Group Theory 6.734J & 8.510J (2002 spring)

Problem Set #5 Solution

1. (a)

$$\chi^{a.s}_{(tot)} = \underbrace{A_{1g} + B_{1g} + B_{2u} + B_{3u}}_{H} + \underbrace{A_{1g} + B_{3u}}_{C}$$

$$= 2A_{1g} + B_{1g} + B_{2u} + 2B_{3u}$$

The symmetries of vibrational modes are obtained by

$$\chi^{a.s}_{(tot)} \otimes \chi_{vector} - \chi_{translation} - \chi_{rotation}$$

From the character table,

$$\chi_{translation} = B_{1u} + B_{2u} + B_{3u}$$

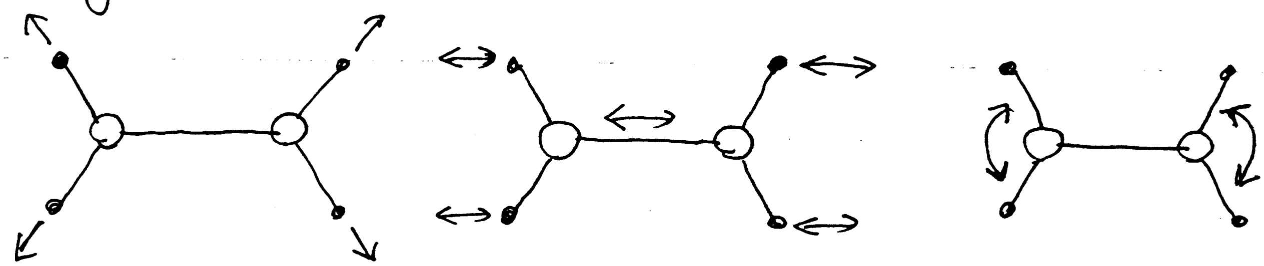
$$\chi_{rotation} = B_{1g} + B_{2g} + B_{3g}$$

$$\therefore \chi^{a.s}_{vibration} = (2A_{1g} + B_{1g} + B_{2u} + 2B_{3u}) \otimes (B_{1u} + B_{2u} + B_{3u}) - B_{1g} + B_{2g} + B_{3g} - B_{1u} - B_{2u} - B_{3u}$$

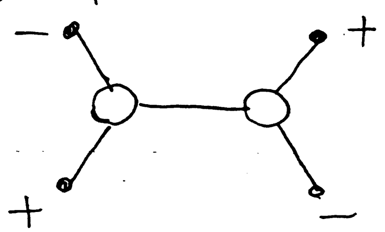
$$\begin{aligned} = {} & 2B_{1u} + 2B_{2g} + B_{3g} + A_{1u} \\ & + 2B_{2u} + 2A_{1g} + B_{1g} + B_{3u} \\ & + 2B_{3u} + 2B_{1g} + A_{1g} + B_{2u} \\ & - B_{1u} - B_{2u} - B_{3u} - B_{1g} - B_{2g} - B_{3g} \end{aligned}$$

$$= \underbrace{3A_{1g} + 2B_{1g} + B_{2g}}_{even} + \underbrace{B_{1u} + 2B_{2u} + 2B_{3u} + A_{1u}}_{odd}$$

(b) $3A_{1g}$

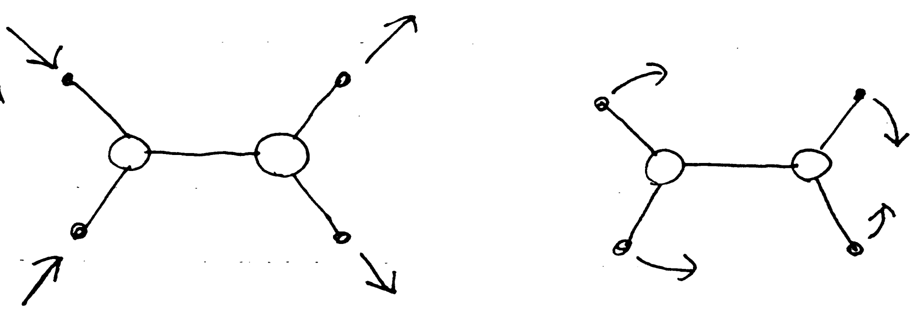


A_{1u}

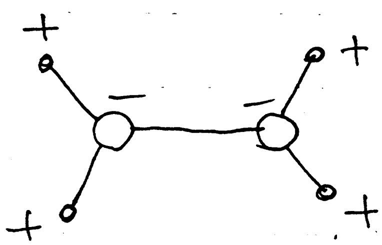


(up (+) & down (-) thru plane of paper.)

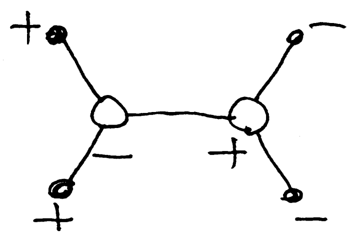
$2B_{3u}$



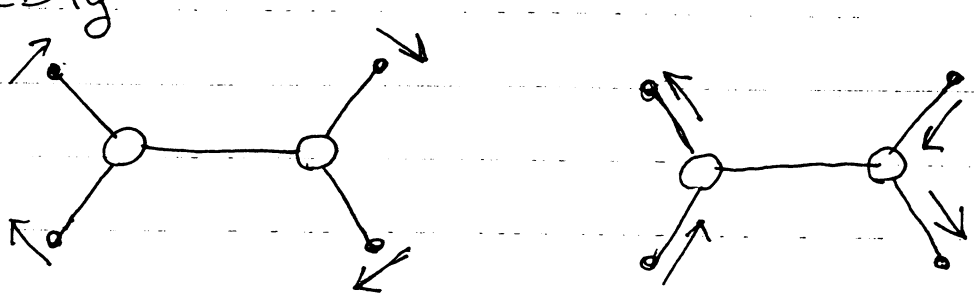
B_{1u}



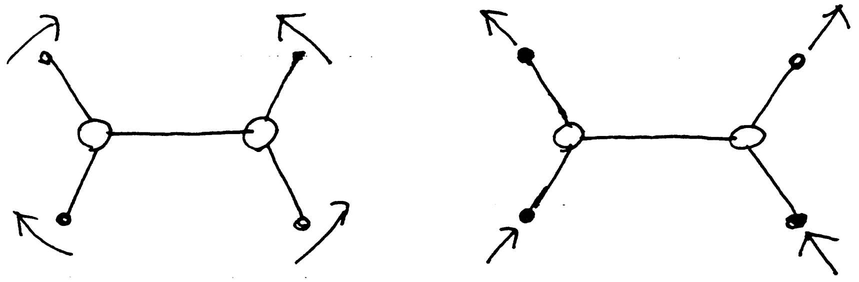
B_{2g}



$2B_{1g}$



$2B_{2u}$



(c)

For infrared active vibration modes, they must have symmetry B_{1u} or B_{2u} or B_{3u}.

∴ The vibration modes in $B_{1u} + 2B_{2u} + 2B_{3u}$ are infrared active.

Since B_{1u}, B_{2u}, B_{3u} transforms like z, y, z respectively,

B_{1u} vibration mode is active only to z polarized light.

$2B_{2u}$ " " " " " y " "

$2B_{3u}$ " " " " " x " "

For Raman active modes, they must transform like x^2, y^2, z^2, xz, yz, zx. That is, they must have symmetry A_{1g} or B_{1g} or B_{2g} or B_{3g}.

∴ all the even modes : $3A_{1g} + 2B_{1g} + B_{2g}$ are Raman active.

Since $x^2+y^2+z^2$ transforms as A_{1g}, the three A_{1g} modes will have diagonal components $(\vec{E}_i \parallel \vec{E}_s)$.

B_{1g}, B_{2g} transform like xy and yz, ∴ The two B_{1g} modes have off-diagonal components $(\vec{E}_i \perp \vec{E}_s)$ and $\vec{E}_i$, $\vec{E}_s$ are all in the x-y plane.

The B_{2g} mode has off-diagonal component $(\vec{E}_i \perp \vec{E}_s)$ and one of them ($\vec{E}_i$ or $\vec{E}_s$) must be perpendicular to the plane.

A_{1u} is silent mode.

2(a) Point Groups for CO_2 and N_2O:

CO_2 : $D_{\infty h}$

N_2O : $C_{\infty v}$

(b) For CO_2:

$D_{\infty h}$	E	$2C_\phi$	C_2'	i	$2iC_\phi$	iC_2'
$\chi^{a.s.}$	3	3	1	1	1	3

$$\therefore \chi^{a.s.} = 2A_{1g} + A_{2u}$$

$$\begin{aligned} \chi_{m.v.} &= \chi^{a.s.} \otimes \chi_{vector} - \chi_{translation} - \chi_{rotation} \\ &= \underbrace{(2A_{1g} + A_{1u}) \otimes (A_{2u} + E_{1u})}_{2A_{2u} + 2E_{1u} + A_{1g} + E_{1g}} - (A_{2u} + E_{1u}) - (E_{1g}) \\ &= \underline{A_{1g} + A_{2u} + E_{1u}} \ // \end{aligned}$$

For N_2O:

$C_{\infty v}$	E	$2C_\phi$	σ_v
$\chi^{a.s.}$	3	3	3

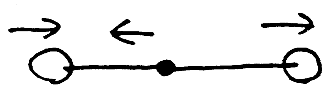
$\chi^{a.s} = 3A_1$

$$\begin{aligned} \chi_{m.v.} &= \chi^{a.s.} \otimes \chi_{vector} - \chi_{trans} - \chi_{rot} \\ &= 3A_1 \otimes (A_1 + E_1) - (A_1 + E_1) - E_1 = \underline{2A_1 + E_1} \ // \end{aligned}$$

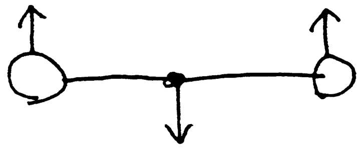
(c) CO_2

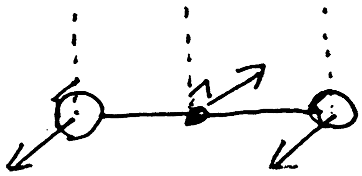
A_{1g}

A_{1u}



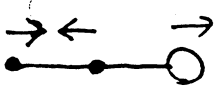
E_{1u}



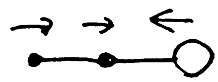


N_2O

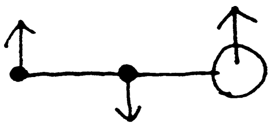
A_{1g} 1

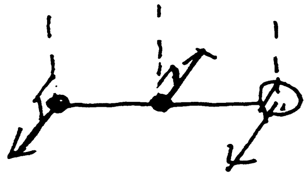


A_{1g} 2



E_1





(d) IR active modes

CO_2: $\Gamma_{IR} = \Gamma_{vector} \otimes \Gamma_{A_{1g}} = A_{2u} + E_{1u}$

N_2O: $\Gamma_{IR} = \Gamma_{vector} \otimes \Gamma_{A_1} = A_1 + E_1$

$\Rightarrow$ In IR Spectra, there are 2 modes (peaks) for CO_2 3 modes (peaks) for N_2O

Raman Active modes

CO_2: $\Gamma_R = (\Gamma_{vector} \otimes \Gamma_{vector}) \otimes \Gamma_{A_{1g}}$

$= 2A_{1g} + A_{2g} + 2E_{1g} + E_{2g}$

compared with $\chi_{m.v.}$, only A_{1g} is Raman active.

N_2O $\Gamma_R = (\Gamma_{vector} \otimes \Gamma_{vector}) \otimes \Gamma_{A_1}$
$= 2A_1 + A_2 + 2E_1 + E_2$

Compared with $\chi_{m.v.}$ all the modes are Raman active $(2A_1 + E_1)$

$\Rightarrow$ difference in Raman spectra:
Three modes for N_2O, while only one mode for CO_2.

(f) Since N_2O has permanent dipole moment while CO_2 doesn't, the rotational modes for N_2O molecule can be excited by infrared or Raman spectroscopy.

(e) For a linear molecule, the equation for the rotation energy spectra can be expressed as

$$E_j = \hbar^2 j(j+1)/2I$$

where I is principal moment of inertia for the molecule.

This equation suggests that CO_2 and N_2O molecules have different spacings in the rotation energy spectra.

3.

(a)

	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}^3$	$12S_{10}$	$20S_3$	15σ
$\chi^{a.s}_{(X)}$	1	1	1	1	1	1	1	1	1	1
$\chi^{a.s}_{(12H)}$	12	2	2	0	0	0	0	0	0	4
$\chi^{a.s}_{(tot)}$	13	3	3	1	1	1	1	1	1	5

Use the decomposition rule,

$$\chi^{a.s}_{(tot)} = 2A_g + F_{1u} + F_{2u} + H_g$$

(b) $\chi^{a.s} \otimes \chi_{vector} = (2A_g + F_{1u} + F_{2u} + H_g) \otimes F_{1u}$

$$= 2F_{1u} + F_{1u} \otimes F_{1u} + F_{1u} \otimes F_{2u} + F_{1u} \otimes H_g$$

	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}^3$	$12S_{10}$	$20S_3$	15σ
$F_{1u} \otimes F_{1u}$	9	$\tau+1$	$2-\tau$	0	1	9	$\tau+1$	$2-\tau$	0	1
$F_{1u} \otimes F_{2u}$	9	-1	-1	0	1	9	-1	-1	0	1
$F_{1u} \otimes F_g$	15	0	0	0	-1	-15	0	0	0	1

$\therefore$ $F_{1u} \otimes F_{1u} = A_{1g} + F_{1g} + H_g$

$F_{1u} \otimes F_{2u} = H_g + G_g$

$F_{1u} \otimes H_g = F_{1u} + F_{2u} + G_u + H_u$

$$\chi_{vibration} = 2F_{1u} + A_{1g} + F_{1g} + 2H_g + G_g + F_{1u} + F_{2u} + G_u + H_u - F_{1g} - F_{1u}$$

$$= A_{1g} + G_g + 2H_g + 2F_{1u} + F_{2u} + G_u + H_u$$

Among these normal modes,

IR active : $2F_{1u}$

Raman active : $A_{1g} + 2H_g$

(c) For the three normal modes in each F_{1u} symmetry, the one that transforms like the x partner can only be excited by the x-polarized light. Similarly, the ones that correspond to the y, z partners can be excited by y-polarized and z-polarized light respectively.

For Raman active modes : A_{1g} and $2H_g$

From the character table we see that A_{1g} has only diagonal elements ($\vec{E}_i \parallel \vec{E}_s$) while H_g can have both diagonal ($\vec{E}_i \parallel \vec{E}_s$) and off-diagonal elements.

4.

(a)
$$P_i P_j = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 5 & 2 & 4 & 1 & 3 \end{pmatrix}$$

$$P_j P_i = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 4 & 2 & 5 & 3 & 1 \end{pmatrix}$$

To check whether the results are consistent with the character table, note that both $P_i P_j$ and $P_j P_i$ are in the class $(4,1)$, while P_i is in class $(2,1^3)$ and P_j is in class $(2^2,1)$

Now, look at the 1 dimensional representations Γ_1^s and Γ_1^a.

the characters are also the representations.

We check that :

$$\Gamma_1^s(P_i)\,\Gamma_1^s(P_j) = 1 \cdot 1 = 1 = \Gamma_1^s(P_i P_j)$$
$$\Gamma_1^a(P_i)\,\Gamma_1^a(P_j) = -1 \cdot 1 = -1 = \Gamma_1^a(P_i P_j)$$

Similarly we check that

$$\Gamma_1^s(P_j)\,\Gamma_1^s(P_i) = \Gamma_1^s(P_j P_i)$$
$$\Gamma_1^a(P_j)\,\Gamma_1^a(P_i) = \Gamma_1^a(P_j P_i)$$

$\therefore$ The results are consistent !!

4(b) Using eq. (10.9)

$$\frac{q!}{1^{\lambda_1}\lambda_1! \cdot 2^{\lambda_2}\lambda_2! \cdots r^{\lambda_r}\lambda_r!}$$

we get for the class $(2, 1^3)$, there are

$$\frac{5!}{1^3 3! \cdot 2^1 1!} = 10$$

elements, while for the class $(3, 2)$, there are

$$\frac{5!}{2^1 \cdot 1! \cdot 3^1 \cdot 1!} = 20$$

elements.

(c) If we consider ${}^5p$ state as an hole in the p orbit, the spin of the allowed state must be $S = s = 1/2$ and the total angular momentum is $L = l = 1$, because there is only one hole.
$\therefore$ The allowed state is ${}^2P$, which is exactly same as the result in Table 10.6.

(d) The irreducible representation for $(\uparrow\uparrow\downarrow\downarrow\downarrow)$ is $\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2)$
By decomposing (see part (f))

$$\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2) = \Gamma_1^S + \Gamma_4 + \Gamma_5$$

According to Table 10.6, Γ_1^S corresponds to $S = 5/2$, Γ_4 corresponds to $S = 3/2$ and Γ_5 corresponds to $S = 1/2$.

(e) Hund's rule

$\Rightarrow$ d^5

	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
m_l :	-2	-1	0	1	2

$\Rightarrow$ Total angular momentum $L = 0$

$\Rightarrow$ Total spin $S = 5/2$

$\Rightarrow$ ${}^6S$ state

From Table 10.6, we find

$$\chi_{L=0} = \Gamma_1^a + \Gamma_4 + \Gamma_{5'} + \Gamma_6$$

$$\chi_{S=5/2} = \Gamma_1^S$$

We can check whether this is an allowed state by taking the direct product.

$$\chi_{L=0} \otimes \chi_{S=5/2} = (\Gamma_1^a + \Gamma_4 + \Gamma_{5'} + \Gamma_6) \otimes \Gamma_1^S$$

$$= \Gamma_1^a + \Gamma_4 + \Gamma_{5'} + \Gamma_6$$

We can see that this is an allowed state since the direct product contains Γ_1^a.

To make life easier, we first work out the irreducible representations contained in each $\chi_{perm.}$

The results are:

$$\chi_{(perm)}(\psi_1\psi_1\psi_1\psi_1\psi_1) = \Gamma_1^s$$

$$\chi_{perm.}(\psi_1\psi_1\psi_1\psi_1\psi_2) = \Gamma_1^s + \Gamma_4$$

$$\chi_{perm.}(\psi_1\psi_1\psi_1\psi_2\psi_2) = \Gamma_1^s + \Gamma_4 + \Gamma_5$$

$$\chi_{perm.}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$$

$$\chi_{perm.}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_5' + \Gamma_6$$

$$\chi_{perm.}(\psi_1\psi_1\psi_2\psi_3\psi_4) = \Gamma_1^s + 3\Gamma_4 + \Gamma_4' + 3\Gamma_5 + 2\Gamma_5' + 3\Gamma_6$$

$$\chi_{perm.}(\psi_1\psi_2\psi_3\psi_4\psi_5) = \Gamma_1^s + \Gamma_1^a + 4\Gamma_4 + 4\Gamma_4' + 5\Gamma_5 + 5\Gamma_5' + 6\Gamma_6$$

(f) The charocters for the equivalence transformation for a (3.2) state have been listed in the extended character table,

	(1^5)	$10(2,1^3)$	$15(2^2,1)$	$20(3,1^2)$	.....
$\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2)$	10	4	2	1	.....

To get these, one observes that there are $\binom{5}{2} = 10$ possible ways to form a (3, 2) state, therefore $(\psi_1\psi_1\psi_1\psi_2\psi_2)$ transforms as a 10-dimensional reducible representation of the group P(5) with 10 partners for this state. So we get $\chi_{perm}(1^5) = 10$.

Each of the permutation operations $[10(2,1^3)]$ leaves 4 partners invariant,

10 partners for (3.2) state

↓

(1 2)(3 4 5)
(1 3)(2 4 5)
(1 4)(2 3 5)
(1 5)(2 3 4)
(2 3)(1 4 5)
(2 4)(1 3 5)
(2 5)(1 3 4)
(3 4)(1 2 5)
(3 5)(1 2 4)
(4 5)(1 2 3)

one of $[10(2,1^3)]$ operations

↓

$\xrightarrow{\begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 2 & 1 & 3 & 4 & 5 \end{pmatrix}}$

(1 2)(3 4 5)
(3 4)(1 2 5)
(3 5)(1 2 4)
(4 5)(1 2 3)

are the 4 invariant partners

therefore $\chi_{perm}(2,1^3) = 4$. Similarly,
$\chi_{perm}(2^2,1) = 2$, $\chi_{perm}(3,1^2) = \chi_{perm}(3,2) = 1$
$\chi_{perm}(4,1) = \chi_{perm}(5) = 0$

Clearly. $\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2) \Rightarrow \Gamma_1^S + \Gamma_4 + \Gamma_5$

(f) For p states we have p^+, p^0, p^-, and for d states there are $d^2, d^1, d^0, d^{-1}, d^{-2}$ states. The character of p^3d^2 depends on the which three p states and which two d states are occupied.

(i) $(\psi_1\psi_1\psi_1\psi_2\psi_2)$ type:

$p^+p^+p^+d^2d^2$, $p^0p^0p^0d^2d^2$, $p^-p^-p^-d^2d^2$,
$p^+p^+p^+d^1d^1$, $p^0p^0p^0d^1d^1$, $p^-p^-p^-d^1d^1$

$\vdots \qquad \vdots \qquad \vdots$

$p^+p^+p^+d^{-2}d^{-2}$, $p^0p^0p^0d^{-2}d^{-2}$, $p^-p^-p^-d^{-2}d^{-2}$

totally 15 configurations.

For this type of configuration,

$$\chi = \chi_{perm.}(\psi_1\psi_1\psi_1\psi_2\psi_2) = \Gamma_1^S + \Gamma_4 + \Gamma_5$$

(ii) $(\psi_1\psi_1\psi_1\psi_2\psi_3)$ type:

For this type, three electrons are in the same p state while the 2 d electrons are in different d orbitals. For example, $p^+p^+p^+d^2d^1$, $p^+p^+p^+d^2d^0, \cdots$

$\therefore$ There are $3 \times C_2^5 = 30$ configurations in this type of configuration.

$$\chi = \chi_{perm.}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6$$

(iii) $(\psi_1\psi_1\psi_2\psi_2\psi_3)$ type:

For this case, 2 electrons are in the same p state and one in a different p state. The two d electrons are in the same d state For example, $p^+p^+p^-d^2d^2, \cdots$

There are $C_1^3 \times C_1^2 \times C_1^5 = 30$ configurations.

$$\chi = \chi_{perm.}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_5' + \Gamma_6$$

(iv) $(\psi_1\psi_1\psi_2\psi_3\psi_4)$ type:

For this type, we can have

(1) all p electrons are in different states and d electrons are in the same state.

(2) two p electrons are in the same state, the rest three electrons are all in different states.

The number of configurations is $1 \times C_1^5 + C_1^3 \times C_1^2 \times C_4^5 = 35$

$$\chi = \chi_{perm.}(\psi_1\psi_1\psi_2\psi_3\psi_4) = \Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_5' + \Gamma_6$$

(V) $(\psi_1\psi_2\psi_3\psi_4\psi_5)$ type:

all electrons are in different p or d states.

For example, $p^+p^-p^\circ d^1 d^2$, ...

The number of configurations is $1 \times C_2^5 = 10$.

$$\therefore \chi = \chi_{perm.}(\psi_1\psi_2\psi_3\psi_4\psi_5)$$

$$= \Gamma_1^s + \Gamma_1^a + 4\Gamma_4 + 4\Gamma_4' + 5\Gamma_5 + 5\Gamma_5' + 6\Gamma_6$$

Appedix.

Configuration	State	Irreducible Representation	Allowed State
(↑↑↑↓↓)	$S = 1/2$	Γ_5	
(↑↑↑↑↓)	$S = 3/2$	Γ_4	
(↑↑↑↑↑)	$S = 5/2$	Γ_1^s	
s^5	$L = 0$	Γ_1^s	–
$1s^4 2s$	$L = 0$	$\Gamma_1^s + \Gamma_4$	–
$1s^2 2s^2 3s$	$L = 0$	$\Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$	^2S
p^5	$L = 0$	Γ_6	–
p^5	$L = 1$	$\Gamma_1^s + \Gamma_4 + \Gamma_5 + \Gamma_{5'}$	^2P
p^5	$L = 2$	$\Gamma_4 + \Gamma_5 + \Gamma_6$	–
p^5	$L = 3$	$\Gamma_1^s + \Gamma_4 + \Gamma_5$	–
p^5	$L = 4$	Γ_4	–
p^5	$L = 5$	Γ_1^s	–
d^5	$L = 0$	$\Gamma_1^a + \Gamma_4 + \Gamma_{5'} + \Gamma_6$	^2S, ^6S
d^5	$L = 1$	$\Gamma_1^s + 2\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + \Gamma_{5'} + 2\Gamma_6$	^2P, ^4P
d^5	$L = 2$	$2\Gamma_1^s + 3\Gamma_4 + \Gamma_{4'} + 4\Gamma_5 + 3\Gamma_{5'} + 2\Gamma_6$	^2D, ^2D, ^2D, ^4D
d^5	$L = 3$	$\Gamma_1^s + 4\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 4\Gamma_6$	^2F, ^2F, ^4F
d^5	$L = 4$	$2\Gamma_1^s + 4\Gamma_4 + \Gamma_{4'} + 4\Gamma_5 + 2\Gamma_{5'} + 2\Gamma_6$	^2G, ^2G, ^4G
d^5	$L = 5$	$\Gamma_1^s + 3\Gamma_4 + 3\Gamma_5 + \Gamma_{5'} + 3\Gamma_6$	^2H
d^5	$L = 6$	$2\Gamma_1^s + 3\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$	^2I
d^5	$L = 7$	$\Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$	–
d^5	$L = 8$	$\Gamma_1^s + \Gamma_4 + \Gamma_5$	–
d^5	$L = 9$	Γ_4	–
d^5	$L = 10$	Γ_1^s	–

S_5	Irreducible representations
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_1\psi_1)$	$\Rightarrow \Gamma_1^s$
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_1\psi_2)$	$\Rightarrow \Gamma_1^s + \Gamma_4$
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_2\psi_2)$	$\Rightarrow \Gamma_1^s + \Gamma_4 + \Gamma_5$
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_2\psi_3)$	$\Rightarrow \Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_2\psi_2\psi_3)$	$\Rightarrow \Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_2\psi_3\psi_4)$	$\Rightarrow \Gamma_1^s + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6$
$\chi_{\text{perm.}}(\psi_1\psi_2\psi_3\psi_4\psi_5)$	$\Rightarrow \Gamma_1^s + \Gamma_1^a + 4\Gamma_4 + 4\Gamma_{4'} + 5\Gamma_5 + 5\Gamma_{5'} + 6\Gamma_6$

(g) For p^3d^2, the total orbital angular momentum can be $L = 1+1+1+2+2 = 7$ to $L = 0$

(1). $L=7$, the configuration can only be $p^+p^+p^+d^2d^2$ to make $M_\ell = 7$.

$$\therefore \chi_{L=7} = \chi_{perm.}(\psi_1\psi_1\psi_1\psi_2\psi_2)$$
$$= \Gamma_1^S + \Gamma_4 + \Gamma_5$$

(2) $L=6$; to make $M_\ell = 6$, we can use $p^+p^+p^+d^2d^1$, $p^0p^+p^+d^2d^2$ only.

$$\therefore \chi_{M_\ell=6} = \chi_{perm.}(\psi_1\psi_1\psi_2\psi_2\psi_3)$$
$$= \Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_5' + \Gamma_6$$

We have to substract the representations that go to $L=7$.

$$\therefore \chi_{L=6} = \Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_5' + \Gamma_6 - (\Gamma_1^S + \Gamma_4 + \Gamma_5)$$
$$= \Gamma_4 + \Gamma_5 + \Gamma_5' + \Gamma_6$$

(3) $L=5$, the $M_\ell = 5$ state can be constructed from $p^-p^+p^+d^2d^2$, $p^0p^0p^+d^2d^2$, $p^0p^+p^+d^1d^2$. $p^+p^+p^+d^0d^2$

$$\therefore \chi_{M_\ell=5} = 2\chi_{perm.}(\psi_1\psi_1\psi_2\psi_2\psi_3) + \chi_{perm.}(\psi_1\psi_1\psi_2\psi_3\psi_4) + \chi_{perm.}(\psi_1\psi_1\psi_1\psi_2\psi_3$$
$$= 2(\Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_5' + \Gamma_6) + (\Gamma_1^S + 3\Gamma_4 + \Gamma_4' + 3\Gamma_5 + 2\Gamma_5' + 3\Gamma_6)$$
$$+ (\Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6)$$
$$= 4\Gamma_1^S + 9\Gamma_4 + \Gamma_4' + 8\Gamma_5 + 4\Gamma_5' + 6\Gamma_6$$

$$\chi_{L=5} = \chi_{M_\ell=5} - \chi_{L=7} - \chi_{L=6}$$
$$= 3\Gamma_1^S + 7\Gamma_4 + \Gamma_4' + 6\Gamma_5 + 3\Gamma_5' + 5\Gamma_6$$

We stop here and check if there are allowed states for $L=7$ or 6 or 5 —

From Table 10.6, $\chi_{S=1/2} = \Gamma_5$, $\chi_{S=3/2} = \Gamma_4$, $\chi_{S=5/2} = \Gamma_1^s$.

For $L=7$,

$$\chi_{L=7} \otimes \chi_{S=1/2} = (\Gamma_1^s + \Gamma_4 + \Gamma_5) \otimes \Gamma_5$$

$$= \Gamma_5 + (\Gamma_4' + \Gamma_5 + \Gamma_5' + \Gamma_6) + (\Gamma_1^s + \Gamma_4 + \Gamma_4' + \Gamma_5 + \Gamma_5' + \Gamma_6)$$

$$\chi_{L=7} \otimes \chi_{S=3/2} = (\Gamma_1^s + \Gamma_4 + \Gamma_5) \otimes \Gamma_4$$

$$= \Gamma_4 + (\Gamma_1^s + \Gamma_4 + \Gamma_5 + \Gamma_6) + (\Gamma_4' + \Gamma_5 + \Gamma_5' + \Gamma_6)$$

$$\chi_{L=7} \otimes \chi_{S=5/2} = (\Gamma_1^s + \Gamma_4 + \Gamma_5) \otimes \Gamma_1^s$$

$$= (\Gamma_1^s + \Gamma_4 + \Gamma_5)$$

$\therefore$ There is no allowed states for $L=7$ since no Γ_1^a appears in the representations.

For $L=6$,

$$\chi_{L=6} \otimes \chi_{S=1/2} = (\Gamma_4 + \Gamma_5 + \Gamma_5' + \Gamma_6) \otimes \Gamma_5$$

$$\chi_{L=6} \otimes \chi_{S=3/2} = (\Gamma_4 + \Gamma_5 + \Gamma_5' + \Gamma_6) \otimes \Gamma_4$$

$$\chi_{L=6} \otimes \chi_{S=5/2} = (\Gamma_4 + \Gamma_5 + \Gamma_5' + \Gamma_6) \otimes \Gamma_1^s$$

We only have to look at $\Gamma_5' \otimes \Gamma_5$, $\Gamma_5 \otimes \Gamma_6$, $\Gamma_5' \otimes \Gamma_4$, $\Gamma_6 \otimes \Gamma_4$ since the others are already known.

$$\Gamma_5' \otimes \Gamma_5 = \Gamma_1^a + \Gamma_4 + \Gamma_4' + \Gamma_5 + \Gamma_5' + \Gamma_6$$

$$\Gamma_5 \otimes \Gamma_6 = \Gamma_4 + \Gamma_4' + \Gamma_5 + \Gamma_5' + 2\Gamma_6$$

$$\Gamma_5' \otimes \Gamma_4 = \Gamma_4' + \Gamma_5 + \Gamma_5' + \Gamma_6$$

$$\Gamma_6 \otimes \Gamma_4 = \Gamma_4 + \Gamma_4' + \Gamma_5 + \Gamma_5' + \Gamma_6$$

So, we see Γ_1^a is contained in $\chi_{L=6} \otimes \chi_{S=1/2}$!

$\therefore$ The Pauli allowed state with the largest L is $L=6$, $S=1/2$, that is, ^2I

(h)

Let's determine the spin states first.

Obviously $(\uparrow\uparrow\uparrow\uparrow\uparrow) \rightarrow \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_1) = \Gamma_1^s$

$S=3/2$ $(\uparrow\uparrow\uparrow\uparrow\downarrow) \rightarrow \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_2)$

$$a_{\Gamma_1^s} = \frac{1}{120}(5+10\times3+15+20\times2+30) = 1.$$

$$a_{\Gamma_4} = \frac{1}{120}(20+60+40) = 1$$

$$\Rightarrow \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_2) = \underset{\substack{M_s=3/2 \\ \text{for } S=5/2}}{\Gamma_1^s} + \underset{S=3/2}{\Gamma_4} \qquad (\uparrow\uparrow\uparrow\uparrow\downarrow) = \Gamma_4$$

$S=1/2$ $(\uparrow\uparrow\uparrow\downarrow\downarrow) \rightarrow \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2)$

$$a_{\Gamma_1^s} = \frac{1}{120}(10+40+30+20+20) = 1$$

$$a_{\Gamma_1^a} = \frac{1}{120}(10-40+30+20-20) = 0$$

$$a_{\Gamma_4} = \frac{1}{120}(40 + 80 + 20 + (-20)) = 1.$$

$$a_{\Gamma_5} = \frac{1}{120}(50 + 40 + 30 - 20 + 20) = 1.$$

$$\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2) = \Gamma_1^S + \Gamma_4 + \Gamma_5$$

Γ_1^S: $M_S = 1/2$ for $S = 5/2$; Γ_4: $M_S = 1/2$ for $S = 3/2$; Γ_5: $S = 1/2$.

Therefore, I get

$$(\uparrow\uparrow\uparrow\uparrow\uparrow) = \Gamma_1^S \qquad (S = 5/2)$$
$$(\uparrow\uparrow\uparrow\uparrow\downarrow) = \Gamma_4 \qquad (S = 3/2)$$
$$(\uparrow\uparrow\uparrow\downarrow\downarrow) = \Gamma_5 \qquad (S = 1/2)$$

For orbital states, consider

$M_L = 10$ $\quad d^{2+}d^{2+}d^{2+}d^{2+}d^{2+} \Rightarrow L = 10$

$$\Rightarrow \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_1) = \Gamma_1^S$$

$\Gamma_1^S \otimes (\Gamma_1^S + \Gamma_4 + \Gamma_5) \Rightarrow$ no Γ_1^a contained $\Rightarrow$ not allowed.

$L = 9$ $\quad d^{2+}d^{2+}d^{2+}d^{2+}d^{+} \Rightarrow \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_2) = \Gamma_4 + \underset{L=10}{\Gamma_1^S}$

$\therefore \Gamma_4 \otimes (\Gamma_1^S + \Gamma_4 + \Gamma_5) \Rightarrow$ no $\Gamma_1^a \Rightarrow$ not allowed.

$L = 8$ $\quad d^{2+}d^{2+}d^{2+}d^{2+}d^{0}$ and $d^{2+}d^{2+}d^{2+}d^{+}d^{+}$

$\Rightarrow \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_2)$ and $\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2)$

$$\Rightarrow \left(\cancel{\Gamma_4}^{L=9} + \cancel{\Gamma_1^s}^{L=10}\right) + \left(\Gamma_5 + \Gamma_4 + \Gamma_1^s\right)$$

$$\left(\Gamma_5 + \Gamma_4 + \Gamma_1^s\right) \otimes \left(\Gamma_1^s + \Gamma_4 + \Gamma_5\right) \Rightarrow \text{no } \Gamma_1^a \text{ contained}$$

$\Rightarrow$ not allowed.

$L=7$ $\quad d^{2+}d^{2+}d^{2+}d^{+}d^{0} \qquad d^{2+}d^{2+}d^{+}d^{+}d^{+}$

$\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) \qquad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2)$

$d^{2+}d^{2+}d^{2+}d^{2+}d^{-} \rightarrow \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_2) = \Gamma_1^s + \Gamma_4$

$$\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6$$

$$a_{\Gamma_1^s} = \frac{1}{120}(20 + 60 + 40) = 1$$

$$a_{\Gamma_1^a} = \frac{1}{120}(20 - 60 + 40) = 0$$

$$a_{\Gamma_4} = \frac{1}{120}(80 + 120 + 40) = 2.$$

$$a_{\Gamma_4'} = \frac{1}{120}(80 - 120 + 40) = 0$$

$$a_{\Gamma_5} = \frac{1}{120}(100 + 60 - 40) = 1$$

$$a_{\Gamma_5'} = \frac{1}{120}(100 - 60 - 40) = 0$$

$$a_{\Gamma_6} = \frac{1}{120}(120) = 1.$$

$$\cancel{\Rightarrow L=7 = \left(\cancel{\Gamma_1^s}^{L=10} + \cancel{2}^{L=9}\Gamma_4 + \Gamma_5 + \Gamma_6\right) + \left(\cancel{\Gamma_1^s} + \cancel{\Gamma_4}^{L=8} + \cancel{\Gamma_5}\right)}$$

$$\cancel{\left(\Gamma_4 + \Gamma_5 + \Gamma_6\right) \otimes \left(\Gamma_1^s + \Gamma_4 + \Gamma_5\right)}$$

$\cancel{\Rightarrow \text{no } \Gamma_1^a \Rightarrow \text{not allowed.}}$

$$L=7 \quad (\overset{L=10}{\cancel{\Gamma_1^s}} + \overset{L=9}{\cancel{2}}\Gamma_4 + \Gamma_5 + \Gamma_6) + (\overset{L=8}{\cancel{\Gamma_1^s} + \cancel{\Gamma_4} + \cancel{\Gamma_5}})$$

$$+ \Gamma_1^s + \Gamma_4$$

$$\Rightarrow \Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$$

$$(\Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6) \otimes (\Gamma_1^s + \Gamma_4 + \Gamma_5)$$

$\Rightarrow$ no Γ_1^a contained $\Rightarrow$ no allowed state.

$L=6$

$d^{2+}d^{2+}d^{2+}d^{0}d^{0}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2) = \Gamma_1^s + \Gamma_4 + \Gamma_5$

$d^{2+}d^{2+}d^{+}d^{+}d^{0}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$d^{2+}d^{+}d^{+}d^{+}d^{+}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_2) = \Gamma_1^s + \Gamma_4$

$d^{2+}d^{2+}d^{2+}d^{+}d^{-}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$

$d^{2+}d^{2+}d^{2+}d^{2+}d^{2-}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_2) = \Gamma_1^s + \Gamma_4$

$L=8$

$$\Rightarrow 2\,\cancel{3}\cancel{4}\underset{L=10}{\cancel{5}}\,\Gamma_1^s + 3\,\cancel{5}\cancel{6}\underset{L=9}{\cancel{7}}\,\Gamma_4 + 2\,\cancel{3}\cancel{4}\,\Gamma_5 + \Gamma_{5'} + \cancel{2}\,\Gamma_6$$

$$\Rightarrow (2\Gamma_1^s + 3\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6) \otimes (\Gamma_1^s + \Gamma_4 + \Gamma_5)$$

contains

$$\Gamma_{5'} \otimes \Gamma_5 = \Gamma_1^a + \Gamma_4 + \Gamma_4' + \Gamma_5 + \Gamma_{5'} + \Gamma_6$$

$\Rightarrow$ There is one allowed state. ^2I

$L=5$ $\quad d^{2+}d^{2+}d^{+}d^{0}d^{0}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$d^{2+}d^{+}d^{+}d^{+}d^{0}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6$

$d^{+}d^{+}d^{+}d^{+}d^{+}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_1) = \Gamma_1^S$

$d^{2+}d^{2+}d^{2+}d^{-}d^{0}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6$

$d^{2+}d^{2+}d^{2+}d^{+}d^{2-}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6$

$d^{2+}d^{2+}d^{+}d^{+}d^{-}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$$\Rightarrow 2\chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) + 3\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) + \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_1)$$

$$= 2(\Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6) + 3(\Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6) + \Gamma_1^S$$

$$= 6\Gamma_1^S + 10\Gamma_4 + 7\Gamma_5 + 2\Gamma_{5'} + 5\Gamma_6$$

$L=10 \sim L=6 \; = 5\Gamma_1^S + 7\Gamma_4 + 4\Gamma_5 + \Gamma_{5'} + 2\Gamma_6$

$L=5 \Rightarrow (\Gamma_1^S + 3\Gamma_4 + 3\Gamma_5 + \Gamma_{5'} + 3\Gamma_6) \otimes (\Gamma_1^S + \Gamma_4 + \Gamma_5)$

Contains one $\Gamma_{5'} \otimes \Gamma_5$

$\Rightarrow$ allowed state $\quad {}^2H$

$L=4$ $\quad d^{2+}d^{2+}d^{0}d^{0}d^{0}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2) = \Gamma_1^S + \Gamma_4 + \Gamma_5$

$d^{2+}d^{2+}d^{+}d^{-}d^{0}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_3\psi_4) = \Gamma_1^S + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6$

$d^{2+}d^{2+}d^{+}d^{+}d^{2-}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$d^{2+}d^{2+}d^{2+}d^{2-}d^{0}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6$

$d^{2+}d^{2+}d^{2+}d^{-}d^{-}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2) = \Gamma_1^S + \Gamma_4 + \Gamma_5$

$d^{2+}d^{+}d^{+}d^{0}d^{0}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$d^{2+}d^{+}d^{+}d^{+}d^{-}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6$

$d^{+}d^{+}d^{+}d^{+}d^{0}$ $\quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_2) = \Gamma_1^S + \Gamma_4$

$$\chi_{perm}(\psi_1\psi_1\psi_2\psi_3\psi_4) = \Gamma_1^s + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6$$

$$a_{\Gamma_1^s} = \frac{1}{120}(60+60) = 1$$

$$a_{\Gamma_4} = \frac{1}{120}(240+120) = 3$$

$$a_{\Gamma_{4'}} = \frac{1}{120}(240-120) = 1$$

$$a_{\Gamma_5} = \frac{1}{120}(300+60) = 3$$

$$a_{\Gamma_{5'}} = \frac{1}{120}(300-60) = 2$$

$$a_{\Gamma_6} = \frac{1}{120}(360) = 3$$

$$\Rightarrow 8\Gamma_1^s + 14\Gamma_4 + \Gamma_{4'} + 11\Gamma_5 + 4\Gamma_{5'} + 5\Gamma_6$$

$$-(6\Gamma_1^s + 10\Gamma_4 + 7\Gamma_5 + 2\Gamma_{5'} + 5\Gamma_6)$$

$$= 2\Gamma_1^s + 4\Gamma_4 + \Gamma_{4'} + 4\Gamma_5 + 2\Gamma_{5'}$$

$$(2\Gamma_1^s + 4\Gamma_4 + \Gamma_{4'} + 4\Gamma_5 + 2\Gamma_{5'}) \otimes (\Gamma_1^s + \Gamma_4 + \Gamma_5)$$

Contains one $\Gamma_{4'} \otimes \Gamma_4 = \Gamma_1^a + \Gamma_{4'} + \Gamma_{5'} + \Gamma_6$

and two $\Gamma_{5'} \otimes \Gamma_5 = \Gamma_1^a + \Gamma_4 + \Gamma_{4'} + \Gamma_5 + \Gamma_{5'} + \Gamma_6$

$\Rightarrow$ There are three allowed states. ^4G, ^2G, ^2G

$L=3$

$d^{2+}d^{2+}d^{+}d^{-}d^{2-}$ $\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$

$d^{2+}d^{2+}d^{+}d^{0}d^{2-}$ $\chi_{perm}(\psi_1\psi_1\psi_2\psi_3\psi_4) = \Gamma_1^s + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6$

$d^{2+}d^{2+}d^{+}d^{-}d^{-}$ $\chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$d^{2+}d^{2+}d^{0}d^{0}d^{-}$ $\chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$d^{2+}d^{+}d^{+}d^{+}d^{2-}$ $\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$

$d^{2+}d^{+}d^{+}d^{0}d^{-}$ $\chi_{perm}(\psi_1\psi_1\psi_2\psi_3\psi_4) = \Gamma_1^s + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6$

$d^{2+}d^{+}d^{0}d^{0}d^{0}$ $\chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$

$d^{+}d^{+}d^{+}d^{+}d^{-}$ $\chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_2) = \Gamma_1^s + \Gamma_4$

$d^+ d^+ d^+ d^0 d^0 \quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2) = \Gamma_1^s + \Gamma_4 + \Gamma_5$

$$\Rightarrow 9\Gamma_1^s + 18\Gamma_4 + 2\Gamma_{4'} + 14\Gamma_5 + 6\Gamma_{5'} + 11\Gamma_6$$
$$- (8\Gamma_1^s + 14\Gamma_4 + \Gamma_{4'} + 11\Gamma_5 + 4\Gamma_{5'} + 5\Gamma_6)$$
$$= \Gamma_1^s + 4\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 6\Gamma_6$$

$$(\Gamma_1^s + 4\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 6\Gamma_6) \otimes (\Gamma_1^s + \Gamma_4 + \Gamma_5)$$

Contains one $\Gamma_{4'} \otimes \Gamma_4 = \Gamma_1^a + \Gamma_{4'} + \Gamma_{5'} + \Gamma_6$

two $\Gamma_{5'} \otimes \Gamma_5 = \Gamma_1^a + \Gamma_4 + \Gamma_{4'} + \Gamma_5 + \Gamma_{5'} + \Gamma_6$

$\Rightarrow$ There are three allowed states ^4F, ^2F, ^2F

$L = 2$

$d^{2+} d^{2+} d^{2+} d^{2-} d^{2-} \quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2) = \Gamma_1^S + \Gamma_4 + \Gamma_5$

$d^{2+} d^{2+} d^{+} d^{-} d^{2-} \quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_3\psi_4) = \Gamma_1^S + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6$

$d^{2+} d^{2+} d^{0} d^{0} d^{2-} \quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$d^{2+} d^{2+} d^{0} d^{-} d^{-} \quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$d^{2+} d^{+} d^{+} d^{0} d^{2-} \quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_3\psi_4) = \Gamma_1^S + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6$

$d^{2+} d^{+} d^{+} d^{-} d^{-} \quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$d^{2+} d^{+} d^{0} d^{0} d^{-} \quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_3\psi_4) = \Gamma_1^S + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6$

$d^{+} d^{+} d^{+} d^{+} d^{2-} \quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_2) = \Gamma_1^S + \Gamma_4$

$d^{+} d^{+} d^{+} d^{0} d^{-} \quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) = \Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6$

$d^{+} d^{+} d^{0} d^{0} d^{0} \quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_2) = \Gamma_1^S + \Gamma_4 + \Gamma_5$

$$\Rightarrow 10\Gamma_1^S + 20\Gamma_4 + 3\Gamma_{4'} + 18\Gamma_5 + 9\Gamma_{5'} + 13\Gamma_6$$
$$-(9\Gamma_1^S + 18\Gamma_4 + 2\Gamma_{4'} + 14\Gamma_5 + 6\Gamma_{5'} + 11\Gamma_6)$$

$$\Rightarrow \left(\Gamma_1^s + 2\Gamma_4 + \Gamma_{4'} + 4\Gamma_5 + 3\Gamma_{5'} + 2\Gamma_6\right) \otimes \left(\Gamma_1^s + \Gamma_4 + \Gamma_5\right)$$

Contains one $\Gamma_{4'} \otimes \Gamma_4 = \Gamma_1^a + \Gamma_{4'} + \Gamma_{5'} + \Gamma_6$

three $\Gamma_{5'} \otimes \Gamma_5 = \Gamma_1^a + \Gamma_4 + \Gamma_{4'} + \Gamma_5 + \Gamma_{5'} + \Gamma_6$

$$\Rightarrow \quad {}^4D, \quad {}^2D, {}^2D, {}^2D$$

$L = 1$

$d^{2+} d^{2+} d^{+} d^{2-} d^{2-}$ $\quad \chi_{perm}(\psi_1 \psi_1 \psi_2 \psi_2 \psi_3)$ $\quad \Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$$\left.\begin{array}{ll} d^{2+} d^{2+} d^{0} d^{-} d^{2-} & \chi_{perm}(\psi_1 \psi_1 \psi_2 \psi_3 \psi_4) \\ d^{2+} d^{+} d^{+} d^{-} d^{2-} & \chi_{perm}(\psi_1 \psi_1 \psi_2 \psi_3 \psi_4) \\ d^{2+} d^{+} d^{0} d^{0} d^{2-} & \chi_{perm}(\psi_1 \psi_1 \psi_2 \psi_3 \psi_4) \\ d^{2+} d^{+} d^{0} d^{-} d^{-} & \chi_{perm}(\psi_1 \psi_1 \psi_2 \psi_3 \psi_4) \end{array}\right\} \Gamma_1^s + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6$$

$$\left.\begin{array}{ll} d^{2+} d^{0} d^{0} d^{0} d^{-} & \chi_{perm}(\psi_1 \psi_1 \psi_1 \psi_2 \psi_3) \\ d^{+} d^{+} d^{+} d^{0} d^{2-} & \chi_{perm}(\psi_1 \psi_1 \psi_1 \psi_2 \psi_3) \end{array}\right\} \Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$$

$d^{+} d^{+} d^{+} d^{-} d^{-}$ $\quad \chi_{perm}(\psi_1 \psi_1 \psi_1 \psi_2 \psi_2)$ $\quad \Gamma_1^s + \Gamma_4 + \Gamma_5$

$d^{+} d^{+} d^{0} d^{0} d^{-}$ $\quad \chi_{perm}(\psi_1 \psi_1 \psi_2 \psi_2 \psi_3)$ $\quad \Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$

$d^{+} d^{0} d^{0} d^{0} d^{0}$ $\quad \chi_{perm}(\psi_1 \psi_1 \psi_1 \psi_1 \psi_2)$ $\quad \Gamma_1 + \Gamma_4$

$$\Rightarrow 10\Gamma_1^s + (2+12+4+4)\Gamma_4 + 4\Gamma_{4'} + (2+12+2+3)\Gamma_5$$

$$+ 10\Gamma_{5'} + (1+12+2+1)\Gamma_6$$

$$= 10\Gamma_1^s + 22\Gamma_4 + 4\Gamma_{4'} + 19\Gamma_5 + 10\Gamma_{5'} + 16\Gamma_6$$

$$- \left(10\Gamma_1^s + 20\Gamma_4 + 3\Gamma_{4'} + 18\Gamma_5 + 9\Gamma_{5'} + 13\Gamma_6\right)$$

$$= 2\Gamma_4 + \Gamma_{4'} + \Gamma_5 + \Gamma_{5'} + 3\Gamma_6$$

$$\left(2\Gamma_4 + \Gamma_{4'} + \Gamma_5 + \Gamma_{5'} + 3\Gamma_6\right) \otimes \left(\Gamma_1^s + \Gamma_4 + \Gamma_5\right)$$

Contains one $\Gamma_4 \otimes \Gamma_{4'}$

one $\Gamma_5 \otimes \Gamma_{5'}$

$\Rightarrow$ There are two allowed states ^4P, ^2P

$L=0$

$$\left.\begin{array}{ll} d^{2+}d^{2+}d^{0}d^{2-}d^{2-} & \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) \\ d^{2+}d^{2+}d^{-}d^{-}d^{2-} & \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) \\ d^{2+}d^{+}d^{+}d^{2-}d^{2-} & \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) \end{array}\right\} \Gamma_1^s+2\Gamma_4+2\Gamma_5+\Gamma_{5'}+\Gamma_6 \quad (A)$$

$$d^{2+}d^{+}d^{0}d^{-}d^{2-} \quad \chi_{perm}(\psi_1\psi_2\psi_3\psi_4\psi_5) \quad \Gamma_1^s+\Gamma_1^a+4\Gamma_4+4\Gamma_{4'}+5\Gamma_5+5\Gamma_{5'}+6\Gamma_6$$

$$d^{2+}d^{0}d^{0}d^{0}d^{2-} \quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) \quad \Gamma_1^s+2\Gamma_4+\Gamma_5+\Gamma_6 \quad (B)$$

$$d^{2+}d^{0}d^{0}d^{-}d^{-} \quad \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) \quad \Gamma_1^s+2\Gamma_4+2\Gamma_5+\Gamma_{5'}+\Gamma_6 \quad (A)$$

$$\left.\begin{array}{ll} d^{+}d^{+}d^{+}d^{-}d^{2-} & \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) \\ d^{2+}d^{+}d^{-}d^{-}d^{-} & \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) \end{array}\right\} \Gamma_1^s+2\Gamma_4+\Gamma_5+\Gamma_6 \quad (B)$$

$$\left.\begin{array}{ll} d^{+}d^{+}d^{0}d^{0}d^{2-} & \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) \\ d^{+}d^{+}d^{0}d^{-}d^{-} & \chi_{perm}(\psi_1\psi_1\psi_2\psi_2\psi_3) \end{array}\right\} (A)$$

$$d^{+}d^{0}d^{0}d^{0}d^{-} \quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_2\psi_3) \quad (B)$$

$$d^{0}d^{0}d^{0}d^{0}d^{0} \quad \chi_{perm}(\psi_1\psi_1\psi_1\psi_1\psi_1) \quad \Gamma_1^s$$

$$\Rightarrow \quad 6\times(A) + 4\times(B) + \chi_{perm}(\psi_1\psi_2\psi_3\psi_4\psi_5) + \Gamma_1^s$$

$$= 6\times(\Gamma_1^s+2\Gamma_4+2\Gamma_5+\Gamma_{5'}+\Gamma_6) + 4(\Gamma_1^s+2\Gamma_4+\Gamma_5+\Gamma_6)$$

$$+\Gamma_1^s+\Gamma_1^a+4\Gamma_4+4\Gamma_{4'}+5\Gamma_5+5\Gamma_{5'}+6\Gamma_6+\Gamma_1^s$$

$$= 12\Gamma_1^s+\Gamma_1^a+(12+8+4)\Gamma_4+4\Gamma_{4'}+(12+4+5)\Gamma_5$$

$$+(6+5)\Gamma_{5'}+(6+4+6)\Gamma_6$$

$$\Rightarrow 12\Gamma_1^s + \Gamma_1^a + 24\Gamma_4 + 4\Gamma_{4'} + 21\Gamma_5 + 11\Gamma_{5'} + 16\Gamma_6$$
$$- (10\Gamma_1^s + 22\Gamma_4 + 4\Gamma_{4'} + 19\Gamma_5 + 10\Gamma_{5'} + 16\Gamma_6)$$
$$= 2\Gamma_1^s + \Gamma_1^a + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'}$$

$$(2\Gamma_1^s + \Gamma_1^a + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'}) \otimes (\Gamma_1^s + \Gamma_4 + \Gamma_{5'})$$

Contains one Γ_1^a

and one $\Gamma_{5'} \otimes \Gamma_5$

$\Rightarrow$ there are two allowed states ^6S, ^2S

To summarize the result, I get the following

d^5	Irreducible rep.	Allowed State
$L=0$	$2\Gamma_1^s + \Gamma_1^a + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'}$	^6S, ^2S
$L=1$	$2\Gamma_4 + \Gamma_{4'} + \Gamma_5 + \Gamma_{5'} + 3\Gamma_6$	^4P, ^2P
$L=2$	$\Gamma_1^s + 2\Gamma_4 + \Gamma_{4'} + 4\Gamma_5 + 3\Gamma_{5'} + 2\Gamma_6$	^4D, ^2D, ^2D, ^2D
$L=3$	$\Gamma_1^s + 4\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 6\Gamma_6$	^4F, ^2F, ^2F
$L=4$	$2\Gamma_1^s + 4\Gamma_4 + \Gamma_{4'} + 4\Gamma_5 + 2\Gamma_{5'}$	^4G, ^2G, ^2G
$L=5$	$\Gamma_1^s + 3\Gamma_4 + 3\Gamma_5 + \Gamma_{5'} + 3\Gamma_6$	^2H
$L=6$	$2\Gamma_1^s + 3\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$	^2I
$L=7$	$\Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$	—
$L=8$	$\Gamma_1^s + \Gamma_4 + \Gamma_5$	—
$L=9$	Γ_4	—
$L=10$	Γ_1^s	—

1 Hund's rule $\rightarrow$ $S = 5/2$.

$\therefore$ Ground state is $\underline{{}^6S}$ //

Since the problem may be asking to do the above calculation taking into account the crystal field spliting in the cubic symmetry, I tried that from the next page.

4(i)

In cubic symmetry, $\Gamma_{l=2}$ orbitals split according to

$$\Gamma_{l=2} = E_g + T_{2g}$$

Let the partners for E_g and T_{2g} be $e_1\, e_2$ and $t_1\, t_2\, t_3$ respectively.

Since we have total 5 electrons, we can assign these electrons in the following way

	E_g	T_{2g}
①	5	0
②	4	1
③	3	2
④	2	3
⑤	1	4
⑥	0	5

Let's look at each case separately

① 5 electrons are in E_g

Spin state

$S = 1/2$ $\quad \Gamma_5$

$S = 3/2$ $\quad \Gamma_4$

$S = 5/2$ $\quad \Gamma_1^S$

Orbital state

$e_1e_1e_1e_1e_1 = \chi_{perm}(1\,1\,1\,1\,1) = \Gamma_1^S$

$e_1e_1e_1e_1e_2 = \chi_{perm}(1\,1\,1\,1\,2) = \Gamma_1^S + \Gamma_4$

$$e_1 e_1 e_2 e_2 e_2 = \chi_{perm}(11122) = \Gamma_1^S + \Gamma_4 + \Gamma_5$$
$$e_1 e_2 e_2 e_2 e_2 = \chi_{perm}(11112) = \Gamma_1^S + \Gamma_4$$
$$e_2 e_2 e_2 e_2 e_2 = \chi_{perm}(11111) = \Gamma_1^S$$

$\Rightarrow$ no allowed state

② 4 electrons are in E_g one electron in T_{2g}

Spin State

$S = 1/2$ Γ_5

$S = 3/2$ Γ_4

$S = 5/2$ Γ_1^S

orbital state $(i = 1, 2, 3)$ $e_1 \leftrightarrow e_2$

$$e_1 e_1 e_1 e_1 t_i = 3 \times (\Gamma_1^S + \Gamma_4) \times 2$$
$$e_1 e_1 e_1 e_2 t_i = 3 \times (\Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6) \times 2$$
$$e_1 e_1 e_2 e_2 t_i = 3 \times (\Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6)$$

$\Rightarrow$ Three allowed states $3 \times \Gamma_{5'} \otimes \Gamma_5$

$\Rightarrow S = 1/2$

$$({}^1E_g + {}^2T_{2g}) \times 3$$

③ 3 electrons are in E_g two electrons in T_{2g}

$(e_1 \leftrightarrow e_2) \times (i = 1, 2, 3)$

$$e_1 e_1 e_1 t_i t_i = 6 \times (\Gamma_1^S + \Gamma_4 + \Gamma_5)$$
$$e_1 e_1 e_2 t_i t_i = 6 \times (\Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6)$$
$$e_1 e_1 e_1 t_i t_j = 6 \times (\Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6)$$
$$e_1 e_1 e_2 t_i t_j = 6 \times (\Gamma_1^S + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6$$

$(i, j) = (1, 2)\ (2, 3)\ (3, 1)$

$\Rightarrow$ allowed states

$6\cdot\Gamma_{5'}\otimes\Gamma_5 \quad (S=1/2) \quad 6\,({}^2E_g + \ldots$

$6\,\Gamma_{4'}\otimes\Gamma_4 \quad (S=3/2) \quad 6$ $S=3/2$ state

$12\,\Gamma_{5'}\otimes\Gamma_5 \quad (S=1/2) \quad 12$ $S=1/2$ state

④ Two electrons in E_g three in T_{2g}

$e_je_j t_it_it_i \; (j=1,2,\; i=1,2,3) = 6\times(\Gamma_1^S + \Gamma_4 + \Gamma_5)$

$e_je_j t_it_it_k \; (j=1,2,\; (i,k)=(1,2),(1,3),(2,1),(2,3),(3,1),(3,2))$

$= 12\times(\Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6)$

$e_je_j t_1t_2t_3 \; (j=1,2) = 2\times(\Gamma_1^S + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6)$

$e_1e_2 t_it_it_i \; (i=1,2,3) = 3\times(\Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6)$

$e_1e_2 t_it_it_j \; ((i,j)=(1,2),(1,3),(2,1),(2,3),(3,1)(3,2))$

$= 6\times(\Gamma_1^S + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6)$

$e_1e_2 t_1t_2t_3 = \Gamma_1^S + \Gamma_1^a + 4\Gamma_4 + 4\Gamma_{4'} + 5\Gamma_5 + 5\Gamma_{5'} + 6\Gamma_6$

Allowed states

$e_je_jt_it_it_k$	$12\times\Gamma_{5'}\otimes\Gamma_5$	$(S=1/2)$	$12\,({}^1E_g + {}^2T_{2g})$
$e_je_jt_1t_2t_3$	$2\times\Gamma_{4'}\otimes\Gamma_4$	$(S=3/2)$	$2\,({}^1E_g + {}^4T_{2g})$
	$4\times\Gamma_{5'}\otimes\Gamma_5$	$(S=1/2)$	$4\,({}^1E_g + {}^2T_{2g})$
$e_1e_2t_it_it_j$	$6\times\Gamma_{4'}\otimes\Gamma_4$	$(S=3/2)$	$6\,({}^2E_g + {}^2T_{2g})$
	$12\times\Gamma_{5'}\otimes\Gamma_5$	$(S=1/2)$	$12\,({}^1E_g + {}^2T_{2g})$
$e_1e_2t_1t_2t_3$	$\Gamma_1^a\otimes\Gamma_1^S$	$(S=5/2)$	1 $S=5/2$ state
	$4\times\Gamma_4\otimes\Gamma_4$	$(S=3/2)$	4 $S=3/2$ states
	$5\times\Gamma_{5'}\otimes\Gamma_5$	$(S=1/2)$	5 $S=1/2$ states

⑤ One electron in E_g and 4 electrons in T_{2g}

$e_i t_j t_j t_j t_j \; (i=1,2,\; j=1,2,3) = 6 \times (\Gamma_1^S + \Gamma_4)$

$e_i t_j t_j t_j t_k (i=1,2,\; (j,k) = (1,2),(1,3),(2,1),(2,3),(3,1)(3,2))$

$= 12 \times (\Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6)$

$e_i t_j t_j t_k t_k \; (i=1,2,\; (j,k) = (1,2),(1,3),(2,3))$

$= 6 \times (\Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6)$

$e_i t_j t_j t_k t_l \; (i=1,2 \quad (j,k,l) = (1,2,3),(2,1,3),(3,1,2))$

$= 6 \times (\Gamma_1^S + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6)$

Allowed states

$e_i t_j t_j t_k t_k$	$6 \times \Gamma_{5'} \otimes \Gamma_5$	$(S=1/2)$	$6 \times (^2E_g + {}^1T_{2g})$
$e_i t_j t_j t_k t_l$	$6 \times \Gamma_{4'} \otimes \Gamma_4$	$(S=3/2)$	$6 \cdot S=3/2$ states
	$12 \times \Gamma_{5'} \otimes \Gamma_5$	$(S=1/2)$	$12 \; S=1/2$ states

⑥ 5 electrons in T_{2g}

$t_i t_i t_i t_i t_i \; (i=1,2,3) = 3 \times \Gamma_1^S$

$t_i t_i t_i t_i t_j \; ((i,j) = (1,2),(1,3),(2,1),(2,3),(3,1),(3,2))$

$= 6 \times (\Gamma_1^S + \Gamma_4)$

$t_i t_i t_i t_j t_j \; (\;\text{''}\;) = 6 \times (\Gamma_1^S + \Gamma_4 + \Gamma_5)$

$t_i t_i t_i t_j t_k \; (i=1,2,3) = 3 \times (\Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6)$

$t_i t_i t_j t_j t_k \; (k=1,2,3) = 3 \times (\Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6)$

$\Rightarrow$ Allowed states

$t_i t_i t_j t_j t_k \quad 3 \times \Gamma_{5'} \otimes \Gamma_5 \quad (S=\frac{1}{2}) \quad 3 \times (^1E_g + {}^2T_{2g})$

The ground state by Hund's rule is

$(E_g)^2 (T_{2g})^3$ $S = 5/2$ state.

(i)

First I will try to find $3d^4 4p$ allowed states

	E_g	T_{2g}	T_{1u}
1	4	0	1
2	3	1	1
3	2	2	1
4	1	3	1
5	0	4	1

(E_g, T_{2g}: 3d; T_{1u}: 4p)

← # of electrons in each level

1 $(E_g)^4 (T_{2g})^0 (T_{1u})^1$

$e_i e_i e_i e_i P_j \; (i=1,2, \; j=x,y,z) = 6 \times (\Gamma_1^S + \Gamma_4)$

$e_i e_i e_i e_k P_j \; (i \neq k, \; '') = 6 \times (\Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6)$

$e_1 e_1 e_2 e_2 P_j \; (j = x,y,z) = 3 \times (\Gamma_1^S + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6)$

$\Rightarrow$ 3 $\Gamma_{5'} \otimes \Gamma_5$ states $(S = 1/2)$

2 $(E_g)^3 (T_{2g})^1 (T_{1u})^1$

$e_i e_i e_i t_j P_k \; (i=1,2, \; j=1,2,3, \; k=x,y,z) = 18 \times (\Gamma_1^S + 2\Gamma_4 + \Gamma_5 + \Gamma_6)$

$e_i e_i e_\ell t_j P_k \; (i=1,2, \; \ell \neq i, \; '') = 18 \times (\Gamma_1^S + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6)$

$\Rightarrow$ 18 $\Gamma_{4'} \otimes \Gamma_4$ $(S = 3/2)$ states

36 $\Gamma_{5'} \otimes \Gamma_5$ $(S = 1/2)$ states.

③ $(E_g)^2 (T_{2g})^2 (T_{1u})^1$

$$e_i e_i t_j t_j p_k \ (i=1,2,\ j=1,2,3,\ k=x,y,z) = 18\,(\Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6)$$

$$e_i e_i t_j t_l p_k \ \left(i=1,2,\ (j,l)=\begin{matrix}(1,2)\\(2,3)\\(3,1)\end{matrix}\ k=x,y,z\right) = 18\times(\Gamma_1^s + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6)$$

$$e_1 e_2 t_j t_j p_k \ (j=1,2,3\ \ k=x,y,z) = 9\times(\Gamma_1^s + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6)$$

$$e_1 e_2 t_j t_l p_k \ \left((j,l)=\begin{matrix}(1,2)\\(2,3)\\(3,1)\end{matrix}\ k=x,y,z\right)$$

$$= 9\times(\Gamma_1^s + \Gamma_1^a + 4\Gamma_4 + 4\Gamma_{4'} + 5\Gamma_5 + 5\Gamma_{5'} + 6\Gamma_6)$$

$\Rightarrow$

18	$\Gamma_{5'}\otimes\Gamma_5$	$(S=1/2)$	States
18	$\Gamma_{4'}\otimes\Gamma_4$	$(S=3/2)$	States
36	$\Gamma_5\otimes\Gamma_5$	$(S=1/2)$	States
9	$\Gamma_{4'}\otimes\Gamma_4$	$(S=3/2)$	States
18	$\Gamma_{5'}\otimes\Gamma_5$	$(S=1/2)$	States

9 $S=5/2$ states   36 $S=3/2$ states   45 $S=1/2$ states

④ $(E_g)^1 (T_{2g})^3 (T_{1u})^1$

$$e_i t_j t_j t_j p_k \Rightarrow 18\times(\Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6)$$

$$e_i t_j t_j t_l p_k \Rightarrow 36\times(\Gamma_1^s + 3\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 3\Gamma_6)$$

$$e_i t_1 t_2 t_3 p_k = 6\times(\Gamma_1^s + \Gamma_1^a + 4\Gamma_4 + 4\Gamma_{4'} + 5\Gamma_5 + 5\Gamma_{5'} + 6\Gamma_6)$$

allowed states

$\Rightarrow$

36	$S=3/2$	states
72	$S=1/2$	states
6	$S=5/2$	states
24	$S=3/2$	states
30	$S=1/2$	states

⑤ $(E_g)^0(T_{2g})^4(T_{1u})^1$

$t_it_it_it_i p_k \; (i=1,2,3,\ k=x,y,z) = 9\times(\Gamma_1^S+\Gamma_4)$

$t_it_it_it_j p_k \; (i=1,2,3,\ j\neq i \;\;'') = 18\times(\Gamma_1^S+2\Gamma_4+\Gamma_5+\Gamma_6)$

$t_it_it_jt_j p_k \; \left((i,j)=\begin{matrix}(1,2)\\(2,3)\\(3,1)\end{matrix} \;\;''\right) = 9\times(\Gamma_1^S+2\Gamma_4+2\Gamma_5+\Gamma_{5'}+\Gamma_6)$

$t_it_it_jt_l p_k \; (i=1,2,3 \;\;'') = 9\times(\Gamma_1^S+3\Gamma_4+\Gamma_{4'}+3\Gamma_5+2\Gamma_{5'}+3\Gamma_6)$

$\Rightarrow$ 9 $S=1/2$ states

9 $S=3/2$ states

18 $S=1/2$ states

Since electric dipole doesn't couple spin states, Spin state has to be conserved.

So the possible transitions are,

$(E_g)^2(T_{2g})^3 \; (S=5/2) \rightarrow \quad 9\,(E_g)^2(T_{2g})^2(T_{1u})^1 \; (S=5/2)$

and $(E_g)^2(T_{2g})^3 \; (S=5/2) \rightarrow \quad 6\,(E_g)^1(T_{2g})^3(T_{1u})^1 \; (S=5/2)$

Actually both are allowed transitions, since

$$E_g \otimes T_{1u} = T_{1u} + T_{2u}$$

initial state — dipole (vector) — final state

$$T_{2g} \otimes T_{1u} = A_{2g} + E_u + T_{1u} + T_{2u}$$

Using the method described in lecture notes, we get the Pauli allowed states for $3d^5$ configuration. Various allowed states are list in the table next page. The decomposition of the reducible equivalence representation are also list, which is performed in part (b).

The three *Hund rules* determine the ground state of an atom whose configuration is given. These rules dictate that to find the ground state:

1. Choose the maximum value of S consistent with the Pauli principle.
2. Choose the maximum value of L consistent with the Pauli principle and rule 1.

3a. If the shell is less than half full, choose $J = J_{min} = |L - S|$.
3b. If the shell is more than half full, choose $J = J_{max} = L + S$.

By Hund's rule, we see that ^6S state is the ground state. in this case, $L=0$, $S=\frac{5}{2}$, therefore $J=\frac{5}{2}$. So the ground state is

$$\boxed{^6S_{\frac{5}{2}}}$$

For electric dipole transitions, according to the following selection rules,

1. Transitions can occur only between configurations which differ in the n and l quantum numbers of a *single* electron. This means that two or more electrons cannot simultaneously make transitions between subshells.
2. Transitions can occur only between configurations in which the change in the l quantum number of that electron satisfies the same restriction that applies to one-electron atoms. (8-37)

$$\Delta l = \pm 1$$

3. Transitions can occur only between states in these configurations for which the changes in the s', l', j' quantum numbers satisfy the restrictions

$$\begin{aligned} \Delta s' &= 0 \\ \Delta l' &= 0, \pm 1 \\ \Delta j' &= 0, \pm 1 \quad \text{(but not } j' = 0 \text{ to } j' = 0) \end{aligned} \qquad (10\text{-}17)$$

the allowed transitions are:

$$^6S_{\frac{5}{2}} \rightarrow {}^6P_{\frac{7}{2}}$$

$$\rightarrow {}^6P_{\frac{5}{2}}$$

$$\rightarrow {}^6P_{\frac{3}{2}}$$