9.4.3 Two d-electrons in an Octahedral field.

Two different starting points:

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

a. Coulomb interaction

Laplace multipole expansion.

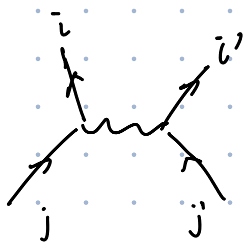
$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \sum_{q=-k}^{k} (-1)^q \frac{r_<^k}{r_>^{k+1}} Y_k^{-q}(\hat{r}) Y_k^{q}(\hat{r}\,')$$

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

The Coulomb interaction

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

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



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

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

$$\langle l_{i'} m_{i'} | C^{(k)}_{q} | l_{j'} m_{j'} \rangle$$

$$\delta_{q, m_j - m_i}\, \delta_{q, m_{i'} - m_{j'}} \xleftarrow[\text{rules}]{\text{selection}}$$

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

(slater integrals)

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

$$u_{ii'ii'} = \sum_{k=0}^{\infty} \underline{F^k(ii)} \langle l_i m_i | C_0^{(k)} | l_i m_i \rangle \langle l_{i'} m_{i'} | C_0^{(k)} | l_{i'} m_{i'} \rangle$$

$$\equiv R^k_{ii'ii'}$$

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

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

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

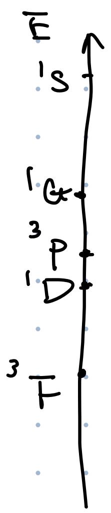
$$\Lambda^2(^2D) = (e-(12))(^2D \otimes {}^2D)$$

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

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



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

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

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

$$E(^3F) = F_0 - \frac{8}{49}F_2 - \frac{1}{49}F_4$$ $\leftarrow$ 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 $L_z \psi_M = M \psi_M$, similarly to the spherical harmonics, the T_1 irrep is constructed as

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

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

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

($M=0$ 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.

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

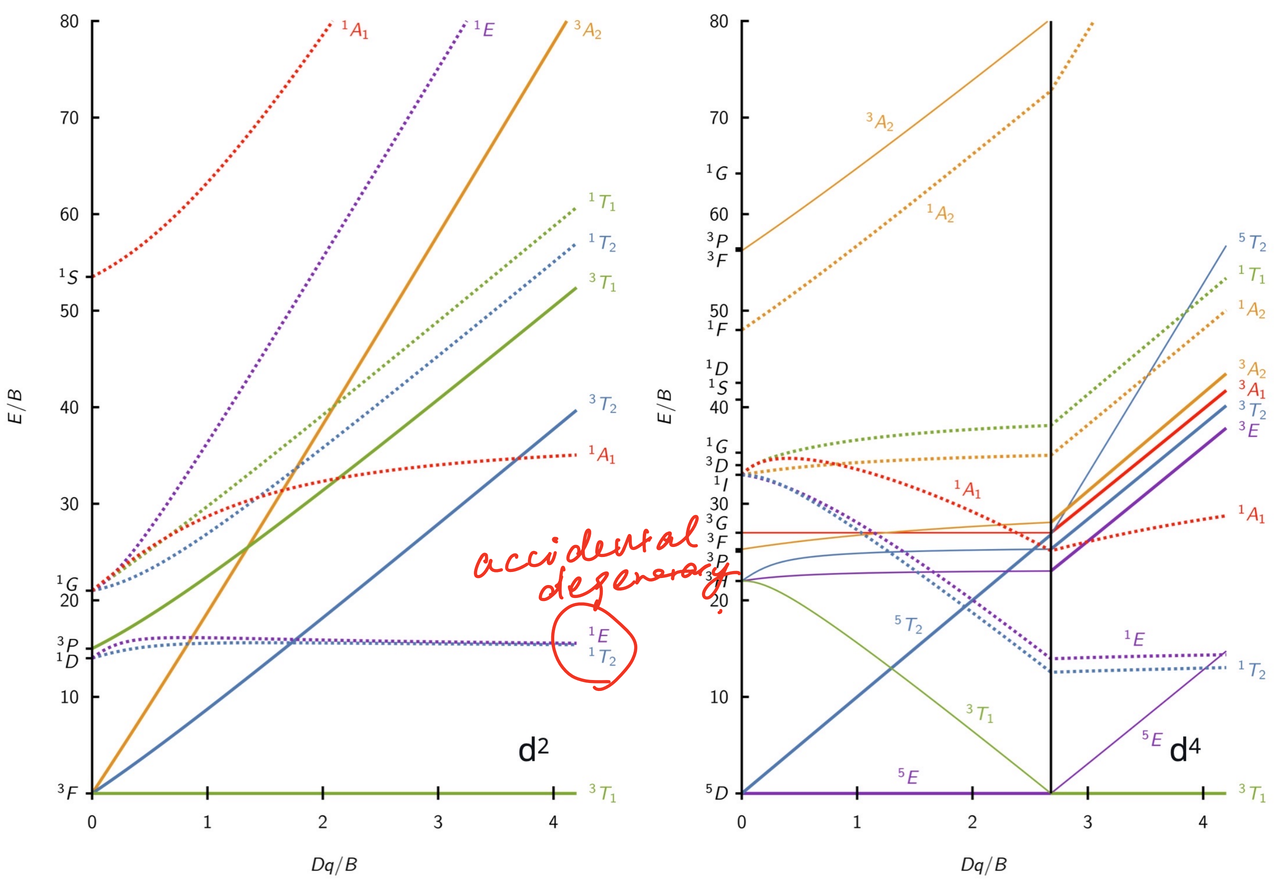
$$E_g \otimes E_g = A_{1g} \oplus A_{2g} \oplus E_g$$

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

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

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

Follows similarly as b.



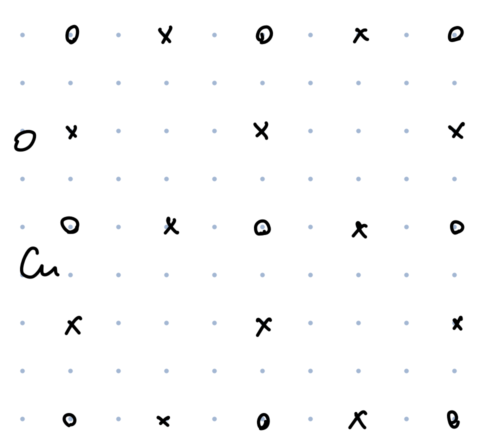
Tanabe-Sugano diagram high-spin vs. low spin

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)



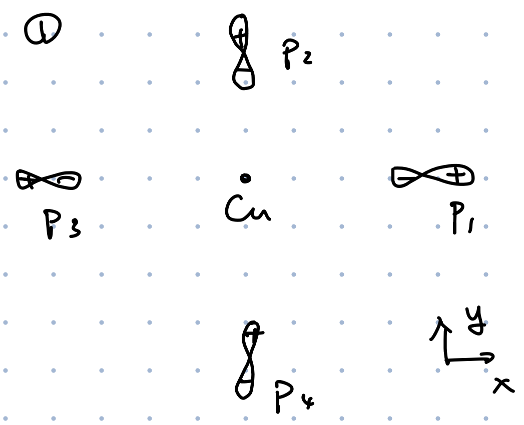
La_2CuO_4

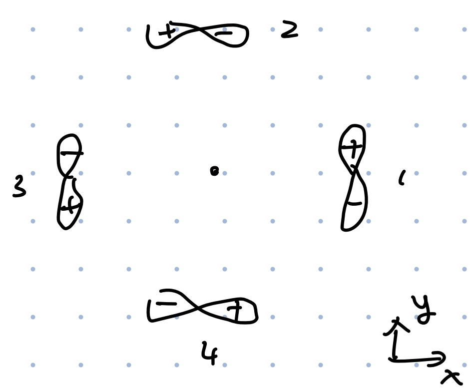
CuO_2 plane

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

	R	iR
g	CT	CT
u	CT	-CT

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

① 

② 

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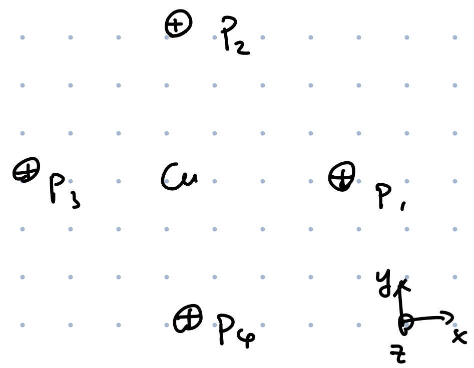


We are looking for a_{1g} . b_{1g} . b_{2g} . e_g

$3z^2-1$ $\quad x^2-y^2$ $\quad xy$ $\quad xz/yz$

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

D_4

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

A_2 : 0

B_1 : 1

B_2 0

E : 1

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

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

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

The projectors to a specific irrep ?

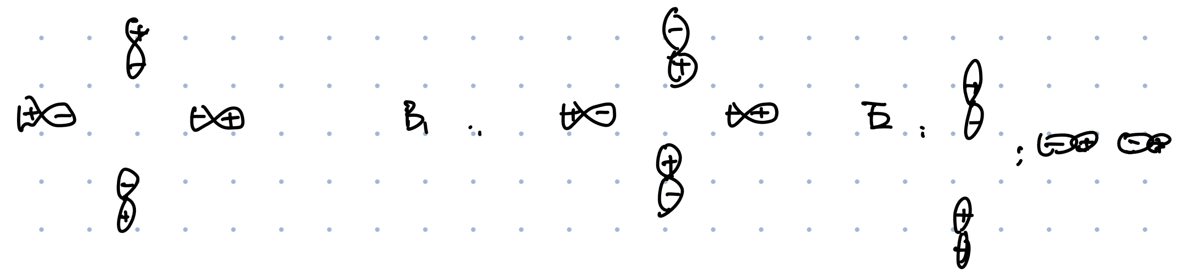
recall that

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

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

see Mathematica notebook for details.

D_4: A_1 : B_1 : E :



in D_{4h} : A_{1g} . B_{1g} . E_u . "p_x", "p_y"