Exercise 12.1

Determine the qualitative form of the molecular orbitals for the square-planar complex $[\text{Ni(CN)}_4]^{2-}$. (Assume that each CN ligand provides one σ-type and two π-type orbitals to the system.)

Solution 12.1

Similar to the section 12.2, we reduce Γ^{AO} (the reducible representation using $1 \times 9 + 4 \times 3 = 21$ atomic orbitals) to the form:

$$\Gamma^{\text{AO}} = \Gamma^{\text{Ni}} \oplus \Gamma^{\text{CN}}. \tag{12.1}$$

where Γ^{Ni} is a reducible representation using all 3d, 4s, 4p atomic orbitals of Ni as basis functions and Γ^{CN} is a reducible representation using the 12 atomic orbitals of the 4 CN ligands as basis functions. By checking the character table for $\mathscr{D}_{4h}$, viz., Table 12.1, we realize that

$$\Gamma^{\text{Ni}} = 2\Gamma^{A_{1g}} \oplus \Gamma^{B_{1g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_g} \oplus \Gamma^{A_{2u}} \oplus \Gamma^{E_u}. \tag{12.2}$$

Table 12.1: Character table for $\mathscr{D}_{4h}$.

$\mathscr{D}_{4h}$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

Due to the different chemical nature of σ and π orbitals, we further reduce Γ^{CN} to the form:

$$\Gamma^{\text{CN}} = \Gamma^{\sigma} \oplus \Gamma^{\pi} = \Gamma^{\sigma} \oplus \Gamma^{\pi\perp} \oplus \Gamma^{\pi//}, \tag{12.3}$$

where Γ^{σ} is the reducible representation using all $\text{Ni}-\text{C}$ bonds while Γ^{π} is the reducible representation using all π orbitals of CN ligands. Furthermore, the representation Γ^{π} can be decomposed into two distinct components based on their spatial orientation: $\Gamma^{\pi\perp}$, which comprises the π orbitals perpendicular to the molecular plane (pointing along the z-axis), and $\Gamma^{\pi//}$, which consists of the π orbitals residing within the molecular plane (orthogonal to the $\text{Ni}-\text{CN}$ σ-bond axis but within the xy-plane). Then, the characters for the ligand representations in $\mathscr{D}_{4h}$ are:

Table 12.2: Characters for the Γ^{CN} of the $\mathscr{D}_{4h}$ point group.

$\mathscr{D}_{4h}$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\chi^{\sigma}(C_i)$	4	0	0	2	0	0	0	4	2	0
$\chi^{\pi\perp}(C_i)$	4	0	0	-2	0	0	0	-4	2	0
$\chi^{\pi//}(C_i)$	4	0	0	-2	0	0	0	4	-2	0

By calculating the systems of linear equations, like in Problem 7.1, we obtain

$$\Gamma^{\sigma} = \Gamma^{A_{1g}} \oplus \Gamma^{B_{1g}} \oplus \Gamma^{E_u}, \tag{12.4}$$
$$\Gamma^{\pi//} = \Gamma^{A_{2g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_u}, \tag{12.5}$$
$$\Gamma^{\pi\perp} = \Gamma^{E_g} \oplus \Gamma^{A_{2u}} \oplus \Gamma^{B_{2u}}. \tag{12.6}$$

Thus, we know that

$$\begin{aligned}\Gamma^{\text{CN}} &= \Gamma^{\sigma} \oplus \Gamma^{\pi\perp} \oplus \Gamma^{\pi//} \\ &= \left[\Gamma^{A_{1g}} \oplus \Gamma^{B_{1g}} \oplus \Gamma^{E_u}\right] \oplus \left[\Gamma^{A_{2g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_u}\right] \oplus \left[\Gamma^{E_g} \oplus \Gamma^{A_{2u}} \oplus \Gamma^{B_{2u}}\right] \\ &= \Gamma^{A_{1g}} \oplus \Gamma^{A_{2g}} \oplus \Gamma^{B_{1g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_g} \oplus \Gamma^{A_{2u}} \oplus \Gamma^{B_{2u}} \oplus 2\Gamma^{E_u}. \end{aligned} \tag{12.7}$$

Summing these contributions, the total representation Γ^{AO} decomposes as:

$$\Gamma^{\text{AO}} = \Gamma^{\text{Ni}} \oplus \Gamma^{\text{CN}}$$

$$= \left[2\Gamma^{A_{1g}} \oplus \Gamma^{B_{1g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_g} \oplus \Gamma^{A_{2u}} \oplus \Gamma^{E_u} \right]$$
$$\oplus \left[\Gamma^{A_{1g}} \oplus \Gamma^{A_{2g}} \oplus \Gamma^{B_{1g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_g} \oplus \Gamma^{A_{2u}} \oplus \Gamma^{B_{2u}} \oplus 2\Gamma^{E_u} \right]$$
$$= 3\Gamma^{A_{1g}} \oplus \Gamma^{A_{2g}} \oplus 2\Gamma^{B_{1g}} \oplus 2\Gamma^{B_{2g}} \oplus 2\Gamma^{E_g} \oplus 2\Gamma^{A_{2u}} \oplus \Gamma^{B_{2u}} \oplus 3\Gamma^{E_u}. \qquad (12.8)$$

The total basis set generates the following molecular orbitals (MO):

- $\Gamma^{A_{1g}}$: 3 non-degenerate MOs. These result from the interaction between the Ni 4s, $3d_{z^2}$ orbitals and the a_{1g} σ-symmetry-adapted linear combinations (SALC) of the CN ligands.

- $\Gamma^{A_{2g}}$: 1 non-degenerate MO. A pure ligand-based MO from the a_{2g} $\pi_{//}$-SALC.

- $\Gamma^{B_{1g}}$: 2 non-degenerate MOs. Mixtures of the Ni $3d_{x^2-y^2}$ and the b_{1g} σ-SALC.

- $\Gamma^{B_{2g}}$: 2 non-degenerate MOs. Mixtures of the Ni $3d_{xy}$ and the b_{2g} $\pi_{//}$-SALC.

- Γ^{E_g}: 2 pairs of doubly degenerate MOs. Each set is a linear combination of the Ni $(3d_{xz}, 3d_{yz})$ orbital pair and the corresponding e_g $\pi_\perp$-SALCs.

- $\Gamma^{A_{2u}}$: 2 non-degenerate MOs. Mixtures of the Ni $4p_z$ and the a_{2u} $\pi_\perp$-SALC.

- $\Gamma^{B_{2u}}$: 1 non-degenerate MO. A pure ligand-based MO from the b_{2u} $\pi_\perp$-SALC.

- Γ^{E_u}: 3 pairs of doubly degenerate MOs. Each set is a linear combination of the Ni $(4p_x, 4p_y)$ orbital pair, and the e_u σ-SALCs, and e_u $\pi_{//}$-SALCs.

Exercise 12.2

Determine the qualitative form of the molecular orbitals for the tetrahedral molecule MnO_4^-. [Assume that each oxygen atom provides just three p-orbitals (set these up so that one points towards the Mn and the other two are perpendicular to each other and to the Mn—O axis) and that the Mn atom provides 4s and 3d orbitals.] You will be on the right track if you find that

$$\Gamma^\sigma = \Gamma^{A_1} \oplus \Gamma^{T_2},$$
$$\Gamma^\pi = \Gamma^E \oplus \Gamma^{T_1} \oplus \Gamma^{T_2}.$$

Solution 12.2

Similar to the section 12.2, we reduce Γ^{AO} (the reducible representation using $1 \times 6 + 4 \times 3 = 18$ atomic orbitals) to the form:

$$\Gamma^{AO} = \Gamma^{Mn} \oplus \Gamma^{O}. \qquad (12.9)$$

where Γ^{Mn} is a reducible representation using all 3d, 4s atomic orbitals of Mn as basis functions and Γ^{O} is a reducible representation using the 12 atomic orbitals of the 4 O ligands as basis functions.
By checking the character table for $\mathscr{T}_d$, viz., Table 12.3, we realize that

$$\Gamma^{Mn} = \Gamma^{A_1} \oplus \Gamma^E \oplus \Gamma^{T_2}. \qquad (12.10)$$

Table 12.3: Character table for $\mathscr{T}_d$.

$\mathscr{T}_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

Due to the different chemical nature of σ and π orbitals, we further reduce Γ^{O} to the form:

$$\Gamma^{O} = \Gamma^\sigma \oplus \Gamma^\pi. \qquad (12.11)$$

where Γ^σ is the reducible representation using all $Mn - O$ bonds while Γ^π is the reducible representation using all π orbitals of O ligands. Then, the characters for these ligand representations in $\mathscr{T}_d$ are:

Table 12.4: Characters for the Γ^{O} of the $\mathscr{T}_{\mathrm{d}}$ point group.

$\mathscr{T}_{\mathrm{d}}$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_{\mathrm{d}}$
$\chi^{\sigma}(C_i)$	4	1	0	0	2
$\chi^{\pi}(C_i)$	8	-1	0	0	0

Though the solution of the character of Γ^{σ} is rather easy. However, here's a difficult point, or rather, a less intuitive one: how to calculate the characters for π orbitals orthogonal to the corresponding $\mathrm{Mn-O}$ bonds. Now I demonstrate the whole process.

- For E, it is obvious that its character is 8.

- For $8C_3$ class, readers can understand in this way. Except for the O atom through which this axis passes, the π orbitals on other O atoms will not coincide with themselves, and the π orbitals on this atom, after rotation, are still a linear combination of the original π orbitals. We can take this axis as a new z-axis, and the two orthogonal π orbitals span a new plane. Using the method for handling the $\mathscr{C}_{3\mathrm{v}}$ point group, the corresponding character is

$$2\cos\frac{2\pi}{3} = 2 \times \left(-\frac{1}{2}\right) = -1.$$

- For $3C_2$ and $6S_4$ classes, it is evident that after rotations (and reflections), no π orbitals will coincide with themselves. Thus both their characters are 0.

- For the $6\sigma_{\mathrm{d}}$ class, as with the $8C_3$ class, we only consider the 2 π orbitals on the atoms lying within σ_{d}. Under this reflection, one π orbital remains invariant (character of $+1$), while the other is antisymmetric and changes sign (character of -1). Consequently, the total character is

$$-1 + 1 = 0.$$

By calculating the systems of linear equations, like in Problem 7.1, we obtain

$$\Gamma^{\sigma} = \Gamma^{A_1} \oplus \Gamma^{T_2}, \tag{12.12}$$
$$\Gamma^{\pi} = \Gamma^{E} \oplus \Gamma^{T_1} \oplus \Gamma^{T_2}. \tag{12.13}$$

These equations are mentioned in the Problem and thus we are on the right way. Now, we know that

$$\Gamma^{\mathrm{O}} = \Gamma^{\sigma} \oplus \Gamma^{\pi} = \left[\Gamma^{A_1} \oplus \Gamma^{T_2}\right] \oplus \left[\Gamma^{E} \oplus \Gamma^{T_1} \oplus \Gamma^{T_2}\right] = \Gamma^{A_1} \oplus \Gamma^{E} \oplus \Gamma^{T_1} \oplus 2\Gamma^{T_2}. \tag{12.14}$$

Summing these contributions, the total representation Γ^{AO} decomposes as:

$$\begin{aligned}\Gamma^{\mathrm{AO}} &= \Gamma^{\mathrm{Mn}} \oplus \Gamma^{\mathrm{O}} \\ &= \left[\Gamma^{A_1} \oplus \Gamma^{E} \oplus \Gamma^{T_2}\right] \oplus \left[\Gamma^{A_1} \oplus \Gamma^{E} \oplus \Gamma^{T_1} \oplus 2\Gamma^{T_2}\right] = 2\Gamma^{A_1} \oplus 2\Gamma^{E} \oplus \Gamma^{T_1} \oplus 3\Gamma^{T_2}.\end{aligned} \tag{12.15}$$

The total basis set generates the following molecular orbitals (MO):

- Γ^{A_1}: 2 non-degenerate MOs. These result from the interaction between the Mn 4s orbital and the a_1 σ-symmetry-adapted linear combinations (SALC) of the O ligands.

- Γ^{E}: 2 pairs of doubly degenerate MOs. These result from the interaction between the Mn ($3\mathrm{d}_{z^2}$, $3\mathrm{d}_{x^2-y^2}$) orbital pair and the e π-SALC.

- Γ^{T_1}: 1 set of triply-degenerate MOs. These are purely ligand-based non-bonding orbitals derived from only the t_1 π-SALC.

- Γ^{T_2}: 3 sets of triply-degenerate MOs. Each set is a linear combination of the Mn ($3\mathrm{d}_{xy}$, $3\mathrm{d}_{xz}$ and $3\mathrm{d}_{yz}$) orbitals, and the t_2 σ-SALCs, and t_2 π-SALCs.

Exercise 12.3

Determine the qualitative form of the molecular orbitals for the eclipsed conformation of ferrocene.

4

Solution 12.3

Similar to the section 12.2, we reduce Γ^{AO} (the reducible representation using $1 \times 9 + 2 \times 5 = 19$ atomic orbitals) to the form:

$$\Gamma^{AO} = \Gamma^{Fe} \oplus \Gamma^{C}. \tag{12.16}$$

where Γ^{Fe} is a reducible representation using all 3d, 4s and 4p atomic orbitals of Fe as basis functions and Γ^{C} is a reducible representation using the 10 π orbitals from 2 carbon rings as basis functions. By checking the character table for $\mathscr{T}_d$, viz., Table 12.5, we realize that

$$\Gamma^{Fe} = 2\Gamma^{A_1'} \oplus \Gamma^{E_1'} \oplus \Gamma^{E_2'} \oplus \Gamma^{A_2''} \oplus \Gamma^{E_1''}. \tag{12.17}$$

Table 12.5: Character table for $\mathscr{D}_{5h}$, where $\alpha = 72°$.

$\mathscr{D}_{5h}$	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$		
A_1'	1	1	1	1	1	1	1	1		$x^2+y^2; z^2$
A_2'	1	1	1	-1	1	1	1	-1	R_z	
E_1'	2	$2\cos\alpha$	$2\cos 2\alpha$	0	2	$2\cos\alpha$	$2\cos 2\alpha$	0	(x,y)	
E_2'	2	$2\cos 2\alpha$	$2\cos\alpha$	0	2	$2\cos 2\alpha$	$2\cos\alpha$	0		(x^2-y^2, xy)
A_1''	1	1	1	1	-1	-1	-1	-1		
A_2''	1	1	1	-1	-1	-1	-1	1	z	
E_1''	2	$2\cos\alpha$	$2\cos 2\alpha$	0	-2	$-2\cos\alpha$	$-2\cos 2\alpha$	0	(R_x, R_y)	(xz, yz)
E_2''	2	$2\cos 2\alpha$	$2\cos\alpha$	0	-2	$-2\cos 2\alpha$	$-2\cos\alpha$	0		

Moreover, due to the same chemical nature of 10 π orbitals of C atoms, we have

$$\Gamma^{C} = \Gamma^{\pi}. \tag{12.18}$$

Then, the characters for these ligand representations in $\mathscr{D}_{5h}$ are:

Table 12.6: Characters for the Γ^{π} of the $\mathscr{D}_{5h}$ point group.

$\mathscr{D}_{5h}$	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$
$\chi^{\pi}(C_i)$	10	0	0	0	0	0	0	2

By calculating the systems of linear equations, like in Problem 7.1, we obtain

$$\Gamma^{C} = \Gamma^{\pi} = \Gamma^{A_1'} \oplus \Gamma^{E_1'} \oplus \Gamma^{E_2'} \oplus \Gamma^{A_2''} \oplus \Gamma^{E_1''} \oplus \Gamma^{E_2''}. \tag{12.19}$$

Summing these contributions, the total representation Γ^{AO} decomposes as:

$$\Gamma^{AO} = \Gamma^{Fe} \oplus \Gamma^{C} = \left[2\Gamma^{A_1'} \oplus \Gamma^{E_1'} \oplus \Gamma^{E_2'} \oplus \Gamma^{A_2''} \oplus \Gamma^{E_1''}\right] \oplus \left[\Gamma^{A_1'} \oplus \Gamma^{E_1'} \oplus \Gamma^{E_2'} \oplus \Gamma^{A_2''} \oplus \Gamma^{E_1''} \oplus \Gamma^{E_2''}\right]$$
$$= 3\Gamma^{A_1'} \oplus 2\Gamma^{E_1'} \oplus 2\Gamma^{E_2'} \oplus 2\Gamma^{A_2''} \oplus 2\Gamma^{E_1''} \oplus \Gamma^{E_2''}. \tag{12.20}$$

The total basis set generates the following molecular orbitals (MO):

- $\Gamma^{A_1'}$: 3 non-degenerate MOs. These result from the interaction between the Fe 4s, $3d_{z^2}$ orbitals and the a_1' π-symmetry-adapted linear combinations (SALC) of the C_5H_5 ligands.

- $\Gamma^{E_1'}$: 2 pairs of doubly degenerate MOs. These result from the interaction between the Fe $(4p_x, 4p_y)$ orbital pair and the e_1' π-SALC.

- $\Gamma^{E_2'}$: 2 pairs of doubly degenerate MOs. These result from the interaction between the Fe $(3d_{x^2-y^2}, 3d_{xy})$ orbital pair and the e_2' π-SALC.

- $\Gamma^{A_2''}$: 2 non-degenerate MOs. These result from the interaction between the Fe $4p_z$ orbital and the a_2'' π-SALC.

- $\Gamma^{E_1''}$: 1 pair of doubly degenerate MOs. These result from the interaction between the Fe $(3d_{xz}, 3d_{yz})$ orbital pair and the e_1'' π-SALC.

- $\Gamma^{E_2''}$: 2 pairs of doubly degenerate MOs. These are purely ligand-based non-bonding orbitals derived from only the e_2'' π-SALC.

In summary, the qualitative forms of the MOs are derived by matching the symmetry of the Fe atomic orbitals with the corresponding C_5H_5 SALCs. While their exact energy ordering requires numerical calculations, this $\mathscr{D}_{5h}$ symmetry analysis defines the fundamental mixing rules and the nodal structure of the electronic framework.

Exercise 12.4

For an octahedral environment the d-orbitals are split into two sets (d_{e_g} and $d_{t_{2g}}$); how would they be split for a square-planar environment?

Solution 12.4

If readers only care about the final result, the solution is listed in the table 12-5.1 in the textbook. State D will be split into 4 irreducible representation $\Gamma^{A_{1g}}$, $\Gamma^{B_{1g}}$, $\Gamma^{B_{2g}}$ and Γ^{E_g}.

Here, I just want to supply another view. The splitting of d-orbitals in a square-planar environment ($\mathscr{D}_{4h}$) can be derived by treating it as a limiting case of an octahedral field ($\mathscr{O}_h$) with the two axial ligands removed. Using the descent in symmetry approach:

- The e_g set ($d_{x^2-y^2}$, d_{z^2}) loses its degeneracy as the z-axis becomes unique. From the Table 12.1, it is evident that now the $d_{x^2-y^2}$ belongs to b_{1g}, maintaining high energy due to direct overlap in the xy-plane, while the d_{z^2} orbital transforms as a_{1g}, with its energy decreasing significantly due to the absence of axial ligands.

- The t_{2g} set (d_{xy}, d_{xz}, d_{yz}) splits into a non-degenerate b_{2g} (d_{xy}) and a doubly-degenerate e_g pair (d_{xz}, d_{yz}). The e_g pair remains lower in energy as these orbitals extend into the vacant axial regions.

Thus, the five-fold degenerate d-orbitals in a spherical field, which split into Γ^{E_g} and $\Gamma^{T_{2g}}$ in an octahedral environment, further split into $\Gamma^{A_{1g}}$, $\Gamma^{B_{1g}}$, $\Gamma^{B_{2g}}$, Γ^{E_g} in a square-planar environment.

By the way, however, the relative energy level of $\Gamma^{A_{1g}}$ and $\Gamma^{B_{2g}}$ are uncertain. In other words, while the descent in symmetry determines the irreducible representations, the relative energy between $\Gamma^{A_{1g}}$ (d_{z^2}) and $\Gamma^{B_{2g}}$ (d_{xy}) depends on the specific nature of the ligands and the metal-ligand distance.

Exercise 12.5

Set up s qualitative correlation diagram for the d^3 configuration in an octahedral environment.

Solution 12.5

Firstly, I will directly deliver all d^3 free-ion terms. In fact, the acquisition of these terms involves angular momentum addition and L-S couplings, which are not covered in this textbook, so I will not go into detail about them here. Only the results are listed in Table 12.7.

Table 12.7: All d^3 free-ion terms and their irreducible representations (irreps). The numbers in parentheses following the irreps are the number of their basis functions. For example, for ^4F, the number is $4 \times (1 + 3 + 3) = 28$. Note that there are two independent ^2D, which are distinguished by adding new subscripts.

States	^4F (28)	^4P (12)	^2G (18)	^2H (22)
Irreps	$^4A_{2g}$, $^4T_{1g}$, $^4T_{2g}$	$^4T_{1g}$	$^2A_{1g}$, ^2E_g, $^2T_{1g}$, $^2T_{2g}$	^2E_g, $^2T_{1g}(2)$, $^2T_{2g}$
States	^2P (6)	$^2D_1$ (10)	^2F (14)	$^2D_2$ (10)
Irreps	$^2T_{1g}$	^2E_g, $^2T_{2g}$	$^2A_{2g}$, $^2T_{1g}$, $^2T_{2g}$	^2E_g, $^2T_{2g}$

From Table 12.7, there are in total 20 irreducible representations, and $28+12+18+22+6+10+14+10 = 120$ basis functions.

Secondly, there are totally $\binom{10}{3} = \frac{10!}{3!7!} = 120$ basis functions in the strong-field configurations, coincidence with the free-ion terms. Moreover, there 4 cases to be discussed separately: t_{2g}^3, $t_{2g}^2e_g^1$, $t_{2g}^1e_g^2$, and e_g^3. The partial product table needed for calculating the direct products between two irreps are:

Table 12.8: Partial product table for $\mathscr{O}_h$ point group.

$\mathscr{O}_h$	$\Gamma^{A_{1g}}$	$\Gamma^{A_{2g}}$	Γ^{E_g}	$\Gamma^{T_{1g}}$	$\Gamma^{T_{2g}}$
$\Gamma^{A_{1g}}$	$\Gamma^{A_{1g}}$	$\Gamma^{A_{2g}}$	Γ^{E_g}	$\Gamma^{T_{1g}}$	$\Gamma^{T_{2g}}$
$\Gamma^{A_{2g}}$	$\Gamma^{A_{2g}}$	$\Gamma^{A_{1g}}$	Γ^{E_g}	$\Gamma^{T_{2g}}$	$\Gamma^{T_{1g}}$
Γ^{E_g}	Γ^{E_g}	Γ^{E_g}	$\Gamma^{A_{1g}} \oplus \Gamma^{A_{2g}} \oplus \Gamma^{E_g}$	$\Gamma^{T_{1g}} \oplus \Gamma^{T_{2g}}$	$\Gamma^{T_{1g}} \oplus \Gamma^{T_{2g}}$
$\Gamma^{T_{1g}}$	$\Gamma^{T_{1g}}$	$\Gamma^{T_{2g}}$	$\Gamma^{T_{1g}} \oplus \Gamma^{T_{2g}}$	$\Gamma^{A_{1g}} \oplus \Gamma^{E_g} \oplus \Gamma^{T_{1g}} \oplus \Gamma^{T_{2g}}$	$\Gamma^{A_{2g}} \oplus \Gamma^{E_g} \oplus \Gamma^{T_{1g}} \oplus \Gamma^{T_{2g}}$
$\Gamma^{T_{2g}}$	$\Gamma^{T_{2g}}$	$\Gamma^{T_{1g}}$	$\Gamma^{T_{1g}} \oplus \Gamma^{T_{2g}}$	$\Gamma^{A_{2g}} \oplus \Gamma^{E_g} \oplus \Gamma^{T_{1g}} \oplus \Gamma^{T_{2g}}$	$\Gamma^{A_{1g}} \oplus \Gamma^{E_g} \oplus \Gamma^{T_{1g}} \oplus \Gamma^{T_{2g}}$

Now we start to discuss various situations. Their handling goes far beyond the scope of this textbook. But I will continue to document them. The methodology for determining multiplet terms of equivalent and non-equivalent configurations is listed below:

- For equivalent configurations, where electrons occupy the same irrep:

  1. Space Construction: Determine the direct product result of the m-dimensional irrep. The number of direct product calculations equals the total number of electrons n, resulting in a tensor space of dimension m^n.

  2. Permutational Symmetry Decomposition: Decompose this m^n-dimensional representation according to the partitions (Young diagrams) of the symmetric group S_n.

  3. Character Calculation via Schur Polynomials: For a specific partition $[\lambda]$, the character $\chi^{[\lambda]}(R)$ for a point group operation R is equivalent to the Schur polynomial $s_{[\lambda]}(x_1, \ldots, x_m)$, where $\{x_1, \ldots, x_m\}$ are the eigenvalues of the point group operation R acting on the m-dimensional irrep basis. This is calculated by summing the weights of all possible Semi-Standard Young Tableaux (SSYT) for that partition.

  4. Reduction to Point Group: Using the derived character, decompose the representation into the irreducible representations of the point group.

  Here, the Pauli Exclusion Principle makes sense. Crucially, the choice of the partition $[\lambda]$ for the spatial part must be the conjugate of the spin part's partition to ensure the total wave function is totally antisymmetric.

- For non-equivalent configurations, where electrons occupy different irreps):

  1. Partial Symmetry Treatment: For each subset of k electrons occupying the same irrep ($k \geq 2$), first perform the S_k decomposition as described above to find the valid terms for that specific sub-shell.

  2. Inter-shell Coupling: For electrons in different irreps, since they are spatially distinct, perform a simple direct product of their respective resulting irreps (coupling of irreducible representations) to find the final states.

After introducing the methods, I will treat 4 situations.

1. t_{2g}^3: It is an equivalent configuration, including two multiplicity. One corresponds to the quartet state, and the other to the doublet state. Moreover, $\Gamma^{T_{2g}} \otimes \Gamma^{T_{2g}} \otimes \Gamma^{T_{2g}}$ is a $3^3 = 27$ dimensional representation. However, it generates all 5 *gerade* irreps from Table 12.8. What is more, S_3 has 3 partitions, $[3]$, $[2,1]$ and $[1^3]$, which are 10, 16, 1-dimensional, respectively, calculated by the hook content formula. Due to no anti-symmetric spin states, the representation $[3]$ makes nonsense.

   - The quartet state requires the representation $[1^3]$, whose character is $x_1 x_2 x_3$ for its only SSYT. Due to

     $$x_1 x_2 x_3 = \frac{1}{6}\left[(x_1 + x_2 + x_3)^3 - 3(x_1 + x_2 + x_3)(x_1^2 + x_2^2 + x_3^2) + 2(x_1^3 + x_2^3 + x_3^3)\right],$$

     we have convert the character of $[1^3]$ to the power sums of eigenvalues. An important truth is that for any n-dimensional square matrix A with eigenvalues $a_1, a_2, \ldots, a_n$, the matrix power A^m has eigenvalues $a_1^n, a_2^n, \ldots, a_n^m$. Thus, we have

     $$\begin{aligned}
     \chi^{[1^3]}(R) &= x_1 x_2 x_3 \\
     &= \frac{1}{6}\left[(x_1 + x_2 + x_3)^3 - 3(x_1 + x_2 + x_3)(x_1^2 + x_2^2 + x_3^2) + 2(x_1^3 + x_2^3 + x_3^3)\right] \\
     &= \frac{1}{6}\left[\chi^{T_{2g}}(R)^3 - 3\chi^{T_{2g}}(R)\chi^{T_{2g}}(R^2) + 2\chi^{T_{2g}}(R^3)\right].
     \end{aligned} \tag{12.21}$$

   By this equation, we obtain the character of $[1^3]$:

   Table 12.9: Characters of the $\Gamma^{[1^3]}$ of the $\mathscr{O}_\mathrm{h}$ point group.

$\mathscr{O}_\mathrm{h}$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
$\chi^{[1^3]}(C_i)$	1	1	1	-1	-1

Compared to the partial character table of $\mathscr{O}_h$, viz.Table 12.10, it is evident that

$$\Gamma^{[1^3]} = \Gamma^{A_{2g}}. \tag{12.22}$$

Table 12.10: Partial character table for $\mathscr{O}_h$.

$\mathscr{O}_h$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
A_{1g}	1	1	1	1	1
A_{2g}	1	1	1	-1	-1
E_g	2	-1	2	0	0
T_{1g}	3	0	-1	1	-1
T_{2g}	3	0	-1	-1	1

Thus, we know that there is only one quartet strong-field term, $^4A_{2g}$.

- The doublet state requires the representation $[2, 1]$, whose character is $s_{[2,1]}(x_1, x_2, x_3)$. Using Jacobi-Trudi Identity, we obtain

$$s_{[2,1]}(x_1, x_2, x_3) = \begin{vmatrix} h_2 & h_3 & h_4 \\ 1 & h_1 & h_2 \\ 0 & 0 & 1 \end{vmatrix} = h_1 h_2 - h_3,$$

where $h_n(x_1, x_2, x_3)$ is the complete homogeneous symmetric polynomial,

$$h_n \equiv h_n(x_1, x_2, x_3) \equiv \sum_{m_1+m_2+m_3=n} \prod_{j=1}^{3} x^{m_j}.$$

With Newton Identity about h_n and power sums $p_n = \sum_{j=1}^{3} x_j^n$, we have

$$h_1 = p_1,$$
$$2h_2 = h_1 p_1 + p_2,$$
$$3h_3 = h_2 p_1 + h_1 p_2 + p_3.$$

Then we can express h_3 as various combinations of p_n.

$$h_1 = p_1,$$
$$h_2 = \frac{1}{2}(h_1 p_1 + p_2) = \frac{1}{2}(p_1 p_1 + p_2) = \frac{1}{2}(p_2 + p_1^2),$$
$$h_3 = \frac{1}{3}(h_2 p_1 + h_1 p_2 + p_3) = \frac{1}{3}\left[\frac{1}{2}(p_2 + p_1^2)p_1 + p_1 p_2 + p_3\right] = \frac{1}{3}p_3 + \frac{1}{2}p_1 p_2 + \frac{1}{6}p_1^3.$$

And now we can express $s_{[2,1]}(x_1, x_2, x_3)$ as

$$s_{[2,1]}(x_1, x_2, x_3) = h_1 h_2 - h_3$$
$$= \frac{1}{2}(p_2 + p_1^2)p_1 - \left(\frac{1}{3}p_3 + \frac{1}{2}p_1 p_2 + \frac{1}{6}p_1^3\right)$$
$$= \frac{1}{3}p_1^3 - \frac{1}{3}p_3 = \frac{1}{3}(p_1^3 - p_3).$$

Thus, we have

$$\chi^{[2,1]}(R) = s_{[2,1]}(x_1, x_2, x_3) = \frac{1}{3}(p_1^3 - p_3) = \frac{1}{3}\left(\chi^{T_{2g}}(R)^3 - \chi^{T_{2g}}(R^3)\right). \tag{12.23}$$

By this equation, we obtain the character of $[2, 1]$:

Table 12.11: Characters of the $\Gamma^{[2,1]}$ of the $\mathscr{O}_h$ point group.

$\mathscr{O}_h$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
$\chi^{[2,1]}(C_i)$	8	-1	0	0	0

By calculating the systems of linear equations, like in Problem 7.1, with Table 12.10, we obtain

$$\Gamma^{[2,1]} = \Gamma^{E_g} \oplus \Gamma^{T_{1g}} \oplus \Gamma^{T_{2g}}. \tag{12.24}$$

Therefore, we know that there are only three doublet strong-field terms, ^2E_g, $^2T_{1g}$, and $^2T_{2g}$.

Summing these terms, the total representation of t_{2g}^3 decomposes as:

$$\Gamma^{t_{2g}^3} = \Gamma^{^4A_{2g}} \oplus \Gamma^{^2E_g} \oplus \Gamma^{^2T_{1g}} \oplus \Gamma^{^2T_{2g}}. \tag{12.25}$$

2. $t_{2g}^2 e_g^1$: It is a non-equivalent configuration, including two multiplicity. One corresponds to the quartet state, and the other to the doublet state. However, these arise from the coupling between the t_{2g}^2 parent term and the e_g^1 electron: the quartet stems from the coupling of the t_{2g}^2 triplet state with the e_g^1 doublet, while the doublet involves the t_{2g}^2 singlet or triplet states.

For the t_{2g}^2 part, the $3^2 = 9$-dimensional spatial part has 4 kinds of irreps from Table 12.8.

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

Moreover, the spatial wavefunctions are classified by the S_2 partitions [2] and $[1^2]$. Using the hook content formula for $N = 3$ (the degeneracy of t_{2g}), these yield 6-dimensional (symmetric) and 3-dimensional (antisymmetric) orbital spaces respectively. Following the principle of parentage, we first determine the irreducible representations of the t_{2g}^2 configuration and then perform the direct product with the Γ^{E_g} representation.

- The triplet state requires the representation $[1^2]$, whose character is $s_{[1^2]}(x_1, x_2, x_3)$. Using Jacobi-Trudi Identity, we also obtain

$$s_{[1^2]}(x_1, x_2, x_3) = \begin{vmatrix} h_1 & h_2 \\ 1 & h_1 \end{vmatrix} = h_1^2 - h_2 = p_1^2 - \frac{1}{2}\left(p_2 + p_1^2\right) = \frac{1}{2}\left(-p_2 + p_1^2\right).$$

Therefore, we have

$$\chi^{[1^2]}(R) = s_{[1^2]}(x_1, x_2, x_3) = \frac{1}{2}\left(-p_2 + p_1^2\right) = \frac{1}{2}\left(-\chi^{T_{2g}}(R^2) + \chi^{T_{2g}}(R)^2\right). \tag{12.26}$$

By this equation, we obtain the character of $[1^2]$:

Table 12.12: Characters of the $\Gamma^{[1^2]}$ of the $\mathscr{O}_h$ point group.

$\mathscr{O}_h$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
$\chi^{[1^2]}(C_i)$	3	0	-1	1	-1

Compared to the partial character table of $\mathscr{O}_h$, viz., Table 12.10, it is evident that

$$\Gamma^{[1^2]} = \Gamma^{T_{1g}}. \tag{12.27}$$

Therefore, we know that there is only one triplet strong-field terms, $^3T_{1g}$.

- The singlet state requires the representation [2], whose character is $s_{[2]}(x_1, x_2, x_3)$. Using Jacobi-Trudi Identity, we also obtain

$$s_{[2]}(x_1, x_2, x_3) = \left|h_2\right| = h_2 = \frac{1}{2}\left(p_2 + p_1^2\right).$$

Therefore, we have

$$\chi^{[2]}(R) = s_{[2]}(x_1, x_2, x_3) = \frac{1}{2}\left(p_2 + p_1^2\right) = \frac{1}{2}\left(\chi^{T_{2g}}(R^2) + \chi^{T_{2g}}(R)^2\right). \tag{12.28}$$

By this equation, we obtain the character of [2]:

Table 12.13: Characters of the $\Gamma^{[2]}$ of the $\mathscr{O}_h$ point group.

$\mathscr{O}_h$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
$\chi^{[2]}(C_i)$	6	0	2	0	2

By calculating the systems of linear equations, like in Problem 7.1, with Table 12.10, we obtain

$$\Gamma^{[2]} = \Gamma^{A_{1g}} \oplus \Gamma^{E_g} \oplus \Gamma^{T_{2g}}. \tag{12.29}$$

Therefore, we know that there are only three singlet strong-field terms, $^1A_{1g}$, ^1E_g, and $^1T_{2g}$.

It is turn to calculate the couplings of states of t_{2g}^2 and e_g parts. With Table 12.8, finally we obtain results:

Table 12.14: Couplings between t_{2g}^2 and e_g parts.

Irreps' direct product	Vector addition	Result
$^3T_{1g} \otimes {}^2E_g$	$1 + \frac{1}{2} = \frac{3}{2}$	$^4T_{1g}$, $^4T_{2g}$
$^3T_{1g} \otimes {}^2E_g$	$1 - \frac{1}{2} = \frac{1}{2}$	$^2T_{1g}$, $^2T_{2g}$
$^1A_{1g} \otimes {}^2E_g$	$0 + \frac{1}{2} = \frac{1}{2}$	^2E_g
$^1E_g \otimes {}^2E_g$	$0 + \frac{1}{2} = \frac{1}{2}$	$^2A_{1g}$, $^2A_{2g}$, ^2E_g
$^1T_{2g} \otimes {}^2E_g$	$0 + \frac{1}{2} = \frac{1}{2}$	$^2T_{1g}$, $^2T_{2g}$

Summing these terms, the total representation of $t_{2g}^2 e_g$ decomposes as:

$$\Gamma^{t_{2g}^2 e_g} = \Gamma^{^4T_{1g}} \oplus \Gamma^{^4T_{2g}} \oplus \Gamma^{^2A_{1g}} \oplus \Gamma^{^2A_{2g}} \oplus 2\Gamma^{^2E_g} \oplus 2\Gamma^{^2T_{1g}} \oplus 2\Gamma^{^2T_{2g}}. \tag{12.30}$$

3. $t_{2g}^1 e_g^2$: It is also a non-equivalent configuration, including two multiplicity. One corresponds to the quartet state, and the other to the doublet state. However, these arise from the coupling between the e_g^2 parent term and the t_{2g}^1 electron: the quartet stems from the coupling of the e_g^2 triplet state with the t_{2g}^1 doublet, while the doublet involves the e_g^2 singlet or triplet states.

For the e_g^2 part, the $2^2 = 4$-dimensional spatial part has 3 kinds of irreps from Table 12.8.

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

Moreover, the spatial wavefunctions are also classified by the S_2 partitions [2] and $[1^2]$. Using the hook content formula for $N = 2$ (the degeneracy of e_g), these yield 3-dimensional (symmetric) and 1-dimensional (antisymmetric) orbital spaces respectively. Following the principle of parentage, we first determine the irreducible representations of the e_g^2 configuration and then perform the direct product with the $\Gamma^{T_{2g}}$ representation.

- The triplet state requires the representation $[1^2]$, whose character is $s_{[1^2]}(x_1, x_2, x_3)$. Similarly, we can obtain the equation of characters of $[1^2]$:

$$\chi^{[1^2]}(R) = \frac{1}{2}\left(-\chi^{E_g}(R^2) + \chi^{E_g}(R)^2\right). \tag{12.31}$$

By this equation, we obtain the character of $[1^2]$:

Table 12.15: Characters of the $\Gamma^{[1^2]}$ of the $\mathscr{O}_{\mathrm{h}}$ point group.

$\mathscr{O}_{\mathrm{h}}$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
$\chi^{[1^2]}(C_i)$	1	1	1	-1	-1

Compared to the partial character table of $\mathscr{O}_{\mathrm{h}}$, viz., Table 12.10, it is evident that

$$\Gamma^{[1^2]} = \Gamma^{A_{2g}}. \tag{12.32}$$

Therefore, we know that there is only one triplet strong-field terms, $^3A_{1g}$.

- The singlet state requires the representation [2], whose character is $s_{[2]}(x_1, x_2, x_3)$. Similarly, we can obtain the equation of characters of [2]:

$$\chi^{[2]}(R) = \frac{1}{2}\left(\chi^{T_{2g}}(R^2) + \chi^{T_{2g}}(R)^2\right). \tag{12.33}$$

By this equation, we obtain the character of [2]:

Table 12.16: Characters of the $\Gamma^{[2]}$ of the $\mathscr{O}_\mathrm{h}$ point group.

$\mathscr{O}_\mathrm{h}$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
$\chi^{[2]}(C_i)$	3	0	3	1	1

By calculating the systems of linear equations, like in Problem 7.1, with Table 12.10, we obtain

$$\Gamma^{[2]} = \Gamma^{A_{1g}} \oplus \Gamma^{E_g}. \tag{12.34}$$

Therefore, we know that there are only two singlet strong-field terms, $^1A_{1g}$, ^1E_g.

It is turn to calculate the couplings of states of t_{2g} and e_g^2 parts. With Table 12.8, finally we obtain results:

Table 12.17: Couplings between t_{2g} and e_g^2 parts.

Irreps' direct product	Vector addition	Result
$^2T_{2g} \otimes {}^3A_{2g}$	$1 + \frac{1}{2} = \frac{3}{2}$	$^4T_{1g}$
$^2T_{2g} \otimes {}^3A_{2g}$	$1 - \frac{1}{2} = \frac{1}{2}$	$^2T_{1g}$
$^2T_{2g} \otimes {}^1A_{1g}$	$0 + \frac{1}{2} = \frac{1}{2}$	$^2T_{2g}$
$^2T_{2g} \otimes {}^1E_g$	$0 + \frac{1}{2} = \frac{1}{2}$	$^2T_{1g}, {}^2T_{2g}$

Summing these terms, the total representation of $t_{2g}e_g^2$ decomposes as:

$$\Gamma^{t_{2g}^2 e_g} = \Gamma^{^4T_{1g}} \oplus 2\Gamma^{^2T_{1g}} \oplus 2\Gamma^{^2T_{2g}}. \tag{12.35}$$

4. e_g^3: It is also an equivalent configuration but including only doublet. Moreover, $\Gamma^{E_g} \otimes \Gamma^{E_g} \otimes \Gamma^{E_g}$ is a $2^3 = 8$ dimensional representation. Luckily, it generates only 3 *gerade* irreps, $\Gamma^{A_{1g}}$, $\Gamma^{A_{2g}}$ and Γ^{E_g}, from Table 12.8. What is more, S_3 has 3 partitions, $[3]$, $[2,1]$ and $[1^3]$, which are 10, 16, 1-dimensional, respectively, calculated by the hook content formula. Because currently only doublet states are needed, it is enough to calculate the partition $[2,1]$ only. Its character is $s_{[2,1]}(x_1, x_2, x_3)$ and similarly, we can obtain the equation of characters of $[2,1]$:

$$\chi^{[2,1]}(R) = \frac{1}{3} \left(\chi^{T_{2g}}(R)^3 - \chi^{T_{2g}}(R^3) \right). \tag{12.36}$$

By this equation, we obtain the character of $[2,1]$:

Table 12.18: Characters of the $\Gamma^{[2,1]}$ of the $\mathscr{O}_\mathrm{h}$ point group.

$\mathscr{O}_\mathrm{h}$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
$\chi^{[2,1]}(C_i)$	2	-1	2	0	0

Compared to the partial character table of $\mathscr{O}_\mathrm{h}$, viz., Table 12.10, it is evident that

$$\Gamma^{[2,1]} = \Gamma^{E_g}. \tag{12.37}$$

Therefore, we know that there is only one doublet strong-field terms, ^2E_g, and thus

$$\Gamma^{e_g^3} = \Gamma^{E_g}. \tag{12.38}$$

Now, summing these information, the belonging of strong-field terms is clear:

Strong-field configurations	Dimension	Strong-field terms
t_{2g}^3	20	$^4A_{2g}, {}^2E_g, {}^2T_{1g}, {}^2T_{2g}$
$t_{2g}^2 e_g$	60	$^4T_{1g}, {}^4T_{2g}, {}^2A_{1g}, {}^2A_{2g}, {}^2E_g(2), {}^2T_{1g}(2), {}^2T_{2g}(2)$
$t_{2g}e_{2g}^2$	36	$^4T_{1g}, {}^2T_{1g}(2), {}^2T_{2g}(2)$
e_{2g}^3	4	^2E_g

Finally, the correlation diagram for a d³ ion in an octahedral environment can be painted. However, the relative position of various terms are uncertain.

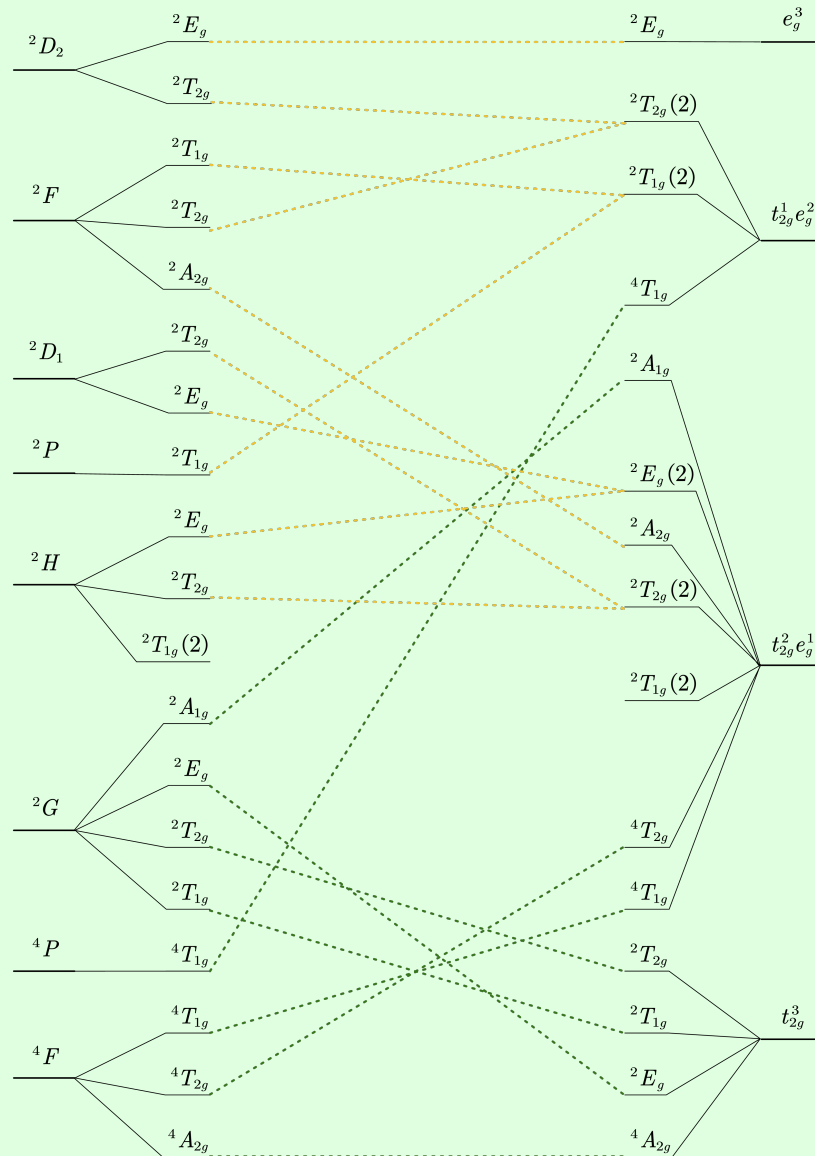

Figure 12.1: Correlation diagram (not to scale) for a d³ ion in an octahedral environment. The position of the left and right terms connected by green lines is also confirmed by B. N. Figgis *Introduction to ligand fields* but the position of the left and right terms connected by orange lines is uncertain.

Remark

The diagram 3.2 in B. N. Figgis *Introduction to ligand fields* has an error. From the top to the bottom, the third term should be ^2D rather than ^2P. The contents can be borrowed from https://archive.org.