Advanced Physical Chemistry II
HW

王石嵘
161240065

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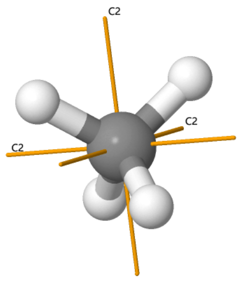
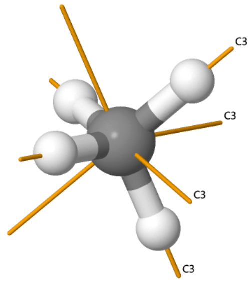
Contents

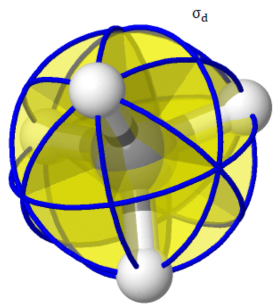
12 Group Theory: the Exploitation of Symmetry

4, 12, 18, 24, 26, 31, 33, 34, 37, 40

12-4 The symmetry elements of CH_4 is as follows. (each S_4 axis is coincident with C_2 axis)[1]







12-12

$$C_3\sigma_v = \sigma_v' \tag{12.1}$$
$$C_3\sigma_v'' = \sigma_v \tag{12.2}$$

12-18 For the irreducible representation of C_{3v},

$$\hat{E}\begin{pmatrix} u_x \\ u_y \end{pmatrix} = \begin{pmatrix} u_x \\ u_y \end{pmatrix} \tag{12.3}$$

Set the z-axis as C_3 axis, we have

$$\hat{C}_3\begin{pmatrix} u_x \\ u_y \end{pmatrix} = \begin{pmatrix} \cos\frac{-\pi}{3} & \sin\frac{-\pi}{3} \\ -\sin\frac{-\pi}{3} & \cos\frac{-\pi}{3} \end{pmatrix}\begin{pmatrix} u_x \\ u_y \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}\begin{pmatrix} u_x \\ u_y \end{pmatrix} \tag{12.4}$$

$$\hat{C}_3^2\begin{pmatrix} u_x \\ u_y \end{pmatrix} = \begin{pmatrix} \cos\frac{-2\pi}{3} & \sin\frac{-2\pi}{3} \\ -\sin\frac{-2\pi}{3} & \cos\frac{-2\pi}{3} \end{pmatrix}\begin{pmatrix} u_x \\ u_y \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}\begin{pmatrix} u_x \\ u_y \end{pmatrix} \tag{12.5}$$

Set the x-axis on σ_v, we have

$$\begin{cases} \hat{\sigma}_v u_x & = u_x \\ \hat{\sigma}_v u_y & = -u_y \end{cases} \Rightarrow \hat{\sigma}_v\begin{pmatrix} u_x \\ u_y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} u_x \\ u_y \end{pmatrix} \tag{12.6}$$

Similarly, we get

$$\hat{\sigma}_v'\begin{pmatrix} u_x \\ u_y \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}\begin{pmatrix} u_x \\ u_y \end{pmatrix} \tag{12.7}$$

$$\hat{\sigma}_v''\begin{pmatrix} u_x \\ u_y \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}\begin{pmatrix} u_x \\ u_y \end{pmatrix} \tag{12.8}$$

Thus, (u_x, u_y) forms a joint basis for the irreducible representation of C_{3v}.

[1]The pictures are taken from chemtube3d.

12-24 No, because $2p_{zN}$ and $1s_{H_A} + 1s_{H_B} + 1s_{H_C}$ both belongs to A_1.

12-26

•

$$\begin{aligned}\frac{\sqrt{12}}{6}(2\phi_4 - \phi_3) &= \frac{\sqrt{12}}{6}\left[2\frac{1}{\sqrt{12}}(\psi_1 + 2\psi_2 + \psi_3 - \psi_4 - 2\psi_5 - \psi_6) - \frac{1}{\sqrt{12}}(2\psi_1 + \psi_2 - \psi_3 - 2\psi_4 - \psi_5 + \psi_6)\right] \\ &= \frac{1}{6}(0 + 3\psi_2 + 3\psi_3 + 0 - 3\psi_5 - 3\psi_6) \\ &= \frac{1}{2}(\psi_2 + \psi_3 - \psi_5 - \psi_6) \\ &= \phi_4' \end{aligned} \tag{12.9}$$

•

$$\begin{aligned}\langle \phi_4' \mid \phi_4' \rangle &= \frac{1}{3}\langle 2\phi_4 - \phi_3 \mid 2\phi_4 - \phi_3 \rangle \\ &= \frac{1}{3}(4 + 1 - 4\langle \phi_4 \mid \phi_3 \rangle)\end{aligned} \tag{12.10}$$

while

$$\begin{aligned}\langle \phi_4 \mid \phi_3 \rangle &= \frac{1}{12}\langle \psi_1 + 2\psi_2 + \psi_3 - \psi_4 - 2\psi_5 - \psi_6 \mid 2\psi_1 + \psi_2 - \psi_3 - 2\psi_4 - \psi_5 + \psi_6 \rangle \\ &= \frac{1}{12}(2 + 2 - 1 + 2 + 2 - 1) \\ &= \frac{1}{2}\end{aligned} \tag{12.11}$$

thus

$$\langle \phi_4' \mid \phi_4' \rangle = \frac{1}{3}\left(5 - 4 \times \frac{1}{2}\right) = 1 \tag{12.12}$$

$\therefore$ ϕ_4' is normalized.

•

$$S_{33}' = S_{44}' = 1 \tag{12.13}$$

$$S_{34}' = S_{43}' = \frac{\sqrt{12}}{6}\langle \phi_3 \mid 2\phi_4 - \phi_3 \rangle = 0 \tag{12.14}$$

$$H_{33}' = \left\langle \phi_3 \middle| \widehat{\mathrm{H}} \middle| \phi_3 \right\rangle = \frac{1}{12}(12\alpha + 12\beta) = \alpha + \beta \tag{12.15}$$

$$H_{44}' = \left\langle \phi_4 \middle| \widehat{\mathrm{H}} \middle| \phi_4 \right\rangle = \frac{1}{4}(4\alpha + 4\beta) = \alpha + \beta \tag{12.16}$$

$$H_{34}' = H_{43}' = \left\langle \phi_3 \middle| \widehat{\mathrm{H}} \middle| \phi_4 \right\rangle = \frac{1}{2\sqrt{12}}(0 + 0) = 0 \tag{12.17}$$

thus

$$\begin{vmatrix} \alpha + \beta - E & 0 \\ 0 & \alpha + \beta - E \end{vmatrix} = 0 \Rightarrow E = \alpha + \beta \tag{12.18}$$

12-31

• Since $H_{ii} = \alpha$, $H_{12} = H_{23} = \beta$, $S_{ij} = \delta_{ij}$, we have

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = \beta^3 \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \tag{12.19}$$

thus

$$x^3 - 2x = 0 \Rightarrow x = 0, \pm\sqrt{2} \tag{12.20}$$

- C_{2v} group has 4 operators, $\hat{E}, \hat{C}_2, \hat{\sigma}_v, \hat{\sigma}'_v$.

$$\hat{E}\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix} = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix} \tag{12.21}$$

$$\hat{C}_2\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix} = \begin{pmatrix}0&0&-1\\0&-1&0\\-1&0&0\end{pmatrix}\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix} \tag{12.22}$$

$$\hat{\sigma}_v\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix} = \begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix} \tag{12.23}$$

$$\hat{\sigma}'_v\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix} = \begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix} \tag{12.24}$$

Collect the traces of the matrices above, we get

$$\Gamma = 3 \quad -1 \quad 1 \quad -3 \tag{12.25}$$

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$$a_{A_1} = \frac{1}{4}[3\times 1 + (-1)\times 1 + 1\times 1 + (-3)\times 1] = 0 \tag{12.26}$$

$$a_{A_2} = \frac{1}{4}[3\times 1 + (-1)\times 1 + 1\times (-1) + (-3)\times (-1)] = 1 \tag{12.27}$$

$$a_{B_1} = \frac{1}{4}[3\times 1 + (-1)\times (-1) + 1\times 1 + (-3)\times (-1)] = 2 \tag{12.28}$$

$$a_{B_2} = \frac{1}{4}[3\times 1 + (-1)\times (-1) + 1\times (-1) + (-3)\times 1] = 0 \tag{12.29}$$

thus

$$\Gamma = A_2 + 2B_2 \tag{12.30}$$

which means the secular determinant can be written as the combination of a 1D block and a 2D block.

- Now we generate the symmetric orbitals

$$\widehat{\mathbf{P}}_{A_2}\,\psi_1 = \frac{1}{4}(\psi_1 - \psi_3 - \psi_3 + \psi_1) = \frac{1}{2}(\psi_1 - \psi_3) \tag{12.31}$$

$$\widehat{\mathbf{P}}_{B_1}\,\psi_1 = \frac{2}{4}(\psi_1 + \psi_3 + \psi_3 + \psi_1) = \psi_1 + \psi_3 \tag{12.32}$$

$$\widehat{\mathbf{P}}_{B_1}\,\psi_2 = \frac{2}{4}(\psi_2 + \psi_2 + \psi_2 + \psi_2) = 2\psi_2 \tag{12.33}$$

$$\tag{12.34}$$

After normalization,

$$\phi_1 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_3) \tag{12.35}$$

$$\phi_2 = \psi_2 \tag{12.36}$$

$$\phi_3 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_3) \tag{12.37}$$

$$\tag{12.38}$$

Thus,

$$\begin{vmatrix}\alpha - E & 0 & 0\\ 0 & \alpha - E & \sqrt{2}\beta\\ 0 & \sqrt{2}\beta & \alpha - E\end{vmatrix} = \beta^3\begin{vmatrix}x & 0 & 0\\ 0 & x & \sqrt{2}\\ 0 & \sqrt{2} & x\end{vmatrix} = 0 \tag{12.39}$$

i.e.

$$x(x^2 - 2) = 0 \tag{12.40}$$

$\therefore$

$$E = 0, \pm\sqrt{2} \tag{12.41}$$

i.e.

$$E = \alpha, \alpha \pm \sqrt{2}\beta \tag{12.42}$$

12-33

1. $i = j = A_1$

$$\sum_R \Gamma_{A_1}(R)_{11}\Gamma_{A_1}(R)_{11} = 1+1+1+1+1+1 = \frac{6}{1} \tag{12.43}$$

2. $i = j = A_2$

$$\sum_R \Gamma_{A_2}(R)_{11}\Gamma_{A_2}(R)_{11} = 1+1+1+1+1+1 = \frac{6}{1} \tag{12.44}$$

3. $i = j = E$

$$\sum_R \Gamma_E(R)_{11}\Gamma_E(R)_{11} = 1+\frac{1}{4}+\frac{1}{4}+1+\frac{1}{4}+\frac{1}{4} = \frac{6}{2} \tag{12.45}$$

$$\sum_R \Gamma_E(R)_{22}\Gamma_E(R)_{22} = 1+\frac{1}{4}+\frac{1}{4}+1+\frac{1}{4}+\frac{1}{4} = \frac{6}{2} \tag{12.46}$$

$$\sum_R \Gamma_E(R)_{12}\Gamma_E(R)_{12} = 0+\frac{3}{4}+\frac{3}{4}+0+\frac{3}{4}+\frac{3}{4} = \frac{6}{2} \tag{12.47}$$

$$\sum_R \Gamma_E(R)_{11}\Gamma_E(R)_{12} = 0+\frac{\sqrt{3}}{4}-\frac{\sqrt{3}}{4}+0-\frac{\sqrt{3}}{4}+\frac{\sqrt{3}}{4} = 0 \tag{12.48}$$

$$\sum_R \Gamma_E(R)_{11}\Gamma_E(R)_{22} = 1+\frac{1}{4}+\frac{1}{4}-1-\frac{1}{4}-\frac{1}{4} = 0 \tag{12.49}$$

$$\sum_R \Gamma_E(R)_{12}\Gamma_E(R)_{22} = 0+\frac{\sqrt{3}}{4}-\frac{\sqrt{3}}{4}+0+\frac{\sqrt{3}}{4}-\frac{\sqrt{3}}{4} = 0 \tag{12.50}$$

4. $i = A_1, j = A_2$

$$\sum_R \Gamma_{A_1}(R)_{11}\Gamma_{A_2}(R)_{11} = 1+1+1-1-1-1 = 0 \tag{12.51}$$

5. $i = A_1, j = E$

$$\sum_R \Gamma_{A_1}(R)_{11}\Gamma_E(R)_{11} = 1-\frac{1}{2}-\frac{1}{2}+1-\frac{1}{2}-\frac{1}{2} = 0 \tag{12.52}$$

$$\sum_R \Gamma_{A_1}(R)_{11}\Gamma_{A_2}(R)_{12} = 0-\frac{\sqrt{3}}{2}+\frac{\sqrt{3}}{2}+0+\frac{\sqrt{3}}{2}-\frac{\sqrt{3}}{2} = 0 \tag{12.53}$$

$$\sum_R \Gamma_{A_1}(R)_{11}\Gamma_{A_2}(R)_{22} = 1-\frac{1}{2}-\frac{1}{2}-1+\frac{1}{2}+\frac{1}{2} = 0 \tag{12.54}$$

6. $i = A_2, j = E$

$$\sum_R \Gamma_{A_1}(R)_{11}\Gamma_{A_2}(R)_{11} = 1-\frac{1}{2}-\frac{1}{2}-1+\frac{1}{2}+\frac{1}{2} = 0 \tag{12.55}$$

$$\sum_R \Gamma_{A_1}(R)_{11}\Gamma_{A_2}(R)_{12} = 0-\frac{\sqrt{3}}{2}+\frac{\sqrt{3}}{2}+0-\frac{\sqrt{3}}{2}+\frac{\sqrt{3}}{2} = 0 \tag{12.56}$$

$$\sum_R \Gamma_{A_1}(R)_{11}\Gamma_{A_2}(R)_{22} = 1-\frac{1}{2}-\frac{1}{2}+1-\frac{1}{2}-\frac{1}{2} = 0 \tag{12.57}$$

12-34

a.

$$\sum_R \Gamma_i(R)_{nn}\Gamma_i(R)_{n'n'} = \frac{h}{d_i}\delta_{nn'} \tag{12.58}$$

Since

$$\sum_n\sum_{n'}\sum_R \Gamma_i(R)_{nn}\Gamma_i(R)_{n'n'} = \sum_R\left(\sum_n \Gamma_i(R)_{nn}\right)\left(\sum_{n'}\Gamma_i(R)_{n'n'}\right) = \sum_R[\chi_i(R)]^2 \tag{12.59}$$

and

$$\sum_n\sum_{n'}\frac{h}{d_i}\delta_{nn'} = \frac{h}{d_i}d_i = h \tag{12.60}$$

thus

$$\sum_R[\chi_i(R)]^2 = h \tag{12.61}$$

b.

$$\sum_R \Gamma_i(R)_{nn}\Gamma_j(R)_{n'n'} = \frac{h}{d_i}\delta_{ij}\delta_{nn'} \tag{12.62}$$

Since

$$\sum_n\sum_{n'}\sum_R \Gamma_i(R)_{nn}\Gamma_j(R)_{n'n'} = \sum_R\left(\sum_n \Gamma_i(R)_{nn}\right)\left(\sum_{n'}\Gamma_j(R)_{n'n'}\right) = \sum_R \chi_i(R)\chi_j(R) \tag{12.63}$$

and

$$\sum_n\sum_{n'}\frac{h}{d_i}\delta_{ij}\delta_{nn'} = \frac{h}{d_i}\delta_{ij}d_i = h\delta_{ij} \tag{12.64}$$

thus

$$\sum_R \chi_i(R)\chi_j(R) = h\delta_{ij} \tag{12.65}$$

i.e.

$$\sum_R \chi_i(R)\chi_j(R) = 0 \quad (i \neq j) \tag{12.66}$$

c. That has been obtained in 12-34.b.

12-37 The point group is D_{3h} and $\Gamma = 4 \quad 1 \quad -2 \quad -4 \quad -1 \quad 2$.

$$a_{A_1'} = \frac{1}{12}(4+2-6-4-2+6) = 0 \tag{12.67}$$

$$a_{A_2'} = \frac{1}{12}(4+2+6-4-2-6) = 0 \tag{12.68}$$

$$a_{E'} = \frac{1}{12}(8-2+0-8+2+0) = 0 \tag{12.69}$$

$$a_{A_1''} = \frac{1}{12}(4+2-6+4+2-6) = 0 \tag{12.70}$$

$$a_{A_2''} = \frac{1}{12}(4+2+6+4+2+6) = 2 \tag{12.71}$$

$$a_{E''} = \frac{1}{12}(8-2+0+8-2+0) = 1 \tag{12.72}$$

thus

$$\Gamma = 2A_2'' + E'' \tag{12.73}$$

$$\widehat{\mathbf{P}}_{A_2''}\psi_1 = \frac{1}{12}(\psi_1 + 2\psi_1 + 3\psi_1 + \psi_1 + 2\psi_1 + 3\psi_1) = \psi_1 \tag{12.74}$$

$$\begin{aligned}\widehat{\mathbf{P}}_{A_2''}\psi_2 &= \frac{1}{12}[\psi_2 + (\psi_3+\psi_4) + (\psi_2+\psi_3+\psi_4) + \psi_2 + (\psi_3+\psi_4) + (\psi_2+\psi_3+\psi_4)] \\ &= \frac{1}{3}(\psi_2+\psi_3+\psi_4)\end{aligned} \tag{12.75}$$

$$\widehat{\mathbf{P}}_{E''}\psi_1 = \frac{1}{12}(2\psi_1 - 2\psi_1 + 0 + 2\psi_1 - 2\psi_1 + 0) = 0 \tag{12.76}$$

$$\widehat{\mathbf{P}}_{E''}\psi_2 = \frac{1}{12}[2\psi_2 - (\psi_3+\psi_4) + 0 + 2\psi_2 - (\psi_3+\psi_4) + 0] = \frac{1}{6}(2\psi_2 - \psi_3 - \psi_4) \tag{12.77}$$

$$\widehat{\mathbf{P}}_{E''}\psi_3 = \frac{1}{12}[2\psi_3 - (\psi_2+\psi_4) + 0 + 2\psi_3 - (\psi_2+\psi_4) + 0] = \frac{1}{6}(2\psi_3 - \psi_2 - \psi_4) \tag{12.78}$$

$$\widehat{\mathbf{P}}_{E''}\psi_4 = \frac{1}{12}[2\psi_4 - (\psi_3+\psi_2) + 0 + 2\psi_4 - (\psi_3+\psi_2) + 0] = \frac{1}{6}(2\psi_4 - \psi_2 - \psi_3) \tag{12.79}$$

Remove linear dependence and do normalization, we get

$$\phi_1 = \psi_1 \tag{12.80}$$

$$\phi_2 = \frac{1}{\sqrt{3}}(\psi_2+\psi_3+\psi_4) \tag{12.81}$$

$$\phi_3 = \frac{1}{\sqrt{6}}(2\psi_2 - \psi_3 - \psi_4) \tag{12.82}$$

$$\phi_4 = \frac{1}{\sqrt{6}}(2\psi_3 - \psi_2 - \psi_4) \tag{12.83}$$

thus

$$\begin{vmatrix} \alpha - E & \sqrt{3}\beta & 0 & 0 \\ \sqrt{3}\beta & \alpha - E & 0 & 0 \\ 0 & 0 & \alpha - E & -\alpha/2 - E/2 \\ 0 & 0 & -\alpha/2 - E/2 & \alpha - E \end{vmatrix} = \beta^4 \begin{vmatrix} x & \sqrt{3} & 0 & 0 \\ \sqrt{3} & x & 0 & 0 \\ 0 & 0 & x & -x/2 \\ 0 & 0 & -x/2 & x \end{vmatrix} = 0 \tag{12.84}$$

i.e.

$$(x^2 - 3)x^2 = 0 \tag{12.85}$$

thus

$$x = 0, \pm\sqrt{3} \tag{12.86}$$

i.e.

$$E = \alpha, \alpha \pm \sqrt{3}\beta \tag{12.87}$$

Since there are 4 π electrons,

$$E_\pi = 2(\alpha + \sqrt{3}\beta) + 2\alpha = 4\alpha + 2\sqrt{3}\beta \tag{12.88}$$

12-40

$$a_{A_1'} = \frac{1}{12}(3+0+3+3+0+3) = 1 \tag{12.89}$$

$$a_{A_2'} = \frac{1}{12}(3+0-3+3+0-3) = 0 \tag{12.90}$$

$$a_{E'} = \frac{1}{12}(6+0+0+6+0+0) = 1 \tag{12.91}$$

$$a_{A_1''} = \frac{1}{12}(3+0+3-3+0-3) = 0 \tag{12.92}$$

$$a_{A_2''} = \frac{1}{12}(3+0-3-3+0+3) = 0 \tag{12.93}$$

$$a_{E''} = \frac{1}{12}(6+0+0-6+0+0) = 0 \tag{12.94}$$

thus

$$\Gamma = A_1' + E' \tag{12.95}$$

From the character table of D_{3h}, we can see that A_1' is corresponding to s orbital and E' is corresponding to p_x, p_y or $d_{x^2-y^2}, d_{xy}$ orbitals.