CHAPTER 11

Hybrid Orbitals

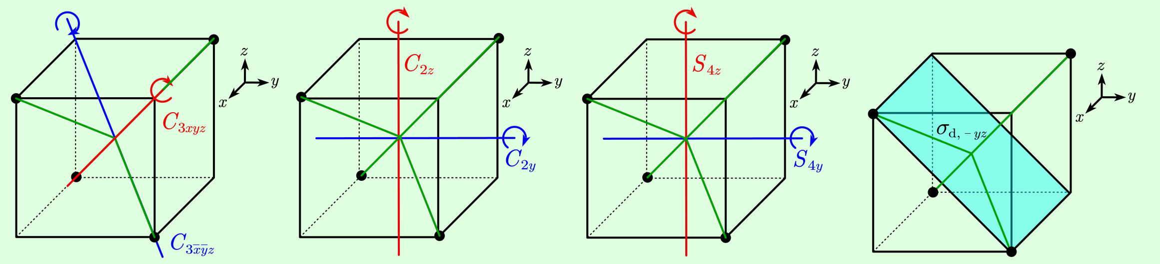
Exercise 11.1

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

Solution 11.1

Firstly, the information of seven (un-normalized) f-orbitals is listed below and they are marked in my symbols.

angular function	f-orbital symfol	my symbol
$\sin\theta\cos\phi(5\sin^2\theta\cos^2\phi-3)$	$\mathrm{f}_{x(5x^2-3r^2)}$ or f_{x^3}	f_1
$\sin\theta\sin\phi(5\sin^2\theta\sin^2\phi-3)$	$\mathrm{f}_{y(5y^2-3r^2)}$ or f_{y^3}	f_2
$5\cos^3\theta-3\cos\theta$	$\mathrm{f}_{z(5z^2-3r^2)}$ or f_{z^3}	f_3
$\sin\theta\cos\phi(\cos^2\theta-\sin^2\theta\sin^2\phi)$	$\mathrm{f}_{x(z^2-y^2)}$	f_4
$\sin\theta\sin\phi(\cos^2\theta-\sin^2\theta\cos^2\phi)$	$\mathrm{f}_{y(z^2-x^2)}$	f_5
$\sin^2\theta\cos\phi\cos 2\phi$	$\mathrm{f}_{z(x^2-y^2)}$	f_6
$\sin^2\theta\cos\phi\sin 2\phi$	f_{xyz}	f_7



class $\{C_3\}$ class $\{C_2\}$ class $\{S_4\}$ class $\{\sigma_\mathrm{d}\}$

Figure 11.1: aaaaaaa

Then, the definition of all operation R is demonstrated below, and they are classified according to their classes. Note that $R(x',y',z')$ means that x, y, z are converted to x', y', z', respectively.

- class E

  There is only one element, i.e. identical operation E, which is $E(x,y,z)$.

- class C_3

  There are 8 elements, whose information is listed below.

$C_{3xyz}(y,z,x)$	rotate $\frac{2\pi}{3}$ clockwise around $\boldsymbol{i}+\boldsymbol{j}+\boldsymbol{k}$
$C_{3\bar{x}\bar{y}z}^{-1}(z,x,y)$	rotate $\frac{4\pi}{3}$ clockwise around $\boldsymbol{i}+\boldsymbol{j}+\boldsymbol{k}$
$C_{3\bar{x}\bar{y}z}(y,\bar{z},\bar{x})$	rotate $\frac{2\pi}{3}$ clockwise around $-\boldsymbol{i}-\boldsymbol{j}+\boldsymbol{k}$
$C_{3\bar{x}\bar{y}z}^{-1}(\bar{z},x,\bar{y})$	rotate $\frac{4\pi}{3}$ clockwise around $-\boldsymbol{i}-\boldsymbol{j}+\boldsymbol{k}$
$C_{3\bar{x}y\bar{z}}(\bar{y},\bar{z},x)$	rotate $\frac{2\pi}{3}$ clockwise around $-\boldsymbol{i}+\boldsymbol{j}-\boldsymbol{k}$
$C_{3\bar{x}y\bar{z}}^{-1}(z,\bar{x},\bar{y})$	rotate $\frac{4\pi}{3}$ clockwise around $-\boldsymbol{i}+\boldsymbol{j}-\boldsymbol{k}$
$C_{3x\bar{y}\bar{z}}(\bar{y},z,\bar{x})$	rotate $\frac{2\pi}{3}$ clockwise around $\boldsymbol{i}-\boldsymbol{j}-\boldsymbol{k}$
$C_{3x\bar{y}\bar{z}}^{-1}(\bar{z},\bar{x},y)$	rotate $\frac{4\pi}{3}$ clockwise around $\boldsymbol{i}-\boldsymbol{j}-\boldsymbol{k}$

- class C_2

  There are 3 elements, whose information is listed below.

$C_{2x}(x, \bar{y}, \bar{z})$	rotate π clockwise around x-axis
$C_{2y}(\bar{x}, y, \bar{z})$	rotate π clockwise around y-axis
$C_{2z}(\bar{x}, \bar{y}, z)$	rotate π clockwise around z-axis

- class S_4

  There are 6 elements, whose information is listed below.

$S_{4x}(\bar{x}, \bar{z}, y)$	rotate $\frac{\pi}{2}$ clockwise around x-axis and then perform horizontal mirror reflection
$S_{4x}^3(\bar{x}, z, \bar{y})$	rotate $\frac{3\pi}{2}$ clockwise around x-axis and then perform horizontal mirror reflection
$S_{4y}(z, \bar{y}, \bar{x})$	rotate $\frac{\pi}{2}$ clockwise around y-axis and then perform horizontal mirror reflection
$S_{4y}^3(\bar{z}, \bar{y}, x)$	rotate $\frac{3\pi}{2}$ clockwise around y-axis and then perform horizontal mirror reflection
$S_{4z}(\bar{y}, x, \bar{z})$	rotate $\frac{\pi}{2}$ clockwise around z-axis and then perform horizontal mirror reflection
$S_{4z}^3(y, \bar{x}, \bar{z})$	rotate $\frac{3\pi}{2}$ clockwise around z-axis and then perform horizontal mirror reflection

- class σ_{d}

  There are 6 elements, whose information is listed below.

$\sigma_{\mathrm{d},yz}(x, z, y)$	perform mirror reflection about the $y - z = 0$ plane
$\sigma_{\mathrm{d},-yz}(x, \bar{z}, \bar{y})$	perform mirror reflection about the $y + z = 0$ plane
$\sigma_{\mathrm{d},xz}(z, y, x)$	perform mirror reflection about the $x - z = 0$ plane
$\sigma_{\mathrm{d},-xz}(\bar{z}, y, \bar{x})$	perform mirror reflection about the $x + z = 0$ plane
$\sigma_{\mathrm{d},xy}(y, x, z)$	perform mirror reflection about the $x - y = 0$ plane
$\sigma_{\mathrm{d},-xy}(\bar{y}, \bar{x}, z)$	perform mirror reflection about the $x + y = 0$ plane

Next, the result of the transformation of these orbitals under O_R is listed below.

element	E	C_{3xyz}	C_{3xyz}^{-1}	$C_{3\bar{x}\bar{y}z}$	$C_{3\bar{x}\bar{y}z}^{-1}$	$C_{3\bar{x}y\bar{z}}$	$C_{3\bar{x}y\bar{z}}^{-1}$	$C_{3x\bar{y}\bar{z}}$	$C_{3x\bar{y}\bar{z}}^{-1}$	C_{2x}	C_{2y}	C_{2z}
f_1	f_1	f_2	f_3	f_2	$-f_3$	$-f_3$	$-f_2$	f_3	$-f_2$	f_1	$-f_1$	$-f_1$
f_4	f_4	$-f_5$	$-f_6$	$-f_5$	f_6	f_5	$-f_6$	f_5	f_6	f_4	$-f_4$	$-f_4$
f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7
element	S_{4x}	S_{4x}^3	S_{4y}	S_{4y}^3	S_{4z}	S_{4z}^3	$\sigma_{\mathrm{d},yz}$	$\sigma_{\mathrm{d},-yz}$	$\sigma_{\mathrm{d},xz}$	$\sigma_{\mathrm{d},-xz}$	$\sigma_{\mathrm{d},xy}$	$\sigma_{\mathrm{d},-xy}$
f_1	$-f_1$	$-f_1$	f_3	$-f_3$	$-f_2$	f_2	f_1	f_1	f_3	$-f_3$	f_2	$-f_2$
f_4	f_4	f_4	f_6	$-f_6$	$-f_5$	f_5	$-f_4$	$-f_4$	f_6	$-f_6$	f_5	$-f_5$
f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7	f_7

Here, we check the character table of the point group $\mathscr{T}_{\mathrm{d}}$,

$\mathscr{T}_{\mathrm{d}}$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_{\mathrm{d}}$		
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	$(x,\, y,\, z)$	$(xy,\, xz,\, yz)$

and we find the character below for Γ^{hyb} for the $\mathscr{T}_{\mathrm{d}}$ point group.

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

We can calculate the reduction of representation Γ^{hyb},

$$
\begin{aligned}
a_1 &= \frac{1}{24}[1 \times 7 \times 1 + 8 \times 1 \times 1 + 3 \times (-1) \times 1 + 6 \times 1 \times 1 + 6 \times 1 \times 1] = 1, \\
a_2 &= \frac{1}{24}[1 \times 7 \times 1 + 8 \times 1 \times 1 + 3 \times (-1) \times 1 + 6 \times 1 \times (-1) + 6 \times 1 \times (-1)] = 0, \\
e &= \frac{1}{24}[1 \times 7 \times 2 + 8 \times 1 \times (-1) + 3 \times (-1) \times 2 + 6 \times 1 \times 0 + 6 \times 1 \times 0] = 0, \\
t_1 &= \frac{1}{24}[1 \times 7 \times 3 + 8 \times 1 \times 0 + 3 \times (-1) \times (-1) + 6 \times 1 \times 1 + 6 \times 1 \times (-1)] = 1, \\
t_2 &= \frac{1}{24}[1 \times 7 \times 3 + 8 \times 1 \times 0 + 3 \times (-1) \times (-1) + 6 \times 1 \times (-1) + 6 \times 1 \times 1] = 1,
\end{aligned}
$$

and we obtain

$$\Gamma^{\text{hyb}} = \Gamma^{A_1} \oplus \Gamma^{T_1} \oplus \Gamma^{T_2}. \tag{11.1}$$

For simplification, we summarize the operations of the same classes.

$\mathscr{T}_{\text{d}}$	O_E	$\sum_{k=1}^{8} O_{C_{3k}}$	$\sum_{k=1}^{3} O_{C_{2k}}$	$\sum_{k=1}^{6} O_{S_{4k}}$	$\sum_{k=1}^{6} O_{\sigma_{\text{d},k}}$
f_1	f_1	0	$-f_1$	$-2f_1$	$2f_1$
f_4	f_4	0	$-f_4$	$2f_4$	$-2f_4$
f_7	f_7	$8f_7$	$3f_7$	$6f_7$	$6f_7$

$$\begin{aligned}
P^{A_1} f_1 &= (1 \times O_E + 1 \times \sum_{k=1}^{8} O_{C_{3k}} + 1 \times \sum_{k=1}^{3} O_{C_{2k}} + 1 \times \sum_{k=1}^{6} O_{S_{4k}} + 1 \times \sum_{k=1}^{6} O_{\sigma_{\text{d},k}}) f_1 = 0, \\
P^{A_2} f_1 &= (1 \times O_E + 1 \times \sum_{k=1}^{8} O_{C_{3k}} + 1 \times \sum_{k=1}^{3} O_{C_{2k}} + (-1) \times \sum_{k=1}^{6} O_{S_{4k}} + (-1) \times \sum_{k=1}^{6} O_{\sigma_{\text{d},k}}) f_1 = 0, \\
P^{E} f_1 &= (2 \times O_E + (-1) \times \sum_{k=1}^{8} O_{C_{3k}} + 2 \times \sum_{k=1}^{3} O_{C_{2k}} + 0 \times \sum_{k=1}^{6} O_{S_{4k}} + 0 \times \sum_{k=1}^{6} O_{\sigma_{\text{d},k}}) f_1 = 0, \\
P^{T_1} f_1 &= (3 \times O_E + 0 \times \sum_{k=1}^{8} O_{C_{3k}} + (-1) \times \sum_{k=1}^{3} O_{C_{2k}} + 1 \times \sum_{k=1}^{6} O_{S_{4k}} + (-1) \times \sum_{k=1}^{6} O_{\sigma_{\text{d},k}}) f_1 = 0, \\
P^{T_2} f_1 &= (3 \times O_E + 0 \times \sum_{k=1}^{8} O_{C_{3k}} + (-1) \times \sum_{k=1}^{3} O_{C_{2k}} + (-1) \times \sum_{k=1}^{6} O_{S_{4k}} + 1 \times \sum_{k=1}^{6} O_{\sigma_{\text{d},k}}) f_1 = 8f_1.
\end{aligned}$$

Thus, f_1 belongs to T_2, which is a three-dimentional irreducible representation. With

$$C_{3xyz} f_1 = f_2, \quad C_{3xyz}^{-1} f_1 = f_3,$$

we conclude that f_1, f_2 and f_3 belong to T_2.
Similarly, we note

$$P^{A_1} f_4 = 0, \quad P^{A_2} f_4 = 0, \quad P^{E} f_4 = 0, \quad P^{T_1} f_4 = 8f_4, \quad P^{T_2} f_4 = 0.$$

So f_4 belongs to T_1. Besides, with

$$C_{3xyz} f_4 = -f_5, \quad C_{3xyz}^{-1} f_4 = -f_6,$$

we can also conclude that f_4, f_5 and f_6 belong to the same three-dimentional irreducible representation T_1.

$$P^{A_1} f_7 = 24f_7, \quad P^{A_2} f_7 = 0, \quad P^{E} f_7 = 0, \quad P^{T_1} f_7 = 0, \quad P^{T_2} f_7 = 0.$$

Thus, we conclude that f_7 belongs to the one-dimentional irreducible representation A_1.
In conclusion, we find

- $f_1 \equiv \mathrm{f}_{x(5x^2-3r^2)}$, $f_2 \equiv \mathrm{f}_{y(5y^2-3r^2)}$ and $f_3 \equiv \mathrm{f}_{z(5z^2-3r^2)}$ belong to the three-dimentional irreducible representation T_2,
- $f_4 \equiv \mathrm{f}_{x(z^2-y^2)}$, $f_5 \equiv \mathrm{f}_{y(z^2-x^2)}$ and $f_6 \equiv \mathrm{f}_{z(x^2-y^2)}$ belong to the three-dimentional irreducible representation T_1,
- $f_7 \equiv \mathrm{f}_{xyz}$ belongs to the one-dimentional irreducible representation A_1.

Exercise 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 $\mathrm{d}_{x^2-y^2}$.

Solution 11.2

The structure of a general molecule AB_6 of octahedral symmetry is shown in Fig 11.2.

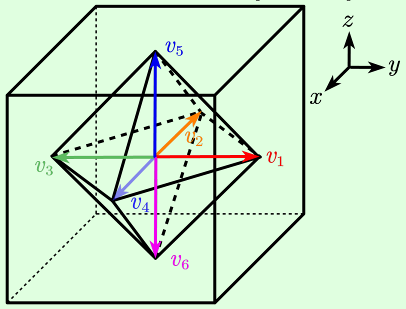


Figure 11.2: A set of vectors v_1, v_2, v_3, v_4, v_5, and v_6 representing the six σ-hybrid orbitals used by the atom A to bond the six B atoms in AB_6.

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

$\mathscr{O}_\mathrm{h}$	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		
4 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		

The character for Γ^{hyb} for the $\mathscr{O}_\mathrm{h}$ point group is

$\mathscr{O}_\mathrm{h}$	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

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

$\Gamma^{A_{1g}}$	Γ^{E_g}	$\Gamma^{T_{1u}}$
s	$(\mathrm{d}_{z^2},\, \mathrm{d}_{x^2-y^2})$	$(\mathrm{p}_x,\, \mathrm{p}_y,\, \mathrm{p}_z)$

In conclusion, we have proved 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 $\mathrm{d}_{x^2-y^2}$.

Exercise 11.3

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

Solution 11.3

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

$\mathscr{D}_{4h}$	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	$(x,\ y)$	

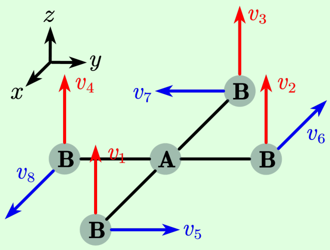


Figure 11.3: rehstrjstfjs

$\mathscr{D}_{4h}$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\chi^{\text{hyb}}(C_i)$	8	0	0	-4	0	0	0	0	0	0
$\chi^{\text{hyb}}_{\text{perp}}(C_i)$	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

$$\Gamma^{\text{hyb}}_{\text{perp}} = \Gamma^{A_{2u}} \oplus \Gamma^{B_{2u}} \oplus \Gamma^{E_g},$$
$$\Gamma^{\text{hyb}}_{\text{plane}} = \Gamma^{A_{2g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_u}.$$

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

Thus, we conclude two conclusions.

- There will be only 3 π-bonds which are formed by p_z, d_{xz}, and d_{yz}, perpendicular to the molecular plane and they are shared equally amongst the 4 B atoms.
- There will be also only 3 π-bonds which are formed by d_{xy}, p_x, and p_y, in the molecular plane and they are shared equally amongst the 4 B atoms.

Exercise 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, $\mathrm{d}_{x^2-y^2}$, p_x, and p_y. Find explicit expressions for the four hybrid orbitals.

Solution 11.4

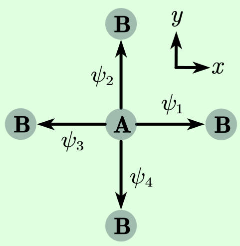


Figure 11.4: fdsgfgsgh