9. Crystalline point groups

Ref: ① Dresselhaus. Chap 5 - 13;
② Bradley & Cracknell.
"The mathematical theory of
symmetry in solids";

In $\mathbb{E}^3$. $\vec{r}' = R(g)\cdot\vec{r}$ $\quad g\cdot\hat{e}_j = \sum_i R(g)_{ij}\,\hat{e}_i$

length/angle invariant after symmetry operation

$$\langle \vec{r}', \vec{s}'\rangle = \vec{r}'^{T}\cdot\vec{s}' = \vec{r}^{T}\cdot R(g)^{T}\cdot R(g)\cdot\vec{s} \equiv \vec{r}^{T}\cdot\vec{s} \quad (\forall \vec{r}, \vec{s})$$

$\Rightarrow R(g)^{T}\cdot R(g) = \mathbb{1}$ $\quad R\in O(3, \mathbb{R})$

$R\in SO(3)$ det $= 1$ proper rotation

$R\in PSO(3)$ det $= -1$ improper rotation:

prop. rot. $\circ$ inversion

Point groups: subgroups of rotation group $O(3)$.

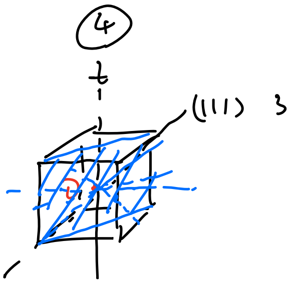
9.1. Symmetry operations (Dresselhaus 3.9)

- E identity
- C_n rotations of $\frac{2\pi}{n}$

$C_2 : \pi \qquad C_3 : \frac{2\pi}{3} \qquad C_3^2 : \frac{4\pi}{3}$ etc.

in crystalline systems: $n = 1.2.3.4$ or 6

- σ : reflection in a plane



σ_h horizontal perp to } principal rot. axis (highest order)

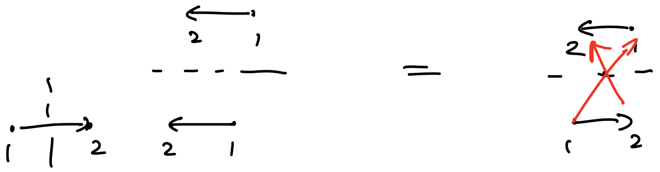
σ_v vertical contains

σ_d "dihedral plane" bisects the angle between 2-fold axes perp. to principal axis

- i : inversion $\vec{r} \to -\vec{r}$

$i = \sigma C_2 (= S_2)$

$S_n := \sigma C_n$



- S_n : $2\pi/n$ rotation + σ_h

n odd. $iC_n^k = \sigma C_2 C_n^k = \sigma(C_{2n}^{n} C_{2n}^{2k}) = \sigma C_{2n}^{n+2k}$

$= S_{2n}^{n+2k}$

n even : $iC_n^k = \sigma C_2 C_n^k = \sigma C_n^{\frac{n}{2}+k}$

$iC_3^\pm = S_6^5 = S_6^\mp$

$iC_4^\pm = S_4^\mp$

$iC_6^\pm = S_3^\mp \, (= \sigma C_6^{3\pm1} = \sigma C_3^\mp \,)$

Above are Schönflies notations

often see Hermann-Mauguin notations

("international notations")

Schönflies	H-M
C_n	n
iC_n	$\bar{n}$
σ	m
σ_h	n/m
σ_v	nm
$\sigma_{v'}$	nmm

Examples.

proper		improper	
S	HM	S	HM
$C_1 = E$	1	$i = S_2$	$\bar{1}$
C_2	2	$iC_2 = \sigma$	$\bar{2}$
C_3^+	3	S_6^-	$\bar{3}$
$C_3^2 = C_3^-$	3_2	S_6	$\bar{3}_2$
C_4	4	S_4^-	$\bar{4}$
C_4^-	4_3	S_4	$\bar{4}_3$
C_6	6	S_3^-	$\bar{6}$
C_6^-	6_5	S_3	$\bar{6}_5$

9.2 Point groups

proper point groups

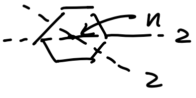
(P.G. of the first kind)

① cyclic groups. sym. elements. only n-fold rot.

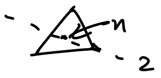
n (C_n)

② dihedral : n-sided prism

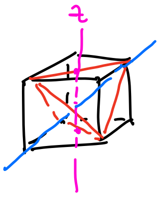
(D_n) { even : n 2 2



odd : n 2



③ tetrahedral regular tetrahedron.



2 3 (T)

3 2-fold // x.y.z . 4 3-fold .

For these.
[001] first
then [111]
then [110]

12 : E + $C_{3j}^{\pm}$ + $C_{2x/y/z}$ = 12

1 + 8 + 3

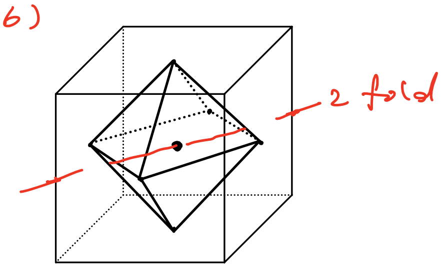
④ octahedral group

2-fold (6)

432 (O)

4-fold (x.y.z)

3-fold (4)



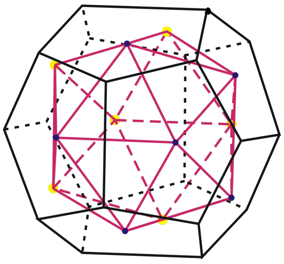
$E + C_{4xyz}^{\pm} + C_{2xyz} + C_{3j}^{\pm} + C_{2p} = 24$

1 6 3 8 6

⑤ icosahedral group.
(二十面体)

$5\,3\,2$ (I)

#6 #10 #15



$$\begin{cases} V = 12 \\ F = 20 \\ E = 30 \end{cases}$$

$$|I| = 1 + 4\times 6 + 2\times 10 + 15 = 60$$

Now we can create more point groups by:

A. add in inversion. $PG \rightarrow PG \otimes \bar{1}$
$\{1, i\}$

① C_n: odd n → $\bar{n}$ (S_{2n})

even → n/m (C_{nh})

② D_n. odd $n2$ → $\bar{n}m$ (D_{nd})
($\bar{n}\,2/m$)

even $n22$ → $n\underline{/m}\ \underline{mm}$ (D_{nh})
($2/m$)

③ 23 (T) → m3 (T_h)
($2/m\ \bar{3}$)

④ 432 (O) → m3m (O_h)
($4/m\ \bar{3}\ 2/m$)

⑤ 532 (I) → 53m (I_h)

B. P.G. P has a normal subgroup Q of index 2

$$P = Q + RQ \quad \text{for some rotation } R.$$

$$\Rightarrow \quad P' = Q + \underline{\underline{iRQ}}$$

① $n \lhd 2n$ $\quad$ n odd $\quad 2n \rightarrow \overline{2n} \quad (C_{nh})$
$(C_n \lhd C_{2n})$ $\quad$ even $\quad 2n \rightarrow \overline{2n} \quad (S_{2n})$

② $n \lhd n22$ or $n2$ $\qquad n22 \rightarrow nmm \quad (C_{nv})$
$\underline{(C_n \lhd D_n)}$ $\qquad n2 \rightarrow nm$

$n22 \lhd (2n)22$ $\quad (2n)22 \longrightarrow (\overline{2n})2m \quad D_{nh}$ odd n
$\underline{\underline{n2}}$ $\qquad D_{nd}$ even

③ T. (23) no subgroup of index 2

④ $23 \lhd 432$ $\qquad \bar{4}3m \quad (T_d)$

⑤ 532 ×

	C_n						D_n			T	O	I
	1	2	3	4	6	222	32	422	622	23	432	532
A.	$\bar{1}$	$2/m$	$\bar{3}$	$4/m$	$6/m$	$2/m\underline{mm}$ (mmm)	$\bar{3}m$	$4/mmm$	$6/mmm$	$m3$	$m3m$	$53m$
B		$\bar{2}$ (m)		$\bar{4}$	$\bar{6}$	$mm2$	$3m$	$4mm$ $\bar{4}2m$	$6mm$ $\bar{6}2m$	×	$\bar{4}3m$	

$\Rightarrow$ 32 crystalline point groups (Bilbao database)

9.3. Character tables

HW 29 $D_4 = \langle r s \mid r^4 = s^2 = (rs)^2 = 1 \rangle$

$= \{ e, r, r^2, r^3, s, \underline{rs}, r^2 s, r^3 s \}$

$\boxed{\underline{r^m s} = s r^{4-m}}$

$\downarrow$

$D_4 = \{e\} \cup \underbrace{\{r, r^3\}}_{①} \cup \underbrace{\{r^2\}}_{②} \cup \underbrace{\{s, r^2 s\}}_{③} \cup \underbrace{\{rs, r^3 s\}}_{④}$

① $\underline{r} s = s^{-1} r^{-1} = s \underline{r}^3$

② $r^2 s = s r^2$

③ $r \underbrace{s r^{-1}} = r \cdot rs = r^2 s$

④ $r(rs)r^{-1} = r^3 s$

class operators. $C_1 = e \quad C_2 = r + r^3. \quad C_3 = r^2$

$C_4 = s + r^2 s \quad C_5 = rs + r^3 s$

	C_1	C_2	C_3	C_4	C_5
C_1	C_1	C_2	C_3	C_4	C_5
C_2		$2C_1 + 2C_3$	C_2	$2C_5$	$2C_4$
C_3			C_1	C_4	C_5
C_4				$2C_1 + 2C_3$	$2C_2$
C_5					$2C_1 + 2C_3$

$$\hat{C}_i \hat{C}_j = \sum_k D_{ij}^k \hat{C}_k$$

$$L_{jk} = \sum_i D_{ij}^k y^i$$

$$L = \begin{pmatrix} y^1 & y^2 & y^3 & y^4 & y^5 \\ 2y^2 & y^1+y^3 & 2y^2 & 2y^5 & 2y^6 \\ y^3 & y^2 & y^1 & y^4 & y^5 \\ 2y^4 & 2y^5 & 2y^4 & y^1+y^3 & 2y^2 \\ 2y^5 & 2y^6 & 2y^5 & 2y^2 & y^1+y^3 \end{pmatrix}$$

$\lambda_a = y^1 \quad - y^3$ $\qquad m_1 = 1$

$\lambda_b = y^1 + 2y^2 + y^3 - 2y^4 - 2y^5$ $\qquad m_2 = 2$

$\lambda_c = y^1 - 2y^2 + y^3 + 2y^4 - 2y^5$ $\qquad m_3 = 1$

$\lambda_d = y^1 - 2y^2 + y^3 - 2y^4 + 2y^5$ $\qquad m_4 = 2$

$\lambda_e = y^1 + 2y^2 + y^3 + 2y^4 + 2y^5$ $\qquad m_5 = 2$

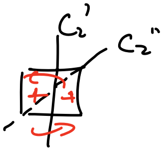
$$\chi_\mu[C_i] = \underline{n_\mu} \frac{\lambda_i^\mu}{m_i}$$

$$\begin{array}{lllllll} & m_i & 1 & 2 & 1 & 2 & 2 \\ \chi_a = n_a & (& 1, & 0, & -1, & 0, & 0) \\ \chi_b = n_b & (& 1, & 1, & 1, & -1, & -1) \\ \chi_c = n_c & (& 1, & -1, & 1, & 1, & -1) \\ \chi_d = n_d & (& 1, & -1, & 1, & -1, & 1) \\ \chi_e = n_c & (& 1, & 1, & 1, & 1, & 1) \end{array}$$

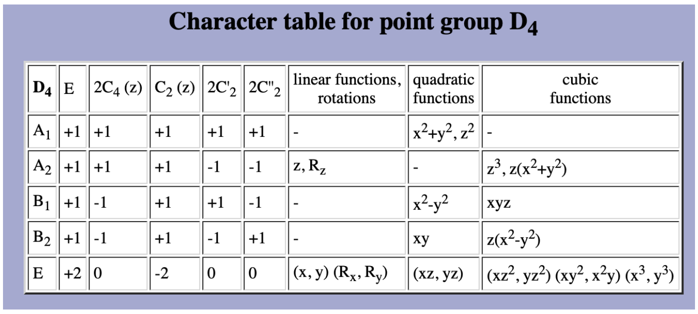
$\langle \chi_\mu . \chi_\mu \rangle = 1 \Rightarrow n_a = 2$

$n_b = n_c = n_d = n_e = 1$

$(\; |D_4| = 1^2 \times 4 + 2^2 \times 1 \;)$



$[r] = C_4(z) \qquad [r^2] = C_2(z) \qquad [s] = C_2' \qquad [rs] = C_2''$



Character table for point group D_4

D_4	E	$2C_4$ (z)	C_2 (z)	$2C'_2$	$2C''_2$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_2	+1	+1	+1	-1	-1	z, R_z	-	z^3, $z(x^2+y^2)$
B_1	+1	-1	+1	+1	-1	-	x^2-y^2	xyz
B_2	+1	-1	+1	-1	+1	-	xy	$z(x^2-y^2)$
E	+2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)	(xz^2, yz^2) (xy^2, x^2y) (x^3, y^3)

Mulliken symbols:

A/B : 1D irreps. symmetric/antisymmetric w.r.t. principal rotation

$\chi(C_n) = \pm 1$

E 2D irrep.

T 3D

G 4D

H 5D

Subscript:

1/2 : symm/antisymm. w.r.t. vertical mirror plane

g/u : $A_1 \rightarrow A_{1g} / A_{1u}$

$E \rightarrow E_g / E_u$

"g" gerade even

"u" ungerade odd.

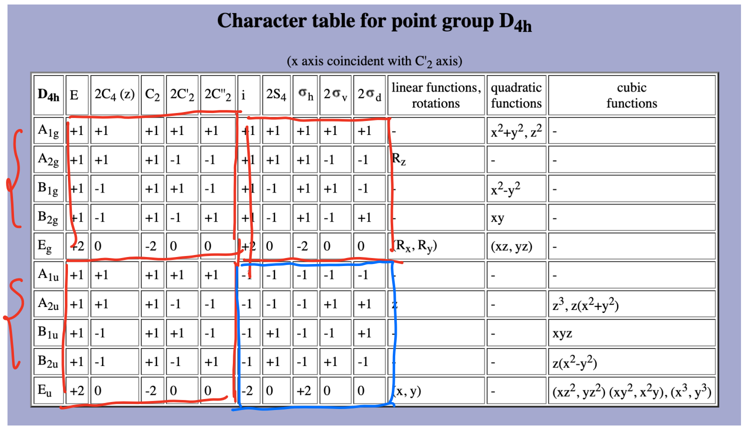
$\chi(i) = \pm 1$

'/'' : sym/antisym σ_h

Examples .

$$D_4 \xrightarrow{D_4 \otimes \bar{1}} D_{4h}$$

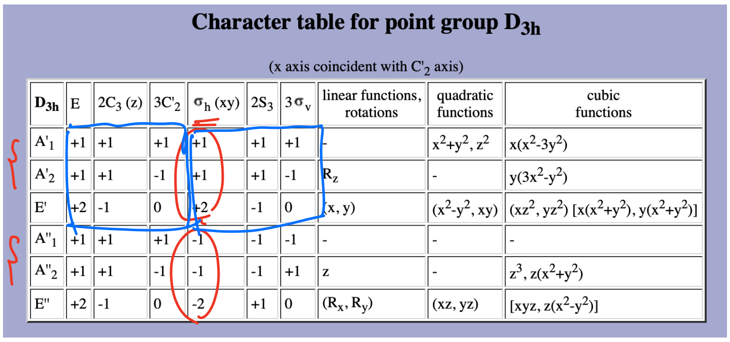
$$422 \longrightarrow 4/mmm$$



Character table for point group D_{4h}

(x axis coincident with C'_2 axis)

D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2	-
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy	-
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)	-
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-	$z^3, z(x^2+y^2)$
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-	xyz
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-	$z(x^2-y^2)$
E_u	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-	(xz^2, yz^2) (xy^2, x^2y), (x^3, y^3)



Character table for point group D_{3h}

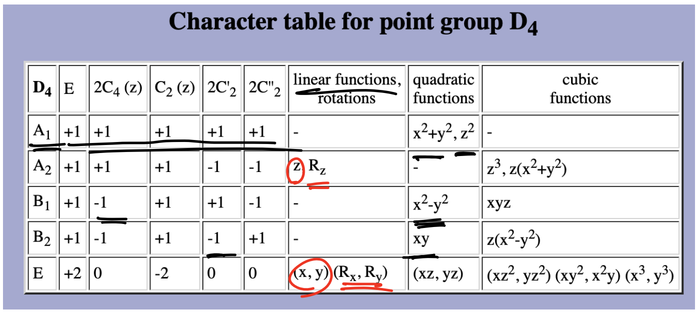
(x axis coincident with C'_2 axis)

D_{3h}	E	$2C_3$ (z)	$3C'_2$	σ_h (xy)	$2S_3$	$3\sigma_v$	linear functions, rotations	quadratic functions	cubic functions
A'_1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	$x(x^2-3y^2)$
A'_2	+1	+1	-1	+1	+1	-1	R_z	-	$y(3x^2-y^2)$
E'	+2	-1	0	+2	-1	0	(x, y)	(x^2-y^2, xy)	(xz^2, yz^2) $[x(x^2+y^2), y(x^2+y^2)]$
A''_1	+1	+1	+1	-1	-1	-1	-	-	-
A''_2	+1	+1	-1	-1	-1	+1	z	-	$z^3, z(x^2+y^2)$
E''	+2	-1	0	-2	+1	0	(R_x, R_y)	(xz, yz)	$[xyz, z(x^2-y^2)]$

$\bar{6}2\ (D_6)$ $\qquad D_3 \triangleleft D_6$

$$D_6 = D_3 \cup \sigma D_3$$

$$\longrightarrow D_{3h} = D_3 \cup i\sigma D_3$$



Character table for point group D_4

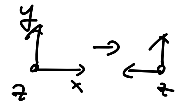
D_4	E	$2C_4$ (z)	C_2 (z)	$2C'_2$	$2C''_2$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_2	+1	+1	+1	-1	-1	z R_z	-	$z^3, z(x^2+y^2)$
B_1	+1	-1	+1	+1	-1	-	x^2-y^2	xyz
B_2	+1	-1	+1	-1	+1	-	xy	$z(x^2-y^2)$
E	+2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)	(xz^2, yz^2) (xy^2, x^2y) (x^3, y^3)

functions

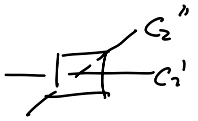
1. linear functions

Rep in $\mathbb{R}^3$ = span $\{e_1, e_2, e_3\}$

$\hat{x}, \hat{y}, \hat{z}$



	e	$2C_4(z)$	$C_2(z)$	$2C_2'$	$2C_2''$
χ_{R_3}	3	1	-1	-1	-1



$n_{A_1} = \langle \chi_{R^3}, \chi_{A_1} \rangle = 0$

$n_{A_2} = 1$, $n_E = 1$

$\Rightarrow \mathbb{R}_3 \cong A_2 \oplus E$

$$\underset{\sim}{E} \quad \underset{\sim}{A_2}$$

The rep matrix
$$e = \left(\begin{array}{cc|c} x & y & z \\ 1 & & 0 \\ & 1 & \\ \hline 0 & & 1 \end{array}\right)$$

$$C_4 = \left(\begin{array}{cc|c} 0 & -1 & 0 \\ 1 & 0 & \\ \hline 0 & & 1 \end{array}\right)$$

$r \to R \cdot r$ — $x, y, z \to$ vector

$r \to (\det R) R r$ — $R_x, R_y, R_z \to$ axial vector

$\boxed{\sigma}$ different

2. quadratic functions.

$xy, xz, yz, x^2, y^2, z^2$

$C_4(z)$ $\quad xy \to y(-x) = \underline{-xy}$ $\qquad x^2 \to y^2$

$xz \to yz$ $\qquad y^2 \to x^2$

$yz \to -xz$ $\qquad \underline{z^2 \to z^2}$

$\chi(C_4) = 0$

$C_2(z)$ $\quad \chi = 2$

$C_2'(x)$ $\quad \chi = 2$

C_2'' $\quad \chi = 2$

$Q \cong 2A_1 \oplus B_1 \oplus B_2 \oplus E$

(recall $P^{\mu} = \int_G dg\, \chi^{\mu}(g)\, M(g) = \frac{1}{|G|} \sum_g \chi(g) \underline{M(g)}$)

$A_1 : x^2 + y^2,\ z^2$ $\qquad B_1 = x^2 - y^2$ $\qquad B_2 = xy$

$E : (yz.\ xz)$

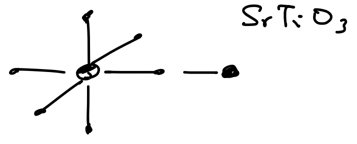
9.4. Splitting of atomic orbitals

Ref. ① Dresselhaus. Chap 5

② Ballhausen. intro. to Ligand field theory Chap 4

③ Cowan. Theory of atomic structure and spectra

Consider an ion inside a crystal



$H = H_f + V_{crystal}$

↑ free ion

① $H_f = \sum_i \left(\frac{p_i^2}{2m} - \frac{Z^* e^2}{r_i} + \sum_j \frac{e^2}{r_{ij}} + \xi_i \vec{l}_i \cdot \vec{s}_i \right)$

↑ kinetic ↑ e-ion Coulomb ↑ e-e ↑ spin-orbit (ignore hyperfine etc.)

with spherical symmetry. We know the solution.

② $V_{crystal}$: external potential due to other ions in the crystal (Madelung potential for ionic systems.) "Crystal field".

a. $V_{crystal} < \xi \vec{l} \cdot \vec{s}$ rare-earths

b. $\xi \vec{l} \cdot \vec{s} < V$ transition metal compounds (Cu. Ni . etc.) magnetism . superconductivity

We focus on the second case. ignore SOC.

In this case. the symmetry-adapted basis functions are a better starting point than the atomic orbitals in spherical harmonics.

9.4.1. Splitting of the V^l rep.

For symmetry analysis. we can ignore the radial part of the basis functions. and consider Spherical harmonics $Y_{lm}(\theta.\phi)$

$$Y_{lm} = \left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} P_l^m(\cos\theta)\, e^{im\phi}$$

$$\left(\int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi\, Y_{lm} \overline{Y_{l'm'}} = \delta_{ll'}\delta_{mm'} \right)$$

each l labels an irrep

$$\hat{O}_R \cdot Y_{l.m} = \Sigma\, D^l(R)_{m'm}\, Y_{lm'} \qquad \text{Wigner D-matrix}$$

① rotation around $\hat{z}$ by α then

$$\hat{O}_R Y_{lm}(\theta.\phi) = Y_{lm}(R^{-1}\cdot(\theta.\phi)) = e^{-im\alpha} Y_{lm}(\theta.\phi)$$

(we've seen it before)

$$\chi^l(\alpha) = \sum_m e^{-im\alpha} \underset{z=e^{-i\alpha/2}}{=} \frac{z^{2j+1} - z^{-2j-1}}{z - z^{-1}} = \frac{\sin(l+\frac{1}{2})\alpha}{\sin\frac{1}{2}\alpha}$$

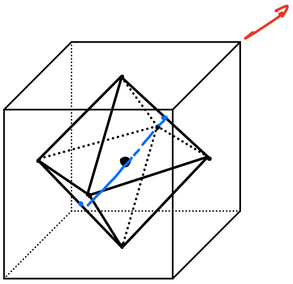
$$= U_l(\cos\frac{\alpha}{2})$$

chebyshev polynomial of the 2nd kind

② inversion $\hat{O}_i \cdot Y_{lm}(\theta,\phi) = Y_{lm}(\pi-\theta, \phi+\pi) = (-1)^l Y_{lm}(\theta,\phi)$

$O_h = m3m$

$4/m \bar{3} 2/m$



$C_3^{\pm}$ 3 body diagonals × ± = 6

C_2 connecting edge midpoints × 6

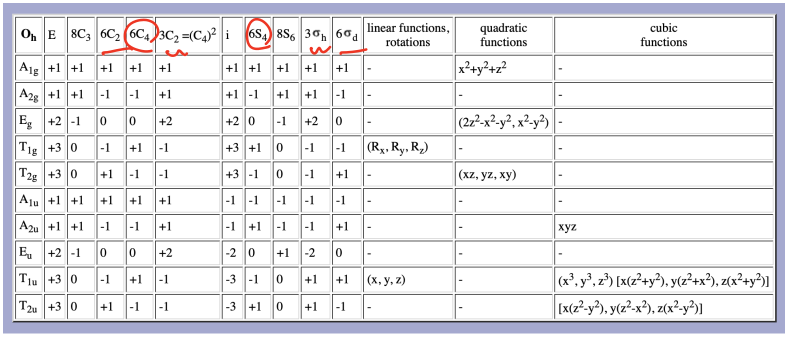
$C_4(z)$ $3 \times C_4^{\pm} = 6$

$C_2(z)$ 3

$24 \times \{e, i\} = 48$

Now consider O_h with the character table below

$C_2(\theta)$



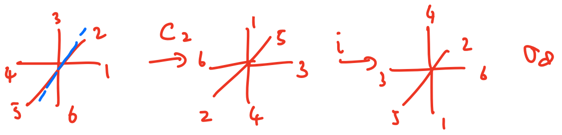
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$	-
A_{2g}	+1	+1	-1	-1	+1	+1	-1	+1	+1	-1	-	-	-
E_g	+2	-1	0	0	+2	+2	0	-1	+2	0	-	$(2z^2-x^2-y^2, x^2-y^2)$	-
T_{1g}	+3	0	-1	+1	-1	+3	+1	0	-1	-1	(R_x, R_y, R_z)	-	-
T_{2g}	+3	0	+1	-1	-1	+3	-1	0	-1	+1	-	(xz, yz, xy)	-
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
A_{2u}	+1	+1	-1	-1	+1	-1	+1	-1	-1	+1	-	-	xyz
E_u	+2	-1	0	0	+2	-2	0	+1	-2	0	-	-	-
T_{1u}	+3	0	-1	+1	-1	-3	-1	0	+1	+1	(x, y, z)	-	(x^3, y^3, z^3) $[x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]$
T_{2u}	+3	0	+1	-1	-1	-3	+1	0	+1	-1	-	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2)]$

$$\left(\frac{\sin(l+\frac{1}{2})\alpha}{\sin\frac{1}{2}\alpha}\right)$$

dim (2l+1)	$\frac{2}{3}\pi$	π	$\frac{\pi}{2}$	π
$\chi(E)$	$\chi(C_3)$	$\chi(C_2)$	$\chi(C_4)$	$\chi(C_2)$
i	$iC_3 = S_6$	$iC_2(xy) = \sigma_d$	$iC_4 = S_4$	$iC_2(z) = \sigma_h$

① $iC_n = \sigma C_2 C_n = \sigma C_{2n}^{n+2} = S_{2n}^{n+2}$ odd: $iC_n = \sigma C_2 C_n = \sigma C_n^{\frac{n}{2}+1} = S_n^{\frac{n}{2}+1}$

②



	dim $(2l+1)$ $\chi(E)$	$\frac{2}{3}\pi$ $\chi(C_3)$	π $\chi(C_2)$	$\frac{\pi}{2}$ $\chi(C_4)$	π $\chi(C_2)$	
	i	S_6	σ_d	S_4	σ_h	
① s-orbital	1	1	1	1	1	$s \to A_{1g}$
$l = 0$	1	1	1	1	1	
② p / $l=1$	3	0	-1	1	-1	$p \to T_{1u}$
	-3	0	1	-1	1	
③ d / $l=2$	5	-1	1	-1	1	$d \to E_g + T_{2g}$
④ f / $l=3$	7	1	-1	-1	-1	$f \to A_{2u} + T_{1u} + T_{2u}$

$$\begin{cases} E_g: & x^2-y^2 .\ 3z^2-r^2 \\ T_{2g}: & xy .\ yz .\ xz \end{cases}$$

9.4.2 Single d-electron in Octahedral field.

$l=2.$ $\quad Y_l^m = \sqrt{\frac{5}{\cancel{4\pi}} \frac{(2-m)!}{(2+m)!}}\, P_l^m(\cos\theta) e^{im\phi}$

ignore

$P_2^2(z) = 3(1-z^2)$ $\qquad P_2^{-m}(z) = (-1)^m \frac{(2-m)!}{(2+m)!} P_2^m$

$P_2^1(z) = -3z(1-z^2)^{1/2}$

$P_2^0(z) = \frac{1}{2}(3z^2-1)$

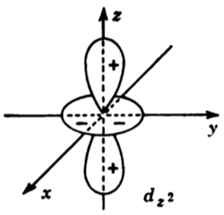
write in x.y.z.

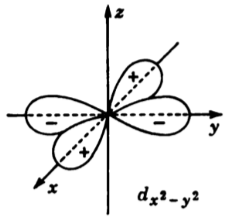
$$\begin{cases} x = \sin\theta\cos\phi \\ y = \sin\theta\sin\phi \\ z = \cos\theta \end{cases}$$

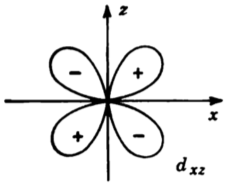
$$\begin{cases} d_{\pm 2} = Y_2^{\pm 2} = \sqrt{\frac{3}{8}}(x \pm iy)^2 \\ d_{\pm 1} = Y_2^{\pm 1} = \mp\sqrt{\frac{3}{2}}(x \pm iy)z \\ d_0 = Y_2^0 = \frac{1}{2}(3z^2-1) \end{cases}$$

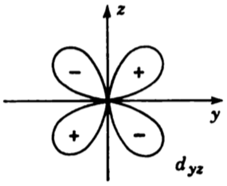
$$E_g : \begin{cases} x^2 - y^2 = \frac{1}{\sqrt{2}} (d_{+2} + d_{-2}) & \sim \sin^2\theta \, (\overset{\cos 2\phi}{\cos^2\phi - s^2\phi}) \\ z^2 \to 3z^2 - 1 = d_0 & \sim \cos\theta \end{cases}$$

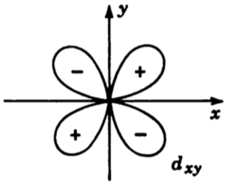
$$t_{2g} \begin{cases} xy & \frac{1}{\sqrt{2} i} (d_{+2} - d_{-2}) & \sim \sin^2\theta (\sin\phi \cos\phi) \\ xz & -\frac{1}{\sqrt{2}} (d_{+1} - d_{-1}) \\ yz & -\frac{1}{\sqrt{2} i} (d_{+1} + d_{-1}) \end{cases}$$

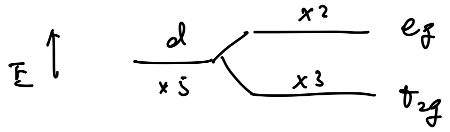












$E = 6Dq$
$E = -4Dq$

historically 10Dq splitting

the sign and amplitude determined by the physical details. $E_{eg} > E_{t_{2g}}$ because of charge distribution skip details ↓

Formally. we can expand $V_{crystal}$ onto spherical harmonics

$$V_c = \sum_i \sum_{lm} Y_l^m(\hat{r}_i) R_{nl}(r_i)$$

$$= V_R + V_O$$

$l=0$ part ↗ ↖ octahedral part.

It should has <u>all symmetries</u> of H. transform as A_{1g}.

$$(V_c = \sum_\mu \lambda^\mu 1_{\Gamma^\mu})$$

The potential for a d-electron:

$$\langle l_1 m_1 | V_c | l_2 m_2 \rangle \sim \begin{pmatrix} 2 & l & 2 \\ m_1 & m & -m_2 \end{pmatrix} \quad l \leq 4$$

we can further ignore odd orders because d electrons are even. ($l=2$)

Remaining terms are Y_2^m and Y_4^m.

Y_2^m : $E_g \oplus T_{2g}$. no A_{1g} component

Y_4^m : $\underline{\underline{A_{1g}}} \oplus E_g \oplus T_{1g} \oplus T_{2g}$

$\Rightarrow$ find that $V_O = Y_4^0 + \sqrt{\frac{5}{14}}(Y_4^4 + Y_4^{-4})$

(axis dependent.)

Check: $\hat{C}_6 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} y \\ -x \\ z \end{pmatrix}$

$\hat{C}_4 Y_4^{\pm 6} = Y_4^{\pm 4}$ $\qquad Y_4^{\pm 4} \propto \sin^4\theta \, e^{\pm i 4\phi}$

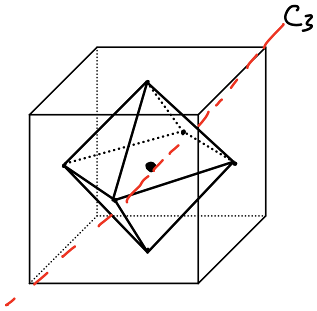
One can then write out the matrix elements of V_o in d_m. ignore prefactors $\langle Y_2^m | Y_4^0 + \sqrt{\frac{3}{14}} (Y_6^4 + Y_6^{-4}) | Y_2^{m'} \rangle$

$$\frac{1}{21} \begin{pmatrix} 1 & & & & 5 \\ & -4 & & & \\ & & 6 & & \\ & & & -4 & \\ 5 & & & & 1 \end{pmatrix}$$

$E(E_g) = \frac{6}{21} = 6Dq$

$E(T_{2g}) = -\frac{4}{21} = -4Dq$

Note that the form of E_g / T_{2g} orbitals depend on the quantization axis. of choosing C_3 as the quantization axis. then



$$E_g = \begin{cases} \sqrt{\frac{1}{3}}\, d_2 + \sqrt{\frac{2}{3}}\, d_{-1} \\ \sqrt{\frac{1}{3}}\, d_{-2} - \sqrt{\frac{2}{3}}\, d_1 \end{cases}$$

$$T_{2g} = \begin{cases} d_0 \\ \sqrt{2/3}\, d_2 - \sqrt{1/3}\, d_1 \\ \sqrt{2/3}\, d_{-2} + \sqrt{1/3}\, d_1 \end{cases}$$

$$V_c = Y_4^0 + \sqrt{\frac{10}{7}} (Y_4^3 - Y_4^{-3})$$

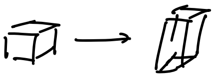
$$(V_c)_{mm'} = \frac{1}{21} \begin{pmatrix} 1 & & & \frac{5}{21}\sqrt{2} & \\ & -4 & & & -\frac{5}{21}\sqrt{2} \\ & & 6 & & \\ \frac{5}{21}\sqrt{2} & & & -4 & \\ & -\frac{5\sqrt{2}}{21} & & & 1 \end{pmatrix}$$

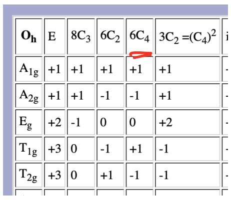
$E(E_g) = -\frac{3}{7}$

$E(T_{2g}) = \frac{2}{7}$

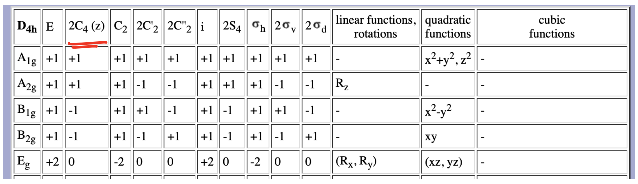
The sign of $10Dq$ is reversed.

Now consider $O_h \longrightarrow D_{4h}$





O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 =(C_4)^2$
A_{1g}	+1	+1	+1	+1	+1
A_{2g}	+1	+1	-1	-1	+1
E_g	+2	-1	0	0	+2
T_{1g}	+3	0	-1	+1	-1
T_{2g}	+3	0	+1	-1	-1



D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2	-
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy	-
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)	-

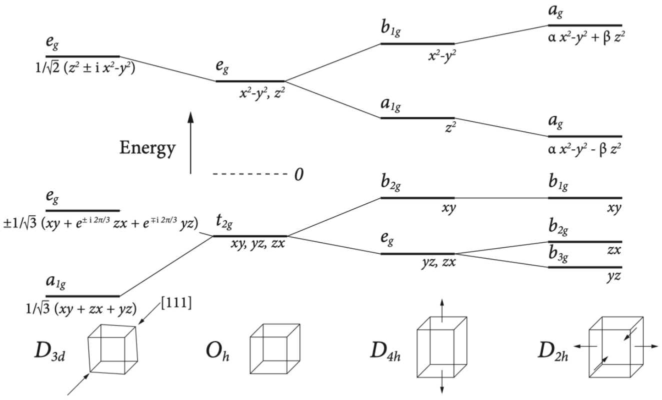
O_h $\tilde{E}_g$ 2 0 2 2 0

$\tilde{T}_{2g}$ 3 1 -1 -1 -1

O_h D_{4h}

$E_g \longrightarrow A_{1g} + B_{1g}$ $\quad$ $T_{2g} \longrightarrow B_{2g} + E_g$

z^2 $\quad x^2-y^2$ $\qquad$ xy $\quad xz, yz$



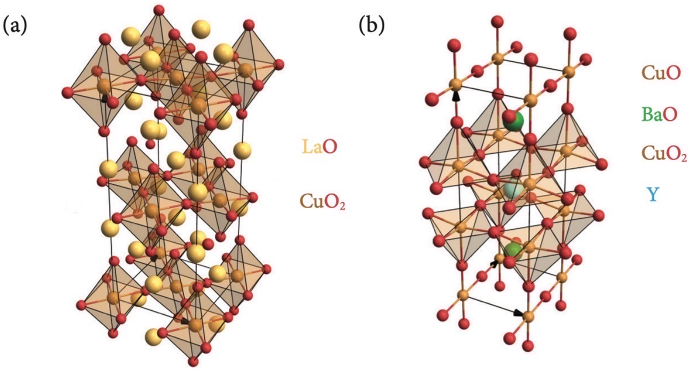


Figure 2.8 | Structures of (a) La_2CuO_4 and (b) $YBa_2Cu_3O_7$.

Cu^{2+}: $3d^9$

b_{2g} ↑ x^2-y^2
a_{1g} ↑↓ $3z^2-r$

b_{2g} ↑↓ xy
e_g ↑↓↑↓ xz/yz

9.4.3 Two d-electrons in an Octahedral field.

Two different starting points:

$e^2/r_{ij} > V_{crystal}$ "weak (crystal) field"

$e^2/r_{ij} < V_{crystal}$ "strong field"

a. Coulomb interaction

Laplace multipole expansion,

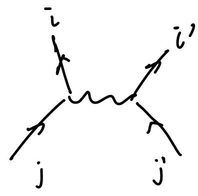
$$\frac{1}{|\vec{r}-\vec{r}'|} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \sum_{q=-k}^{k} (-1)^q \frac{r_<^k}{r_>^{k+1}} Y_k^{-q}(\hat{r}) Y_k^{q}(\hat{r}')$$

Define tensor operators $C^{(k)}_q(\hat{r}) = \sqrt{\frac{4\pi}{2l+1}}\, Y_k^q(\hat{r})$

The Coulomb interaction

$$U_{ii'jj'} = \langle \alpha_i \alpha_{i'} | \frac{1}{r_{ij}} | \alpha_{j'} \alpha_j \rangle$$

$\alpha = |\overset{\text{spin}}{\sigma}\rangle \otimes |n, l, m\rangle$



$$= \delta_{\sigma_i \sigma_j} \delta_{\sigma_{i'} \sigma_{j'}} \sum_{k=0}^{\infty} R^{l}_{ii'jj'} \sum_{q=-k}^{k} (-1)^q \times$$

$$\langle l_i m_i | C^{(k)}_{-q} | l_j m_j \rangle \times$$

$$\delta_{q, m_j - m_i}\, \delta_{q, m_{i'} - m_{j'}} \xleftarrow[\text{rules}]{\text{selection}} \langle l_{i'} m_{i'} | C^{(k)}_{q} | l_{j'} m_{j'} \rangle$$

$$R^{k}_{ii'jj'} = \int_0^{\infty} dr\, r^2 \int_0^{\infty} dr'\, r'^2 \frac{r_<^k}{r_>^{k+1}} R_{n_i l_i}(r) R_{n_{i'} l_{i'}}(r') R_{n_j l_j}(r) R_{n_{j'} l_{j'}}(r')$$

(slater integrals)

Direct term: $i=j \quad i'=j'$

$$U_{ii'ii'} = \sum_{k=0}^{\infty} \underbrace{F^k(ii)}_{\equiv R^k_{ii'ii'}} \langle l_i m_i | C_0^{(k)} | l_i m_i \rangle \langle l_{i'} m_{i'} | C_0^{(k)} | l_{i'} m_{i'} \rangle$$

$$F^k > F^{k+1} > \cdots > 0 \qquad \left(\because \ \frac{r_<^k}{r_>^{k+1}} \right)$$

triangular relation: $\quad k \leq 2 \min[l_i . l_{i'}]$

exchange term: $i = j' . \ i' = j$

$$U_{ijji} = \delta_{\sigma_i \sigma_{i'}} \sum_{k=0}^{\infty} \underbrace{G^k(ij)}_{R^k_{ijji}} | \langle l_i m_i | C_{-q}^{(k)} | l_j m_j \rangle |^2$$

$$\frac{G^k}{2k+1} > \frac{G^{k+1}}{2k+3} > 0 \qquad \text{usually } G^k > G^{k+1} > 0$$

$$k = |l_i - l_j| \cdots , l_i + l_j$$

and $G^k = F^k$ for electrons in the same shell and cancel each other.

Wigner-Eckart theorem

$$\langle l'm' | C_q^{(k)} | l m \rangle = \underbrace{(-1)^{l'-m'} \begin{pmatrix} l' & k & l \\ -m' & q & m \end{pmatrix}}_{\text{angular part}} \underbrace{\langle l' \| C^{(k)} \| l \rangle}_{\text{reduced mat. el.}}$$

with selection rule

$$q = m' - m$$

where $\langle l' \| C^{(k)} \| l \rangle = (-1)^{l'} \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}$

It follows, for d^2: $V^2 \otimes V^2 \cong V^0 \oplus V^1 \oplus V^2 \oplus V^3 \oplus V^4$

$$D \otimes D \cong S \oplus P \oplus D \oplus F \oplus G$$

Consider the spin part: $\frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1$

The fermionic statistics are incooperated by the antisymmetric power $\Lambda^n(V^d)$ $\dim = \frac{d^2-d}{2}$

^{2S+1}L

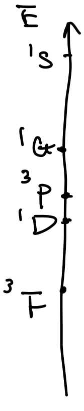
$$\Lambda^2({}^2D) = (e-(12))({}^2D \otimes {}^2D)$$

$$\dim = \frac{100-10}{2} = 45$$

indeed. $\Lambda^2({}^2D) \cong {}^1S \oplus {}^3P \oplus {}^1D \oplus {}^3F \oplus {}^1G$

$$1+9+5+21+9 = 45 = \binom{10}{2}$$

The energies: depend on F^0. F^2. F^4



$$E({}^1S) = F_0 + \frac{2}{7}F_2 + \frac{2}{7}F_4$$

$$E({}^3P) = F_0 + \frac{1}{7}F_2 - \frac{4}{21}$$

$$E({}^1D) = F_0 - \frac{3}{49}F_2 + \frac{4}{49}F_4$$

$$E({}^3F) = F_0 - \frac{8}{49}F_2 - \frac{1}{49}F_4 \quad \Leftarrow \text{ground state.}$$

$$E({}^1G) = F_0 + \frac{4}{49}F_2 + \frac{1}{441}F_4$$

^3F: $S=1$, $L=3$ **Hund's rules** 1: max S

$(|2,\uparrow;1,\uparrow\rangle$ etc.$)$ 2: max L.

(3 min or max J due to SOC.)

b. Weak field : ($V_{crystal} < e^2/r_{ij}$)

Take the spherical limit as the starting point:

$^1S \rightarrow {}^1A_{1g}$

$^3P \rightarrow {}^3T_{1g}$

$^1D \rightarrow {}^1E_g \oplus {}^1T_{2g}$

$^3F \rightarrow {}^3A_{2g} \oplus {}^3T_{1g} \oplus {}^3T_{2g}$ $\Leftarrow$ Contains the GS.

$^1G \rightarrow {}^1A_{1g} \oplus {}^1E_g \oplus {}^1T_{1g} \oplus {}^1T_{2g}$

Consider matrix element $\langle L_1 M_1 | \underline{V_0} | L_2 M_2 \rangle$ for ^3F

$$V_0 = Y_4^0 + \sqrt{\frac{5}{14}} (Y_4^4 + Y_4^{-4})$$

Consider eigenstates $L_M \psi_M = M \psi_M$, similarly to the spherical harmonics, the T_1 irrep is constructed as

$$\begin{cases} \sqrt{\frac{3}{8}}\psi_1 + \sqrt{\frac{3}{8}}\psi_{-3} \\ \sqrt{3/8}\,\psi_{-1} + \sqrt{5/8}\,\psi_3 \\ \psi_0 \end{cases}$$

Let $\psi_0 \equiv |L, M_L; S, M_S\rangle = |3, 0, 1, 1\rangle$

$$\overset{CG}{=} \sqrt{1/10}\,(|2^+, -2^+\rangle - |-2^+, 2^+\rangle) + \sqrt{2/5}\,(|1^+, -1^+\rangle - |-1^+, 1^+\rangle)$$

($M=0$ only couples to $M=0$)

$E({}^3T_{1g}) = \cdots = -6Dq$

Similarly. $E({}^3A_{2g}) = 12\,Dq$. $E({}^3T_{2g}) = 2\,Dq$.

c. strong-field ($V_{crystal} < e^2/r_{ij}$)

Cubic limit.

$$D \cong E_g \oplus T_{2g}$$

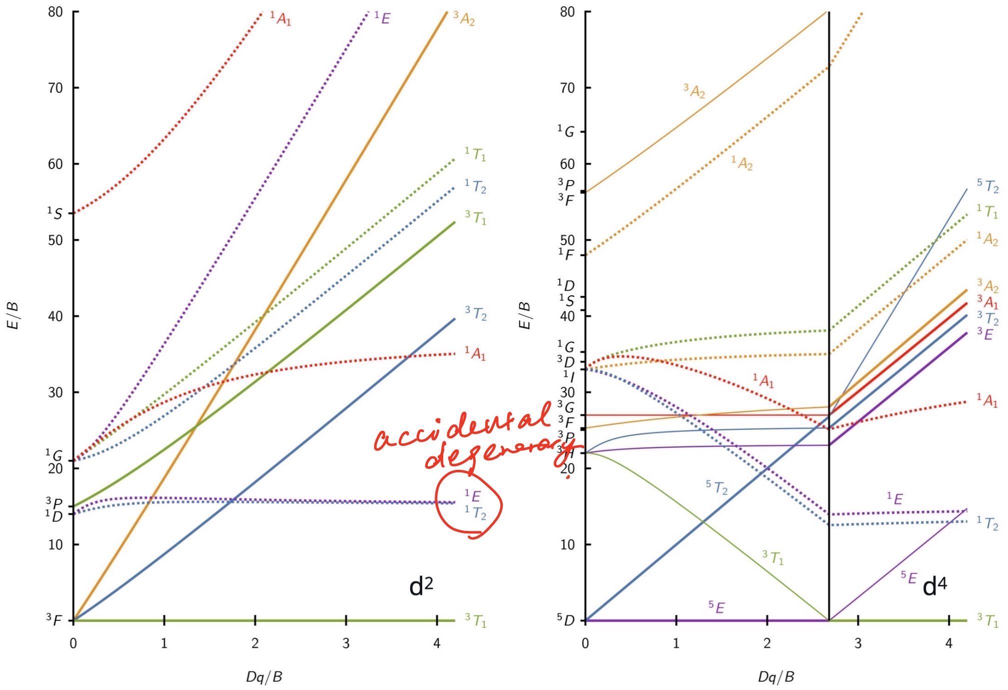
$$E_g \otimes E_g = A_{1g} \oplus A_{2g} \oplus E_g$$

$$E_g \otimes T_{2g} = T_{1g} \oplus T_{2g}$$

$$T_{2g} \otimes T_{2g} = A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$$

treat Coulomb as perturbation. evaluate $U_{ii'jj'}$ in the crystal-field eigen basis.

Follows similarly as b.



accidental degeneracy

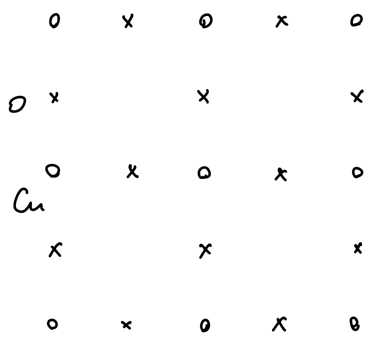
Tanabe-Sugano diagram   high-spin vs. low spin

9.5. Hybridization and molecular orbitals

Dresselhaus 7
Ballhausen 7

Now we move on to larger systems by considering the neighboring ions:

Take D_{4h} as example. (2D square lattice)



La_2CuO_4

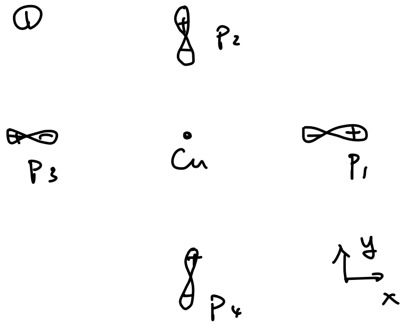
CuO_2 plane

$D_4 \otimes \bar{I} \rightarrow D_{4h}$

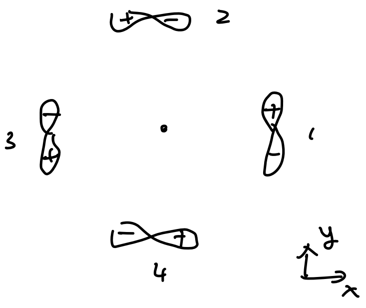
	R	iR
g	CT	CT
u	CT	-CT

How the Cu-d orbitals and O-2p orbitals form "molecular orbitals". (Hybridization)

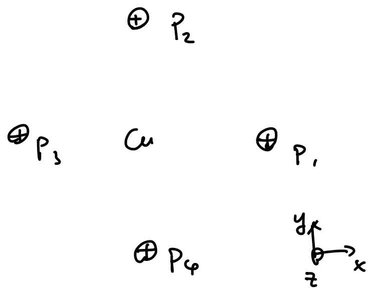
①



②



③



We are looking for	a_{1g} .	b_{1g} .	b_{2g} .	e_g
	$3z^2-1$	x^2-y^2	xy	xz/yz

Set 1 :	E	$2C_4$	C_2	$2C_2'(x)$	$2C_2''(xy)$
	4	0	0	2	0

D_4

A_1 : $\frac{1}{8}(4 + \cdots + 4) = 1$

A_2 : 0

B_1 : 1

B_2 0

E : 1

set 1: $D(E) = \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ & & & 1 \end{pmatrix}$

$$D(C_4^+(z)) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \qquad D(C_4^-(z)) = D(C_4^{3+}(z)) = D(C_4^+(z))^T$$

$$D(C_2(z)) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 \end{pmatrix} \qquad \begin{matrix} 1 \leftrightarrow 3 \\ 2 \leftrightarrow 4 \end{matrix} \qquad \text{etc.}$$

The projectors to a specific irrep?

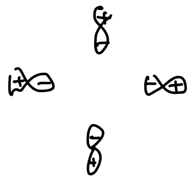
recall that

$$P^\mu_{ij} = \int_G \bar{M}^\mu(g)\, T(g)\, dg$$

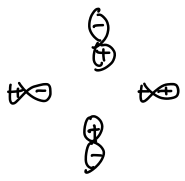
$$P^\mu = \mathrm{Tr}\, P^\mu_{ii} = n_\mu \int_G \bar{\chi}^\mu(g)\, T(g)\, dg$$

see Mathematica notebook for details.

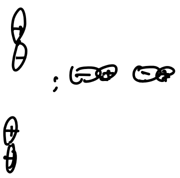
D_4: A_2 :



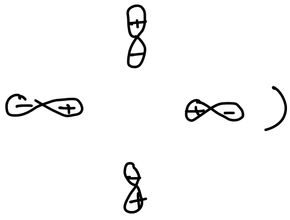
B_1 :



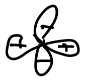
E :



in D_{4h}: A_{1g}. B_{1g}. E_u. "px", "py"



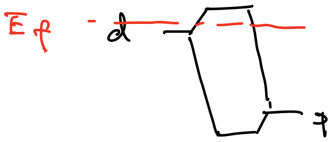
$\frac{1}{2}\left(\quad\right) = \text{``}L_{x^2-y^2}\text{''}$



$= d_{x^2-y^2}$

$\frac{1}{2}\times\left(\frac{\sqrt{3}}{2}pd\sigma\times 4\right) = \sqrt{3}\,pd\sigma$

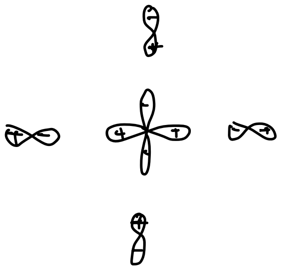
$$H_{dp4} = \begin{pmatrix} \epsilon_d & \sqrt{3}\,pd\sigma \\ \sqrt{3}\,pd\sigma & \epsilon_L \end{pmatrix}$$



$$\frac{\epsilon_d+\epsilon_p}{2} \pm \sqrt{\left(\frac{\epsilon_d-\epsilon_p}{2}\right)^2 + 3\,pd\sigma^2}$$

↓ doping

Zhang-Rice singlet. PRB $\underline{37}$, 3759 (1988)



doping: 1 hole on $d_{x^2-y^2}$

1 hole on Ligand.

forms a singlet hopping on the Cu AFM background.

Low-energy model:

$$H = \sum_{ij} t_{ij}\, c_i^\dagger c_j + U\sum_i n_{i\uparrow} n_{i\downarrow}$$

single-band Hubbard model.