CHAPTER 11

Hybrid Orbitals

Problem 11.1

Determine the irreducible representations of $\mathscr{T}_\mathrm{d}$ to which f-orbitals belong.

Solution 11.1

Firstly, we demonstrate the character table for the $\mathscr{T}_\mathrm{d}$ point group.

Table 11.1: Character table for the $\mathscr{T}_\mathrm{d}$ point group.

$\mathscr{T}_\mathrm{d}$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

Using the conclusion of the remark below this problem, we immediately obtain the characters of the representation Γ^red which uses 7 f-orbitals ($l = 3$) as its basis functions for the $\mathscr{T}_\mathrm{d}$ point group:

$$\begin{aligned}
\chi^\mathrm{red}(E) &= 2l + 1 = 7, \\
\chi^\mathrm{red}(C_3) &= \frac{\sin\frac{2l+1}{3}\pi}{\sin\frac{\pi}{3}} = \frac{\sin\frac{7}{3}\pi}{\sin\frac{\pi}{3}} = 1, \\
\chi^\mathrm{red}(C_2) &= \frac{\sin\frac{2l+1}{2}\pi}{\sin\frac{\pi}{2}} = \frac{\sin\frac{7}{2}\pi}{\sin\frac{\pi}{2}} = -1, \\
\chi^\mathrm{red}(S_4) &= \frac{\cos\frac{2l+1}{4}\pi}{\cos\frac{\pi}{4}} = \frac{\cos\frac{7}{4}\pi}{\cos\frac{\pi}{4}} = 1, \\
\chi^\mathrm{red}(\sigma_\mathrm{d}) &= 1.
\end{aligned}$$

Summarizing these results, we obtain the character for Γ^red of the $\mathscr{T}_\mathrm{d}$ point group:

Table 11.2: Character of the reducible representation Γ^red of the $\mathscr{T}_\mathrm{d}$ point group.

$\mathscr{T}_\mathrm{d}$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\chi^\mathrm{hyb}(C_i)$	7	1	-1	1	1

Hence, Solving the system of linear equations like in Problem 7.1, we arrive at

$$\Gamma^\mathrm{hyb} = \Gamma^{A_1} \oplus \Gamma^{T_1} \oplus \Gamma^{T_2}.$$

At last, we should point all irreducible representations which f-orbitals belong.

- It is evident that only f_{xyz} is invariant under any C_3 operation. Thus, f_{xyz} belongs to the Γ^{A_1}.
- Note that the only two differences in the characters between Γ^{T_1} and Γ^{T_2}, we analyse the behaviours of other f-orbitals under the S_{4z} operation. The S_{4z} operation renders $x \to -y$, $y \to x$ and $z \to -z$, thus we find

$$\begin{array}{ccc} \mathrm{f}_{x^3} \to -\mathrm{f}_{y^3}, & \mathrm{f}_{y^3} \to \mathrm{f}_{x^3}, & \mathrm{f}_{z^3} \to -\mathrm{f}_{z^3}, \\ \mathrm{f}_{x(y^2-z^2)} \to -\mathrm{f}_{y(x^2-z^2)}, & \mathrm{f}_{y(z^2-x^2)} \to \mathrm{f}_{x(z^2-y^2)}, & \mathrm{f}_{z(x^2-y^2)} \to \mathrm{f}_{z(x^2-y^2)}. \end{array}$$

In other words, the character of the 3 S_4 class of the irreducible representation, whose basis functions are $\mathrm{f}_{x(y^2-z^2)}$, $\mathrm{f}_{y(z^2-x^2)}$, and $\mathrm{f}_{x(z^2-y^2)}$, is 1 while that of the irreducible representation, whose basis functions are f_{x^3}, f_{y^3}, and f_{z^3} is -1. This means that $\mathrm{f}_{x(y^2-z^2)}$, $\mathrm{f}_{y(z^2-x^2)}$, and $\mathrm{f}_{x(z^2-y^2)}$ belong to the Γ^{T_1}, while f_{x^3}, f_{y^3}, and f_{z^3} belong to the Γ^{T_2}.

Now we can conclude

- f_{xyz} belongs to the Γ^{A_1},
- $\mathrm{f}_{x(y^2-z^2)}$, $\mathrm{f}_{y(z^2-x^2)}$, and $\mathrm{f}_{x(z^2-y^2)}$ belong to the Γ^{T_1},
- f_{x^3}, f_{y^3}, and f_{z^3} belong to the Γ^{T_2}.

Remark

In quantum mechanics, a set of $2l+1$ spherical harmonics $Y_m^l \equiv Y_m^l(\theta,\phi)$ forms a basis for a representation of the rotation group SO(3). Now I derive the character for this set of all symmetry operations under a general point group.

- E: There are $2l+1$ basis functions and after the identical operation, a general basis function is invariant:
$$\boldsymbol{O}_E Y_m^l(\theta,\phi) = Y_m^l(\theta,\phi). \tag{11.1}$$
Thus, we obtain
$$\chi_l(E) = \sum_{i=-l}^{l} 1 = 2l+1. \tag{11.2}$$

- C_n: When we rotate the system clockwise by an angle $\alpha = 2\pi/n$ about the z-axis, the wavefunctions transform as:
$$\boldsymbol{O}_{C_n} Y_m^l(\theta,\phi) = \hat{R}_z(\alpha) Y_m^l(\theta,\phi) = Y_m^l(\theta,\phi-\alpha) = e^{-im\alpha} Y_m^l(\theta,\phi). \tag{11.3}$$
Since each basis function Y_m^l (where $m = -l,\ldots,0,\ldots,l$) is simply multiplied by a phase factor, the rotation matrix is diagonal. The character $\chi_l(\alpha)$ is the trace of this matrix is
$$\chi_l(\alpha) = \sum_{m=-l}^{l} e^{im\alpha} = e^{-il\alpha} + e^{-i(l-1)\alpha} + \cdots + 1 + \cdots + e^{i(l-1)\alpha} + e^{il\alpha}.$$
This is a geometric series with a starting term of $e^{-il\alpha}$, a common ratio of $e^{i\alpha}$, and a total of $2l+1$ terms. Therefore, we obtain
$$\chi_l(\alpha) = \frac{e^{-il\alpha}(1-e^{i(2l+1)\alpha})}{1-e^{i\alpha}}$$
To simplify this into sines, we "factor out" the half-angle terms $e^{i(l+1/2)\alpha}$ and $e^{i\alpha/2}$ from the numerator and denominator respectively. Applying the famous Euler's formula,
$$\sin\theta = \frac{e^{i\theta}-e^{-i\theta}}{2i} \Leftrightarrow e^{-i\theta} - e^{i\theta} = -2i\sin\theta,$$
the phase factors cancel out, leaving the elegant result:
$$\chi_l(\alpha) = \frac{e^{-il\alpha}e^{i\frac{(2l+1)\alpha}{2}}}{e^{\frac{i\alpha}{2}}} \frac{e^{-\frac{i(2l+1)\alpha}{2}} - e^{\frac{i(2l+1)\alpha}{2}}}{e^{-\frac{i\alpha}{2}} - e^{\frac{i\alpha}{2}}} = \frac{e^{-il\alpha}e^{i(l+\frac{1}{2})\alpha}}{e^{\frac{i\alpha}{2}}} \frac{-2i\sin\left(\frac{2l+1}{2}\alpha\right)}{-2i\sin\frac{\alpha}{2}} = \frac{\sin\frac{2l+1}{2}\alpha}{\sin\frac{\alpha}{2}}.$$
Now we substitute α by $\frac{2\pi}{n}$, we obtain
$$\chi_l(C_n) = \chi_l(\frac{2\pi}{n}) = \frac{\sin\frac{2l+1}{2}\frac{2\pi}{n}}{\sin\frac{1}{2}\frac{2\pi}{n}} = \frac{\sin\frac{2l+1}{n}\pi}{\sin\frac{\pi}{n}}. \tag{11.4}$$

- i: After the inverse operation, the result of a general Y_m^l is:
  - *gerade* (l is an even integer): s, d, g orbitals ($l = 0, 2, 4$) are symmetric under the inversion operation.
  - *ungerade* (l is an odd integer): p, f, h orbitals ($l = 1, 3, 5$) are antisymmetric (change sign) under the inversion operation.

  Therefore, we get two equations. One is the effect of the inverse operator $\boldsymbol{O}_i$:

$$\boldsymbol{O}_i Y_m^l = (-1)^l Y_m^l. \tag{11.5}$$

  The other is the character:

$$\chi_l(i) = \sum_{i=-l}^{l} (-1)^l = (-1)^l \sum_{i=-l}^{l} 1 = (-1)^l (2l+1). \tag{11.6}$$

- σ: A reflection operation is mathematically equivalent to a C_2 rotation operation followed by an inversion operation ($i \cdot C_2$). Thus in the same way, with $\alpha = 2\pi/2 = \pi$, its effect is

$$\begin{aligned} \boldsymbol{O}_\sigma Y_m^l(\theta,\phi) &= \boldsymbol{O}_i \boldsymbol{O}_{C_2} Y_m^l(\theta,\phi) \\ &= \boldsymbol{O}_i Y_m^l(\theta,\phi-\pi) = (-1)^l Y_m^l(\theta,\phi-\pi) = (-1)^l e^{-im\pi} Y_m^l(\theta,\phi). \end{aligned} \tag{11.7}$$

  Hence, similar to the solution of the $\chi_l(C_n)$, we obtain

$$\chi_l(\sigma) = \sum_{m=-l}^{l} (-1)^l e^{im\pi} = (-1)^l \sum_{m=-l}^{l} e^{im\pi} = (-1)^l \chi_l(C_2) = (-1)^l \frac{\sin\frac{2l+1}{2}\pi}{\sin\frac{\pi}{2}}.$$

  Due to

$$\sin\frac{2l+1}{2}\pi = \sin\left(l\pi + \frac{\pi}{2}\right) = \cos l\pi = (-1)^l \cos 0\pi = (-1)^l,$$

  we have

$$\chi_l(\sigma) = (-1)^l \frac{\sin\frac{2l+1}{2}\pi}{\sin\frac{\pi}{2}} = (-1)^l \frac{(-1)^l}{1} = (-1)^{2l} = 1. \tag{11.8}$$

- S_n: A rotation-reflection operation is defined as a C_n operation followed by a reflection operation ($\sigma \cdot C_n = i \cdot C_2 \cdot C_n$). Thus in the same way, substituting α by $\pi + \alpha$, its effect is

$$\begin{aligned} \boldsymbol{O}_{S_n} Y_m^l(\theta,\phi) &= \boldsymbol{O}_i \boldsymbol{O}_{C_n} \boldsymbol{O}_{C_2} Y_m^l(\theta,\phi) = \boldsymbol{O}_i \hat{R}_z(\pi) \hat{R}_z(\alpha) Y_m^l(\theta,\phi) = \boldsymbol{O}_i \hat{R}_z(\pi+\alpha) Y_m^l(\theta,\phi) \\ &= \boldsymbol{O}_i Y_m^l(\theta,\phi-\alpha-\pi) = (-1)^l Y_m^l(\theta,\phi-\alpha-\pi) = (-1)^l e^{-im(\alpha+\pi)} Y_m^l(\theta,\phi). \end{aligned} \tag{11.9}$$

  Hence, similar to the solution of the $\chi_l(C_n)$, we obtain

$$\chi_l^{S_n}(\alpha) = \sum_{m=-l}^{l} (-1)^l e^{im(\alpha+\pi)} = (-1)^l \sum_{m=-l}^{l} e^{im(\alpha+\pi)}.$$

  This is also a geometric series but with a first term of $e^{-il(\alpha+\pi)}$, a common ratio of $e^{i(\alpha+\pi)}$, and a total of $2l+1$ terms. Therefore, we obtain

$$\begin{aligned} \chi_l^{S_n}(\alpha) &= (-1)^l \frac{e^{-il(\alpha+\pi)}(1 - e^{i(2l+1)(\alpha+\pi)})}{1 - e^{i(\alpha+\pi)}} = (-1)^l \frac{\sin\frac{2l+1}{2}(\alpha+\pi)}{\sin\frac{\alpha+\pi}{2}} = (-1)^l \frac{\sin\left(\frac{2l+1}{2}\alpha + l\pi + \frac{\pi}{2}\right)}{\sin\left(\frac{\alpha}{2} + \frac{\pi}{2}\right)} \\ &= (-1)^l \frac{\cos\left(\frac{2l+1}{2}\alpha + l\pi\right)}{\cos\frac{\alpha}{2}} = (-1)^l \frac{(-1)^l \cos\left(\frac{2l+1}{2}\alpha\right)}{\cos\frac{\alpha}{2}} = (-1)^{2l} \frac{\cos\left(\frac{2l+1}{2}\alpha\right)}{\cos\frac{\alpha}{2}} = \frac{\cos\left(\frac{2l+1}{2}\alpha\right)}{\cos\frac{\alpha}{2}}. \end{aligned}$$

  Now we substitute α by $\frac{2\pi}{n}$, we obtain

$$\chi_l(S_n) = \chi_l^{S_n}\left(\frac{2\pi}{n}\right) = \frac{\cos\frac{2l+1}{2}\frac{2\pi}{n}}{\cos\frac{1}{2}\frac{2\pi}{n}} = \frac{\cos\frac{2l+1}{n}\pi}{\cos\frac{\pi}{n}}. \tag{11.10}$$

It is very efficient to deal with similar problems like Problem 5.1 and Problem 7.6, with eqns (11.2), (11.4), (11.6), (11.8) and (11.10).

Problem 11.2

Show that for a molecule of octahedral symmetry the σ-bonding hybrid orbitals on the central atom are composed of six atomic orbitals: s, p_x, p_y, p_z, d_{z^2} and $d_{x^2-y^2}$.

Solution 11.2

The structure of an octahedral AB_6 is shown in Fig 11.1.

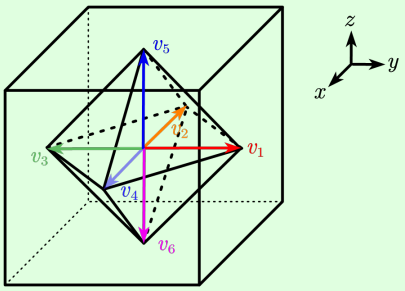

Figure 11.1: Vectors v_1, v_2, v_3, v_4, v_5, and v_6 represent the 6 σ-bonding hybrid orbitals between the A atom to one of 6 B atoms in AB_6.

AB_6 has 3 C_4 axes, and a center of symmetry i but no C_5 axis. Thus it belongs to the $\mathscr{O}_h$ point group. Then, I show the character table of the $\mathscr{O}_h$ point group as below.

Table 11.3: Character table for the $\mathscr{O}_h$ point group.

$\mathscr{O}_h$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
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		
E_g	2	-1	2	0	0	2	-1	2	0	0		$(2z^2-x^2-y^2,\ x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1	$(R_x,\ R_y,\ R_z)$	
T_{2g}	3	0	-1	-1	1	3	0	-1	-1	1		$(xy,\ xz,\ yz)$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1		
E_u	2	-1	2	0	0	-2	1	-2	0	0		
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1	$(x,\ y,\ z)$	
T_{2u}	3	0	-1	-1	1	-3	0	1	1	-1		

After lots of calculation, the character for Γ^{hyb} for the $\mathscr{O}_h$ point group is

Table 11.4: Character for the Γ^{hyb} representation of the $\mathscr{O}_h$ point group.

$\mathscr{O}_h$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
$\chi^{\text{hyb}}(C_i)$	6	0	2	2	0	0	0	4	0	2

Hence, solving the system of linear equations like in Problem 7.1, we arrive at

$$\Gamma^{\text{hyb}} = \Gamma^{A_{1g}} \oplus \Gamma^{E_g} \oplus \Gamma^{T_{1u}}. \tag{11.11}$$

From Table 11.3, we know that only the following 6 atomic orbitals can be used to construct σ-bonding molecular orbitals. In other words, for a molecule of octahedral symmetry the σ-bonding hybrid orbitals on the central atom are composed of six atomic orbitals: s, p_x, p_y, p_z, d_{z^2} and $d_{x^2-y^2}$

$\Gamma^{A_{1g}}$	Γ^{E_g}	$\Gamma^{T_{1u}}$
s	d_{z^2}, $d_{x^2-y^2}$	p_x, p_y, p_z

Problem 11.3

Determine what type of π-bonding hybrid orbitals can be formed for the square planar AB_4 molecule which belongs to the $\mathscr{D}_{4h}$ point group.

Solution 11.3

The structure of a square planar AB_4 with π-bonding hybrid orbitals is shown in Fig 11.2.

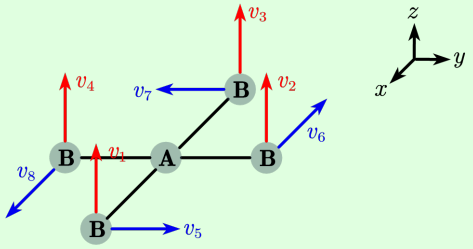

Figure 11.2: Vectors v_1, v_2, v_3, v_4, v_5, v_6, v_7 and v_8 represent the π-bonding hybrid orbitals between the A atom to one of 4 B atoms in AB_4.

The character table of the point group $\mathscr{D}_{4h}$ is shown below.

Table 11.5: Character table for the $\mathscr{D}_{4h}$ point group.

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

After lots of calculation, the character for the $\Gamma^{\text{hyb}}_{\text{perp}}$ representation whose basis functions are v_1, v_2, v_3, and v_4, and $\Gamma^{\text{hyb}}_{\text{plane}}$ representation whose basis functions are v_5, v_6, v_7, and v_8, for the $\mathscr{D}_{4h}$ point group is

Table 11.6: Character for the $\Gamma^{\text{hyb}}_{\text{perp}}$, and $\Gamma^{\text{hyb}}_{\text{plane}}$ representations of the $\mathscr{D}_{4h}$ point group.

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

Hence, solving the system of linear equations like in Problem 7.1, we arrive at

$$\Gamma^{\text{hyb}}_{\text{perp}} = \Gamma^{A_{2u}} \oplus \Gamma^{B_{2u}} \oplus \Gamma^{E_g}, \tag{11.12}$$

$$\Gamma^{\text{hyb}}_{\text{plane}} = \Gamma^{A_{2g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_u}. \tag{11.13}$$

From Table 11.5, we know that only the following 6 atomic orbitals can be used to construct π-bonding molecular orbitals.

$\Gamma^{\text{hyb}}_{\text{perp}}$			$\Gamma^{\text{hyb}}_{\text{plane}}$		
$\Gamma^{A_{2u}}$	$\Gamma^{B_{2u}}$	Γ^{E_g}	$\Gamma^{A_{2g}}$	$\Gamma^{B_{2g}}$	Γ^{E_u}
p_z	none	$(d_{xz},\ d_{yz})$	none	d_{xy}	$(p_x,\ p_y)$

Based on symmetry-adapted linear combinations (SALCs) of the ligand p-orbitals, the π-bonding framework can be summarized as follows:

- Out-of-Plane π-System ($\pi_\perp$): The 4 ligand p_z orbitals transform as $a_{2u} + b_{2u} + e_g$. Symmetry matching confirms that the central atom A utilizes its p_z (a_{2u}) and (d_{xz}, d_{yz}) (e_g) orbitals to form 3 sets of bonding molecular orbitals. These interactions result in π-electron density delocalized above and below the molecular plane across all 4 B atoms. The b_{2u} combination remains non-bonding due to the absence of a valence orbital of the same symmetry on the central atom.

- In-Plane π-System ($\pi_{//}$): The 4 ligand p orbitals lying in the xy-plane transform as $a_{2g}+b_{2g}+e_u$. The primary π-contribution arises from the overlap of the ligand b_{2g} SALC with the central atom A's d_{xy} orbital. While the (p_x, p_y) (e_u) orbitals are symmetry-allowed for π-bonding, they are typically partitioned to the stronger σ-bonding framework, thus their contribution to the π-system is secondary.

Remark

Note that from the next problem, we can know that while p_x, p_y, and p_z of the center atom A are technically available for π-bonding, they are often heavily involved in the primary σ-bonding framework ($a_{1g}+b_{1g}+e_u$). In such cases, the π-interaction is dominated by the d-orbitals (d_{xz}, d_{yz}, d_{xy}).

Problem 11.4

Show that for the square planar AB_4 molecule a possible set of four σ-hybrid orbitals on A is composed of the atomic orbitals: s, $d_{x^2-y^2}$, p_x, and p_y. Find explicit expressions for the four hybrid orbitals.

Solution 11.4

The structure of a square planar AB_4 with π-bonding hybrid orbitals is shown in Fig 11.3.

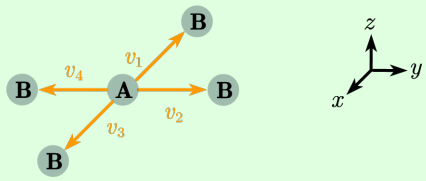

Figure 11.3: Vectors v_1, v_2, v_3, and v_4 represent the σ-bonding hybrid orbitals between the A atom to one of 4 B atoms in AB_4.

The character table of the point group $\mathscr{D}_{4h}$ can be seen in Table 11.5. After lots of calculation, the character for Γ^{hyb} for the $\mathscr{D}_{4h}$ point group is

Table 11.7: Character for the Γ^{hyb} representations of the $\mathscr{D}_{4h}$ point group.

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

Hence, solving the system of linear equations like in Problem 7.1, we arrive at

$$\Gamma^{hyb} = \Gamma^{A_{1g}} \oplus \Gamma^{B_{1g}} \oplus \Gamma^{E_u}. \tag{11.14}$$

From Table 11.5, we know that only the following 6 atomic orbitals can be used to construct π-bonding molecular orbitals.

$\Gamma^{A_{1g}}$	$\Gamma^{B_{1g}}$	Γ^{E_u}
s, d_{z^2}	$d_{x^2-y^2}$	p_x, p_y

Although both s and d_{z^2} belong to the $\Gamma^{A_{1g}}$ irreducible representation, the widely accepted dsp^2 hybridization scheme predominantly incorporates s alongside the $d_{x^2-y^2}$, p_x, and p_y orbitals. This selection is governed not by group theory alone, but by the physical constraints outlined in Molecular Orbital (MO) theory:

- The Symmetry Principle: While d_{z^2} is symmetry-allowed for σ-bonding in the $\mathscr{D}_{4h}$ point group, symmetry is merely a "selection rule" that permits interaction but does not guarantee its strength.
- The Energy Similarity Principle: In a square planar ligand field, the d orbitals undergo significant splitting. It is generally considered that from the energy perspective, $(n-1)d < ns < np$. In a square planar field, d_{z^2} has a lower energy than $d_{x^2-y^2}$, while the energy of s is higher than that of $d_{x^2-y^2}$ and lower than p_x and p_y.
- The Maximum Overlap Principle: s is spherically symmetric, with a large electron cloud distribution in the xy plane; while the main body of d_{z^2} (two large "lobes") points towards the

z-axis, and the ligands of the AB_4 molecule are all in the xy plane. Although d_{z^2} has a central ring region ("doughnut") in the xy plane, the electron cloud density of that ring is much smaller than that of the s orbital, resulting in lower overlap efficiency. This is demonstrated in Fig 11.4.

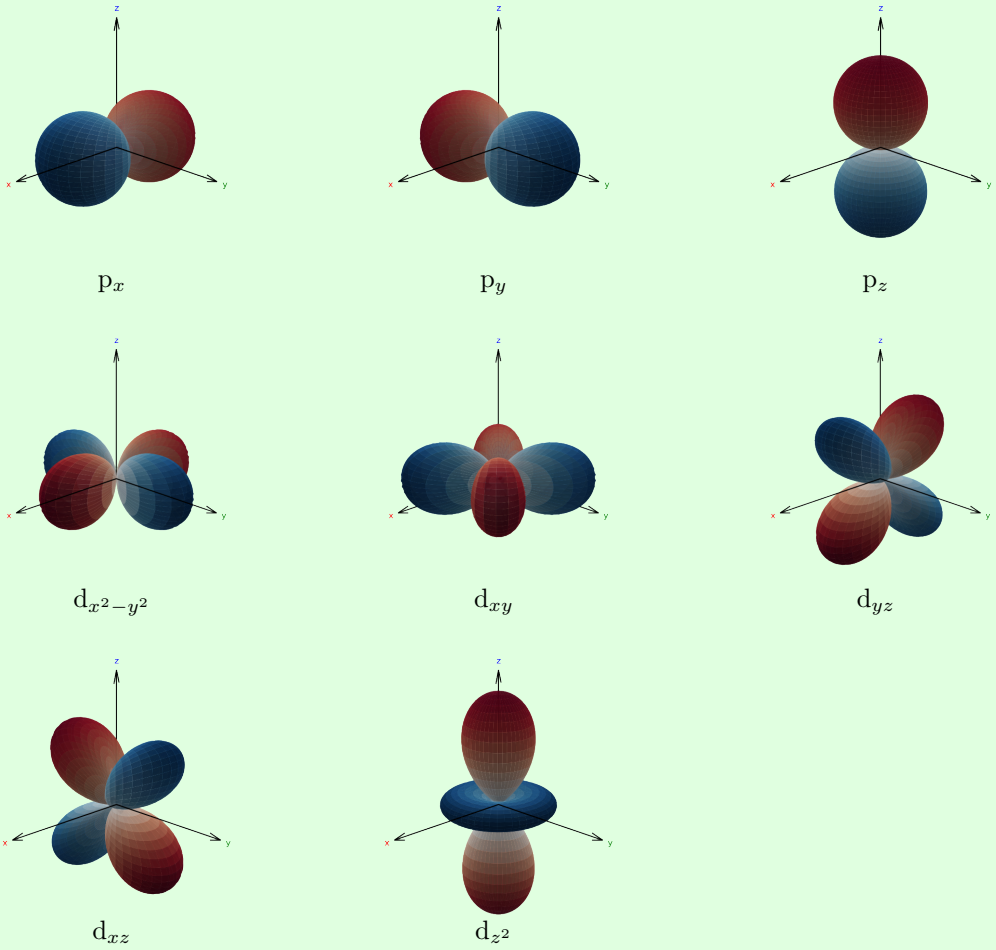

Figure 11.4: Diagrams of 3 2p-orbitals and 5 3d-orbitals.

Consequently, s rather than d_{z^2} takes part in the dsp^2 hybridization scheme, and d_{z^2} is typically regarded as a non-bonding or weakly interacting orbital in the square planar σ-framework, in the general qualitative analysis.
Now we solve the explicit expressions for the 4 hybrid orbitals.

- For the $\Gamma^{A_{1g}}$ representation, we have

$$P^{A_{1g}}v_1 = \sum_R \chi^{A_{1g}*}(R)\boldsymbol{O}_R v_1 = \sum_R \boldsymbol{O}_R v_1 = 4(v_1+v_2+v_3+v_4).$$

  Thus, the only normalized basis function of the $\Gamma^{A_{1g}}$ representation is

$$\psi^{a_{1g}} = \frac{1}{\sqrt{(P^{A_{1g}}v_1|P^{A_{1g}}v_1)}}P^{A_{1g}}v_1 = \frac{1}{8}4(v_1+v_2+v_3+v_4) = \frac{1}{2}(v_1+v_2+v_3+v_4), \qquad (11.15)$$

  and it should be equal to s.

- For the $\Gamma^{B_{1g}}$ representation, similarly, we have

$$P^{B_{1g}}v_1 = \sum_R \chi^{B_{1g}*}(R)\boldsymbol{O}_R v_1 = 4(-v_1+v_2-v_3+v_4).$$

  Thus, the only normalized basis function of the $\Gamma^{A_{1g}}$ representation is

$$\psi^{b_{1g}} = \frac{1}{\sqrt{(P^{B_{1g}}v_1|P^{B_{1g}}v_1)}}P^{B_{1g}}v_1 = \frac{1}{8}4(-v_1+v_2-v_3+v_4) = \frac{1}{2}(-v_1+v_2-v_3+v_4), \qquad (11.16)$$

and it should be equal to $\mathrm{d}_{x^2-y^2}$.

- For the Γ^{E_u} representation, similarly, we have

$$P^{E_u}v_1 = \sum_R \chi^{E_u*}(R)\boldsymbol{O}_R v_1 = 4(v_1 - v_3),$$
$$P^{E_u}v_2 = \sum_R \chi^{E_u*}(R)\boldsymbol{O}_R v_2 = 4(v_2 - v_4).$$

It is easy to verify that these two basis functions are orthogonal. We normalize them:

$$\psi_1^{e_u} = \frac{1}{\sqrt{(P^{E_u}v_1|P^{E_u}v_1)}}P^{E_u}v_1 = \frac{1}{4\sqrt{2}}4(v_1 - v_3) = \frac{1}{\sqrt{2}}(v_1 - v_3),$$
$$\psi_2^{e_u} = \frac{1}{\sqrt{(P^{E_u}v_2|P^{E_u}v_2)}}P^{E_u}v_2 = \frac{1}{4\sqrt{2}}4(v_2 - v_4) = \frac{1}{\sqrt{2}}(v_2 - v_4).$$

Because both v_1 and v_3 are on the x axis while both v_2 and v_4 are on the y axis, thus $\psi_1^{e_u}$, $\psi_2^{e_u}$ should be p_x and p_y, respectively.

Summarizing these contributions, we obtain a system of linear equations:

$$\begin{pmatrix} \mathrm{s} \\ \mathrm{d}_{x^2-y^2} \\ \mathrm{p}_x \\ \mathrm{p}_y \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \end{pmatrix} = A \begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \end{pmatrix}.$$

It is easy to verift that the transition matrix A is an real orthogonal matrix and thus $A^{-1} = \tilde{A}$, viz., eqn (A.4-1.12) at the page 61 in the textbook. Hence, we obtain

$$\begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & \frac{1}{\sqrt{2}} \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \mathrm{s} \\ \mathrm{d}_{x^2-y^2} \\ \mathrm{p}_x \\ \mathrm{p}_y \end{pmatrix}.$$

Now we can demonstrate the explicit expressions for the 4 σ-hybrid orbitals. Now we substitute v_i by ψ_i:

$$\psi_1 = \frac{1}{2}\mathrm{s} - \frac{1}{2}\mathrm{d}_{x^2-y^2} + \frac{1}{\sqrt{2}}\mathrm{p}_x, \tag{11.17}$$
$$\psi_2 = \frac{1}{2}\mathrm{s} + \frac{1}{2}\mathrm{d}_{x^2-y^2} + \frac{1}{\sqrt{2}}\mathrm{p}_y, \tag{11.18}$$
$$\psi_3 = \frac{1}{2}\mathrm{s} - \frac{1}{2}\mathrm{d}_{x^2-y^2} - \frac{1}{\sqrt{2}}\mathrm{p}_x, \tag{11.19}$$
$$\psi_4 = \frac{1}{2}\mathrm{s} + \frac{1}{2}\mathrm{d}_{x^2-y^2} - \frac{1}{\sqrt{2}}\mathrm{p}_y. \tag{11.20}$$

Remark

Through this problem and the subsequent chapter, it becomes evident that while group theory is an indispensable tool in quantum chemistry, its power lies primarily in qualitative symmetry-based predictions. A comprehensive understanding of a specific molecular system's chemical structure can only be achieved by integrating these symmetry principles with quantitative quantum mechanical calculations, which account for the unique energy profiles and electronic environments of the system.