

### Exercise 11.1

Determine the irreducible representations of  $\mathcal{T}_d$  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 symbol	my symbol
$\sin \theta \cos \phi (5 \sin^2 \theta \cos^2 \phi - 3)$	$f_x(5x^2 - 3r^2)$ or $f_{x^3}$	$f_1$
$\sin \theta \sin \phi (5 \sin^2 \theta \sin^2 \phi - 3)$	$f_y(5y^2 - 3r^2)$ or $f_{y^3}$	$f_2$
$5 \cos^3 \theta - 3 \cos \theta$	$f_z(5z^2 - 3r^2)$ or $f_{z^3}$	$f_3$
$\sin \theta \cos \phi (\cos^2 \theta - \sin^2 \theta \sin^2 \phi)$	$f_x(z^2 - y^2)$	$f_4$
$\sin \theta \sin \phi (\cos^2 \theta - \sin^2 \theta \cos^2 \phi)$	$f_y(z^2 - x^2)$	$f_5$
$\sin^2 \theta \cos \phi \cos 2\phi$	$f_z(x^2 - y^2)$	$f_6$
$\sin^2 \theta \cos \phi \sin 2\phi$	$f_{xyz}$	$f_7$

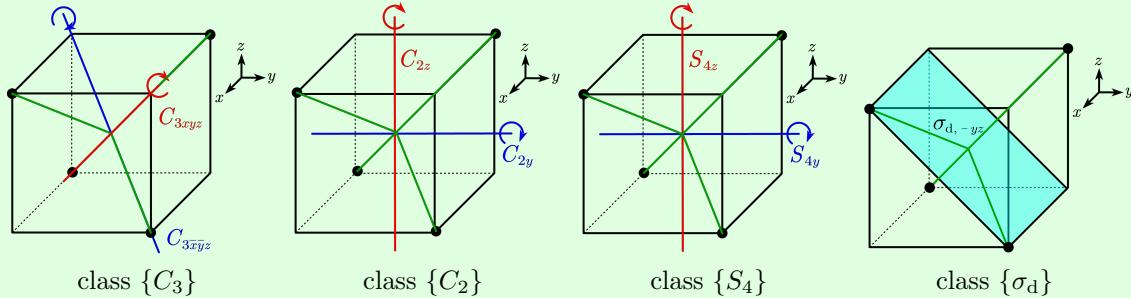


Figure 11.1: aaaaaaa

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

- class  $C_2$

There are 3 elements, whose information is listed below.

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

There are 6 elements, whose information is listed below.

$\sigma_{d,yz}(x, z, y)$	perform mirror reflection about the $y - z = 0$ plane
$\sigma_{d,-yz}(x, \bar{z}, \bar{y})$	perform mirror reflection about the $y + z = 0$ plane
$\sigma_{d,xz}(z, y, x)$	perform mirror reflection about the $x - z = 0$ plane
$\sigma_{d,-xz}(\bar{z}, y, \bar{x})$	perform mirror reflection about the $x + z = 0$ plane
$\sigma_{d,xy}(y, x, z)$	perform mirror reflection about the $x - y = 0$ plane
$\sigma_{d,-xy}(\bar{y}, \bar{x}, z)$	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	$E$	$C_{3xyz}$	$C_{3xyz}^{-1}$	$C_{3\bar{x}\bar{y}z}$	$C_{3\bar{x}\bar{y}z}^{-1}$	$C_{3\bar{y}z\bar{x}}$	$C_{3\bar{y}z\bar{x}}^{-1}$	$C_{3x\bar{y}\bar{z}}$	$C_{3x\bar{y}\bar{z}}^{-1}$	$C_{2x}$	$C_{2y}$	$C_{2z}$
$f_1$	$f_1$	$f_2$	$f_3$	$f_2$	$-f_3$	$-f_3$	$-f_2$	$f_3$	$-f_2$	$f_1$	$-f_1$	$-f_1$
$f_4$	$f_4$	$-f_5$	$-f_6$	$-f_5$	$f_6$	$f_5$	$-f_6$	$f_5$	$f_6$	$f_4$	$-f_4$	$-f_4$
$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$
element	$S_{4x}$	$S_{4x}^3$	$S_{4y}$	$S_{4y}^3$	$S_{4z}$	$S_{4z}^3$	$\sigma_{d,yz}$	$\sigma_{d,-yz}$	$\sigma_{d,xz}$	$\sigma_{d,-xz}$	$\sigma_{d,xy}$	$\sigma_{d,-xy}$
$f_1$	$-f_1$	$-f_1$	$f_3$	$-f_3$	$-f_2$	$f_2$	$f_1$	$f_1$	$f_3$	$-f_3$	$f_2$	$-f_2$
$f_4$	$f_4$	$f_4$	$f_6$	$-f_6$	$-f_5$	$f_5$	$-f_4$	$-f_4$	$f_6$	$-f_6$	$f_5$	$-f_5$
$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$	$f_7$

Here, we check the character table of the point group  $\mathcal{T}_d$ ,

$\mathcal{T}_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
$A_1$	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	$(x, y, z)$
						$(xy, xz, yz)$

and we find the character below for  $\Gamma^{\text{hyb}}$  for the  $\mathcal{T}_d$  point group.

$\mathcal{T}_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\chi^{\text{hyb}}(C_i)$	7	1	-1	1	1

We can calculate the reduction of representation  $\Gamma^{\text{hyb}}$ ,

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

and we obtain

$$\Gamma^{\text{hyb}} = \Gamma^{A_1} \oplus \Gamma^{T_1} \oplus \Gamma^{T_2}. \quad (11.1)$$

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

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

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

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

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

### Exercise 11.2

Show that for a molecule of octahedral symmetry the  $\sigma$ -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 a general molecule  $AB_6$  of octahedral symmetry is shown in Fig 11.2.

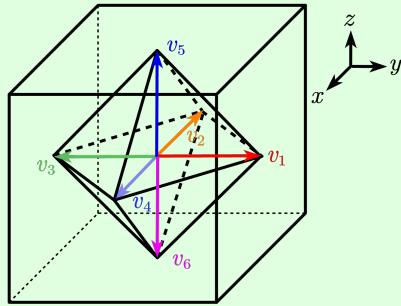


Figure 11.2: A set of vectors  $v_1, v_2, v_3, v_4, v_5$ , and  $v_6$  representing the six  $\sigma$ -hybrid orbitals used by the atom A to bond the six B atoms in  $\text{AB}_6$ .

The character table of the point group  $\mathcal{O}_h$  is shown below.

$\mathcal{O}_h$	$E$	$8C_3$	$3C_2$	$6C_4$	$6C'_2$	$i$	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$	
$A_{1g}$	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	
$4 A_{2u}$	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  $\Gamma^{\text{hyb}}$  for the  $\mathcal{O}_h$  point group is

$\mathcal{O}_h$	$E$	$8C_3$	$3C_2$	$6C_4$	$6C'_2$	$i$	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
$\chi^{\text{hyb}}(C_i)$	6	0	2	2	0	0	0	4	0	2

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

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

In conclusion, we have proved that for a molecule of octahedral symmetry the  $\sigma$ -bonding hybrid orbitals on the central atom are composed of six atomic orbitals, s,  $p_x$ ,  $p_y$ ,  $p_z$ ,  $d_{z^2}$ , and  $d_{x^2-y^2}$ .

### Exercise 11.3

Determine what type of  $\pi$ -bonding hybrid orbitals can be formed for the square planar  $\text{AB}_4$  molecule which belongs to the  $\mathcal{D}_{4h}$  point group.

### Solution 11.3

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

$\mathcal{D}_{4h}$	$E$	$2C_4$	$C_2$	$2C'_2$	$2C''_2$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$	
$A_{1g}$	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	$(R_x, R_y)$
$A_{1u}$	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	$(x, y)$

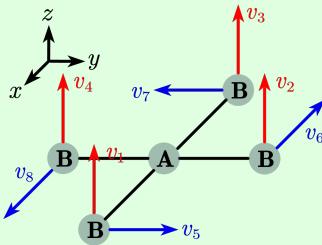


Figure 11.3: rehstrjstfjs

$\mathcal{D}_{4h}$	$E$	$2C_4$	$C_2$	$2C'_2$	$2C''_2$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$	
$\chi^{\text{hyb}}(C_i)$	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	

$$\begin{aligned}\Gamma_{\text{perp}}^{\text{hyb}} &= \Gamma^{A_{2u}} \oplus \Gamma^{B_{2u}} \oplus \Gamma^{E_g}, \\ \Gamma_{\text{plane}}^{\text{hyb}} &= \Gamma^{A_{2g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_u}.\end{aligned}$$

$\Gamma_{\text{perp}}^{\text{hyb}}$			$\Gamma_{\text{plane}}^{\text{hyb}}$		
$\Gamma^{A_{2u}}$	$\Gamma^{B_{2u}}$	$\Gamma^{E_g}$	$\Gamma^{A_{2g}}$	$\Gamma^{B_{2g}}$	$\Gamma^{E_u}$
p <sub>z</sub>	none	(d <sub>xz</sub> , d <sub>yz</sub> )	none	d <sub>xy</sub>	(p <sub>x</sub> , p <sub>y</sub> )

Thus, we conclude two conclusions.

- There will be only 3  $\pi$ -bonds which are formed by p<sub>z</sub>, d<sub>xz</sub>, and d<sub>yz</sub>, perpendicular to the molecular plane and they are shared equally amongst the 4 B atoms.
- There will be also only 3  $\pi$ -bonds which are formed by d<sub>xy</sub>, p<sub>x</sub>, and p<sub>y</sub>, in the molecular plane and they are shared equally amongst the 4 B atoms.

#### Exercise 11.4

Show that for the square planar AB<sub>4</sub> molecule a possible set of four  $\sigma$ -hybrid orbitals on A is composed of the atomic orbitals: s, d<sub>x<sup>2</sup>-y<sup>2</sup></sub>, p<sub>x</sub>, and p<sub>y</sub>. Find explicit expressions for the four hybrid orbitals.

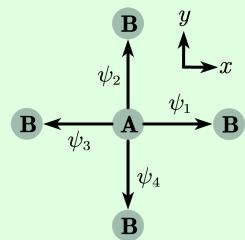
**Solution 11.4**

Figure 11.4: fdsgfgsgh