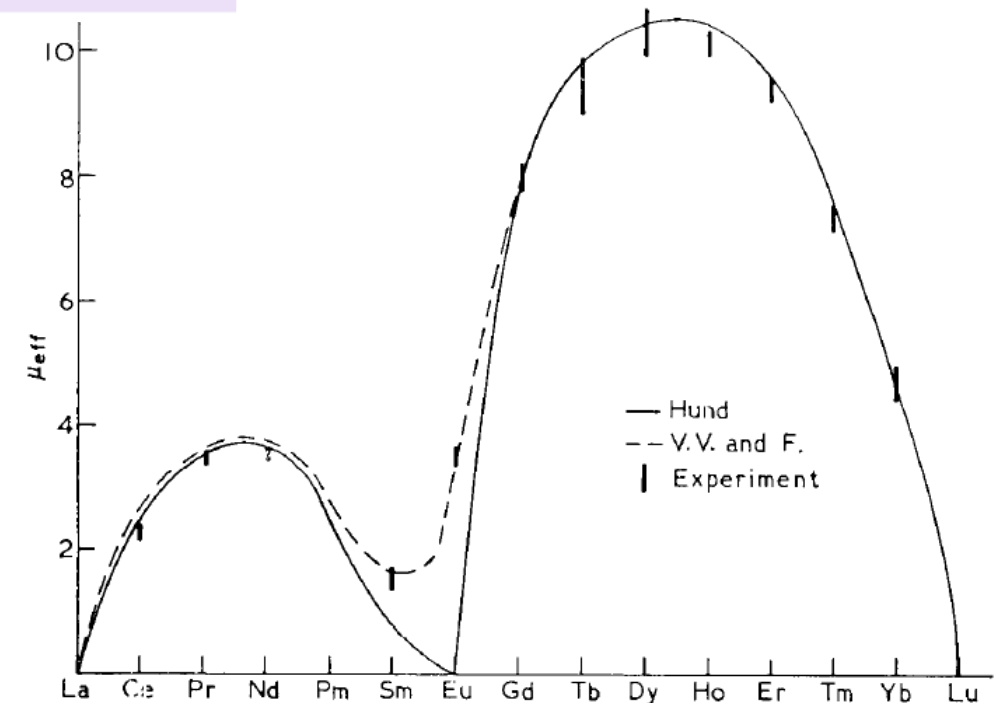


$$\begin{aligned}\mathcal{H}_{\text{SOI}} &= \lambda \mathbf{L} \cdot \mathbf{S} \\ &= \frac{\lambda}{2} [J(J+1) - S(S+1) - L(L+1)]\end{aligned}$$

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

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

Excited state \rightarrow 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 $\xrightarrow{\text{projection}}$ $D(a_i)$ square matrix } Representation of group A
 $a * b = c$ $\xrightarrow{\text{projection}}$ $D(a)D(b) = D(c)$

$D'(a_i) = S^{-1} D(a_i) S$ $D'(a_i), D(a_i)$: 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 ($\mathbf{r} \rightarrow -\mathbf{r}$)
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		examples
		full	abbreviated	
triclinic	C_1	1	1	Al_2SiO_5
	$C_i, (S_2)$	$\bar{1}$	$\bar{1}$	
monoclinic	$C_{1h}, (S_1)$	m	m	KNO_2
	C_2	2	2	
	C_{2h}	$2/m$	$2/m$	
orthorhombic	C_{2v}	$2mm$	mm	I, Ga
	$D_2, (V)$	222	222	
	$D_{2h}, (V_h)$	$2/m2/m2/m$	mmm	
tetragonal	C_4	4	4	CaWO_4
	S_4	4	4	
	C_{4h}	4/m	4/m	
	$D_{2d}, (V_d)$	$\bar{4}2m$	$\bar{4}2m$	
	C_{4v}	$4mm$	$4mm$	
	D_4	422	42	$\text{TiO}_2, \text{In}, \beta\text{-Sn}$
	D_{4h}	$4/m2/m2/m$	$4/mmm$	

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	$\beta\text{-Mn}$
	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}	$102/m$	$102/m$	C_{70}
	I	532	532	
	I_h			C_{60}

Reducible/irreducible representations

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

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

If $\mathcal{A}' = \mathcal{A}$ then \mathcal{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

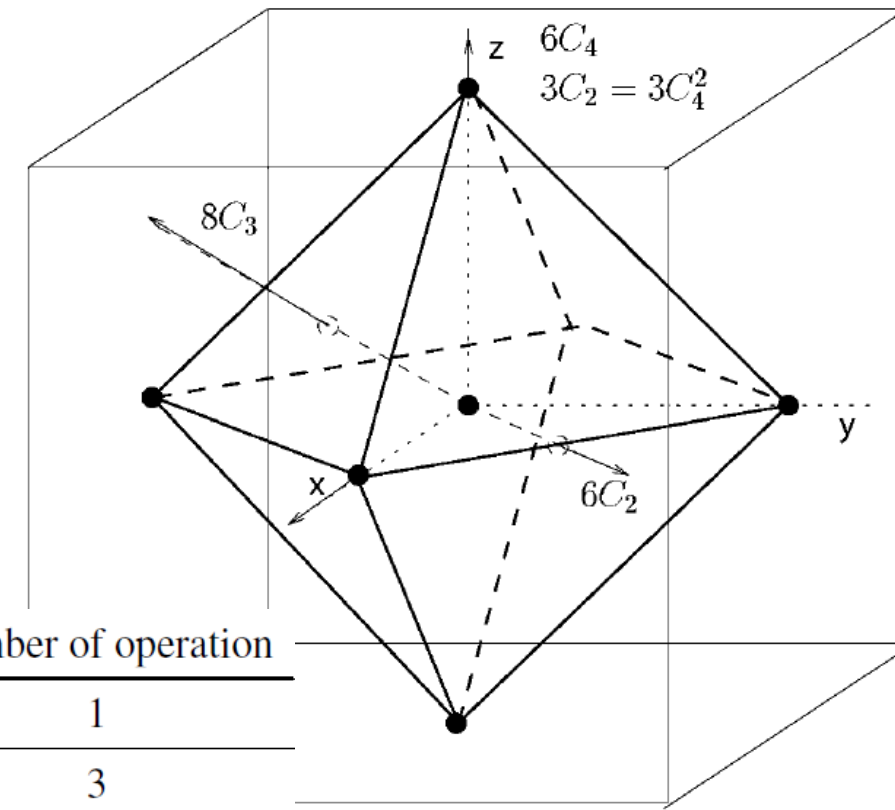
$$SD(R)S^{-1} = \begin{pmatrix} D_1(R) & & 0 \\ & D_2(R) & \\ 0 & & \ddots \end{pmatrix}$$

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

If block diagonalization is impossible:
irreducible representation

$\text{Tr} [D(R)]$: 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	$(0,1,1), (1,0,1), (1,1,0)$ $(0,1,-1), (-1,0,1), (1,-1,0)$	6
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: $\mathcal{O} \xrightarrow{R} \mathcal{O}'$ $\mathcal{O}' R\varphi = R\mathcal{O}\varphi = R\mathcal{O}R^{-1}R\varphi$ $\mathcal{O} \xrightarrow{R} R\mathcal{O}R^{-1}$

Assume the system is invariant by operator R

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

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

$\mathcal{H}R\phi = R\mathcal{H}R^{-1}R\phi = RE\phi = ER\phi$ $R\phi$: eigenfunction of eigenvalue E
Symmetry connected eigenfunctions

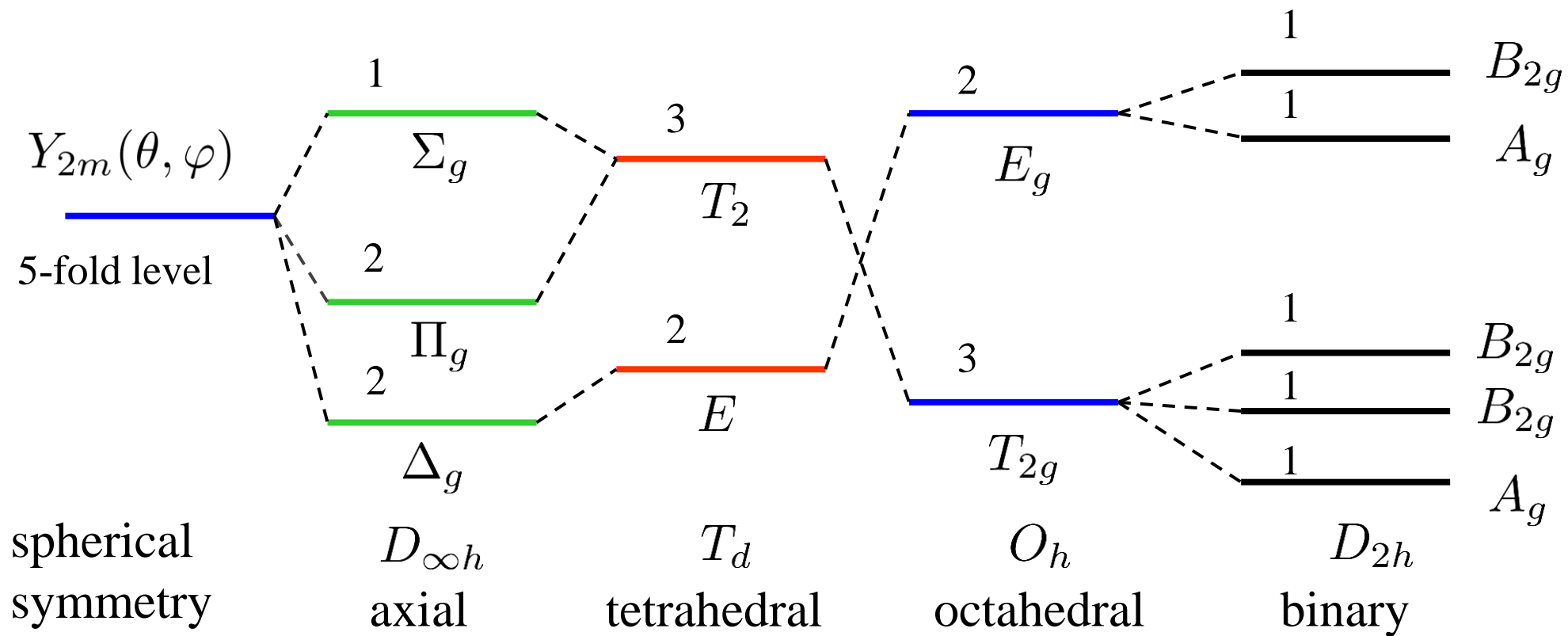
$\{\phi_i\}$: degenerated function set with eigenvalue E of \mathcal{H}

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

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

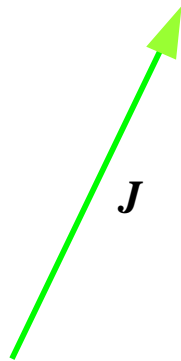
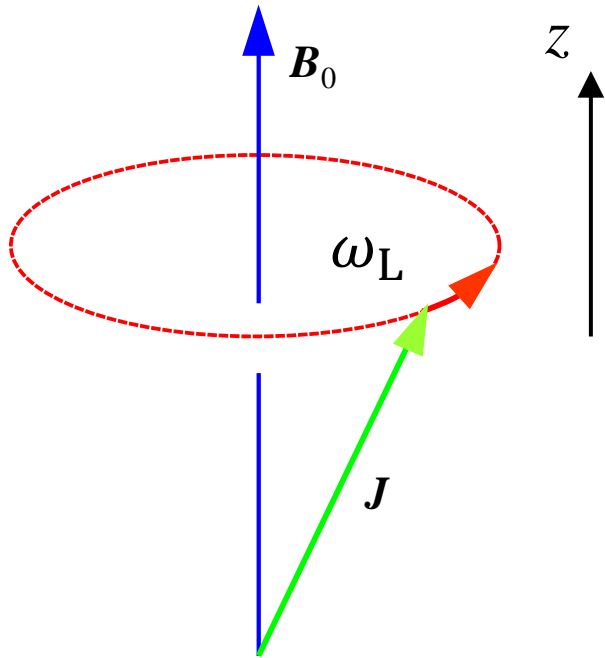
Simplification of representation $\Gamma_{l=2} = E \oplus T_2$



Experiments of magnetic moments on atoms/ions and applications



Magnetic resonance



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

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

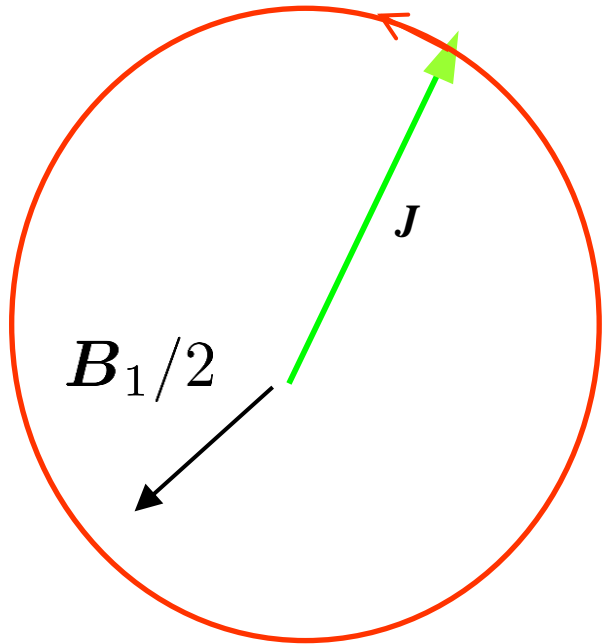
$$\frac{d\mathbf{J}}{dt} = \frac{g_J \mu_B}{\hbar} \mathbf{B}_0 \times \mathbf{J}$$

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

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)



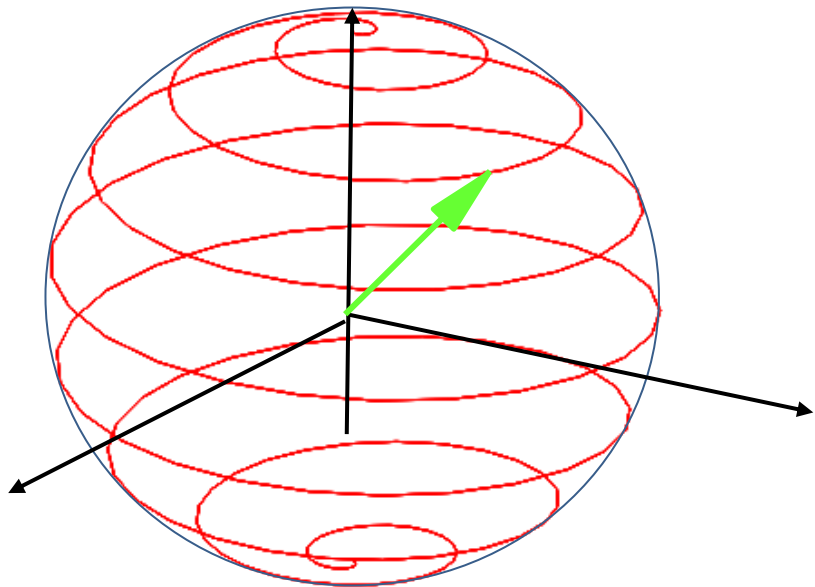
High frequency magnetic field in xy -plane

$$\begin{aligned} \mathbf{B}(t) &= \mathbf{B}_1 \cos(\omega t) \\ &= \frac{\mathbf{B}_1}{2} [\exp(i\omega t) + \exp(-i\omega t)] \end{aligned} \quad \text{Two rotational magnetic fields}$$

when $\omega \approx \omega_L$

On the rotational coordinate: $\omega \approx 0, 2\omega_L$

Ignore $2\omega_L$ component: rotational wave approximation



Precession around \mathbf{B}_1 $\omega_1 = g_j \frac{eB_1}{2m}$

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