

Exercise 10.1

For the following molecules, determine the point group and the symmetry of the MOs for the π -electrons, and, using Hückel theory, obtain the MOs and orbital energies:

- (a) *trans*-1,3-butadiene,
- (b) ethylene,
- (c) cyclobutadiene,
- (d) cyclopentadienyl radical C_5H_5 ,
- (e) naphthalene,
- (f) phenanthrene.

Solution 10.1

I will solve these issues with Hückel theory.

- (a) 1111111111111111

\mathcal{C}_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1
B_g	1	-1	1	-1
A_u	1	1	-1	-1
B_u	1	-1	-1	1

\mathcal{C}_{2h}	E	C_2	i	σ_h
$\chi^{AO}(C_i)$	4	0	0	-4

$$a_g = \frac{1}{4} \sum_R \chi^{AO}(R) \chi^{A_g}(R) = \frac{1}{4} [1 \times 4 \times 1 + 1 \times 0 \times 1 + 1 \times 0 \times 1 + 1 \times (-4) \times 1] = 0,$$

$$b_g = \frac{1}{4} \sum_R \chi^{AO}(R) \chi^{B_g}(R) = \frac{1}{4} [1 \times 4 \times 1 + 1 \times 0 \times (-1) + 1 \times 0 \times 1 + 1 \times (-4) \times (-1)] = 2,$$

$$a_u = \frac{1}{4} \sum_R \chi^{AO}(R) \chi^{A_u}(R) = \frac{1}{4} [1 \times 4 \times 1 + 1 \times 0 \times 1 + 1 \times 0 \times (-1) + 1 \times (-4) \times (-1)] = 2,$$

$$b_u = \frac{1}{4} \sum_R \chi^{AO}(R) \chi^{B_u}(R) = \frac{1}{4} [1 \times 4 \times 1 + 1 \times 0 \times (-1) + 1 \times 0 \times (-1) + 1 \times (-4) \times 1] = 0.$$

$$\Gamma^{AO} = 2\Gamma^{B_g} \oplus 2\Gamma^{A_u}.$$

\mathcal{C}_{2h}	E	C_2	i	σ_h
ϕ_1	ϕ_1	ϕ_4	$-\phi_4$	$-\phi_1$
ϕ_2	ϕ_2	ϕ_3	$-\phi_3$	$-\phi_2$

$$\Gamma^{B_g} \phi_1 = \sum_R \chi^{B_g}(R) O_R \phi_1 = (O_E - O_{C_2} + O_i - O_{\sigma_h}) \phi_1 = \phi_1 - \phi_4 + (-\phi_4) - (-\phi_1) = 2(\phi_1 - \phi_4),$$

$$\Gamma^{B_g} \phi_2 = \sum_R \chi^{B_g}(R) O_R \phi_2 = (O_E - O_{C_2} + O_i - O_{\sigma_h}) \phi_2 = \phi_2 - \phi_3 + (-\phi_3) - (-\phi_2) = 2(\phi_2 - \phi_3).$$

$$\phi'_1 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_4),$$

$$\phi'_2 = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3).$$

$$\begin{aligned}
H'_{11} &= \int_{\omega} \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) H^{\text{eff},\pi} \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) = \frac{1}{2}(\alpha + 0 + 0 + \alpha) = \alpha, \\
H'_{12} &= \int_{\omega} \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) H^{\text{eff},\pi} \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) = \frac{1}{2}(\beta - 0 - 0 + \beta) = \beta, \\
H'_{22} &= \int_{\omega} \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) H^{\text{eff},\pi} \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) = \frac{1}{2}(\alpha - \beta - \beta + \alpha) = \alpha - \beta,
\end{aligned}$$

$$H'_{B_g} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha - \beta \end{pmatrix}.$$

$$\det(H'_{B_g} - \varepsilon^{\pi} S'_{B_g}) = \begin{vmatrix} \alpha - \varepsilon^{\pi} & \beta \\ \beta & \alpha - \beta - \varepsilon^{\pi} \end{vmatrix} = \beta^2 \begin{vmatrix} x & 1 \\ 1 & x - 1 \end{vmatrix} = \beta^2(x^x - x - 1) = 0,$$

where

$$x = \frac{\alpha - \varepsilon^{\pi}}{\beta},$$

$$\Delta_{B_g} = (-1)^2 - 4 \times 1 \times (-1) = 5,$$

$$x_1 = \frac{1 + \sqrt{5}}{2}, \quad x_2 = \frac{1 - \sqrt{5}}{2}.$$

$$\varepsilon_1 = \alpha - x_1 \beta = \alpha - \frac{1 + \sqrt{5}}{2} \beta \approx \alpha - 1.618\beta,$$

$$\varepsilon_2 = \alpha - x_2 \beta = \alpha - \frac{1 - \sqrt{5}}{2} \beta = \alpha + \frac{\sqrt{5} - 1}{2} \beta \approx \alpha + 0.618\beta.$$

$$H'_{B_g} - \varepsilon_1^{\pi} S'_{B_g} = 0$$

$$\begin{pmatrix} 1 & \frac{-1+\sqrt{5}}{2} \\ 0 & 0 \end{pmatrix}$$

$$\Phi_1 = -\frac{\sqrt{5}-1}{2} \phi'_1 + \phi'_2.$$

$$\sum_i c_i^2 = \left(-\frac{\sqrt{5}-1}{2}\right)^2 + 1^2 = \frac{5-\sqrt{5}}{2}.$$

$$\Phi_1^{\pi} = \sqrt{\frac{2}{5-\sqrt{5}}} \Phi_1 = -\frac{\sqrt{5}-1}{2} \phi'_1 + \phi'_2 \quad (10.1)$$

$$= -\sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}} \phi'_1 + \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}} \phi'_2 \quad (10.2)$$

$$= -\frac{1}{2} \sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}} \phi_1 + \frac{1}{2} \sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}} \phi_2 - \frac{1}{2} \sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}} \phi_3 + \frac{1}{2} \sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}} \phi_4 \quad (10.3)$$

$$\approx -0.3717\phi_1 + 0.6015\phi_2 - 0.6015\phi_3 + 0.3717\phi_4. \quad (10.4)$$

$$H'_{B_g} - \varepsilon_2^{\pi} S'_{B_g} = 0$$

$$\begin{pmatrix} 1 & \frac{-1-\sqrt{5}}{2} \\ 0 & 0 \end{pmatrix}$$

$$\Phi_2 = \frac{\sqrt{5}+1}{2}\phi'_1 + \phi'_2.$$

$$\Phi_2^\pi = \sqrt{\frac{2}{5+\sqrt{5}}}\Phi_2 = \frac{\sqrt{5}+1}{2}\phi'_1 + \phi'_2 \quad (10.5)$$

$$= \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}\phi'_1 + \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}\phi'_2 \quad (10.6)$$

$$= \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_1 + \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_2 - \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_3 - \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_4 \quad (10.7)$$

$$\approx 0.6015\phi_1 + 0.3717\phi_2 - 0.3717\phi_3 - 0.6015\phi_4. \quad (10.8)$$

$$\Gamma^{A_u}\phi_1 = \sum_R \chi^{A_u}(R)O_R\phi_1 = (O_E + O_{C_2} - O_i - O_{\sigma_h})\phi_1 = \phi_1 + \phi_4 - (-\phi_4) - (-\phi_1) = 2(\phi_1 + \phi_4),$$

$$\Gamma^{A_u}\phi_2 = \sum_R \chi^{A_u}(R)O_R\phi_2 = (O_E + O_{C_2} - O_i - O_{\sigma_h})\phi_2 = \phi_2 + \phi_3 - (-\phi_3) - (-\phi_2) = 2(\phi_2 + \phi_3).$$

$$\phi'_3 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_4),$$

$$\phi'_4 = \frac{1}{\sqrt{2}}(\phi_2 + \phi_3).$$

$$H'_{A_u} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha + \beta \end{pmatrix}.$$

$$\det(H'_{A_u} - \varepsilon^\pi S'_{A_u}) = \begin{vmatrix} \alpha - \varepsilon^\pi & \beta \\ \beta & \alpha + \beta - \varepsilon^\pi \end{vmatrix} = \beta^2 \begin{vmatrix} x & 1 \\ 1 & x+1 \end{vmatrix} = \beta^2(x^2 + x - 1) = 0,$$

$$\Delta_{A_u} = 1^2 - 4 \times 1 \times (-1) = 5,$$

$$x_3 = \frac{-1+\sqrt{5}}{2}, \quad x_4 = \frac{-1-\sqrt{5}}{2}.$$

$$\varepsilon_3 = \alpha - x_3\beta = \alpha - \frac{-1+\sqrt{5}}{2}\beta \approx \alpha - 0.618\beta,$$

$$\varepsilon_4 = \alpha - x_4\beta = \alpha - \frac{-1-\sqrt{5}}{2}\beta = \alpha + \frac{\sqrt{5}+1}{2}\beta \approx \alpha + 1.618\beta.$$

$$H'_{A_u} - \varepsilon_3^\pi S'_{A_u} = 0$$

$$\begin{pmatrix} 1 & \frac{1+\sqrt{5}}{2} \\ 0 & 0 \end{pmatrix}$$

$$\Phi_3 = -\frac{\sqrt{5}+1}{2}\phi'_3 + \phi'_4.$$

$$\Phi_3^\pi = \sqrt{\frac{2}{5+\sqrt{5}}} \Phi_3 \quad (10.9)$$

$$= -\sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}} \phi'_3 + \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}} \phi'_4 \quad (10.10)$$

$$= -\frac{1}{2} \sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}} \phi_1 + \frac{1}{2} \sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}} \phi_2 + \frac{1}{2} \sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}} \phi_3 - \frac{1}{2} \sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}} \phi_4 \quad (10.11)$$

$$\approx -0.6015\phi_1 + 0.3717\phi_2 + 0.3717\phi_3 - 0.6015\phi_4. \quad (10.12)$$

$$H'_{A_u} - \varepsilon_4^\pi S'_{A_u} = 0$$

$$\begin{pmatrix} 1 & \frac{1-\sqrt{5}}{2} \\ 0 & 0 \end{pmatrix}$$

$$\Phi_4 = \frac{\sqrt{5}-1}{2} \phi'_3 + \phi'_4.$$

$$\Phi_4^\pi = \sqrt{\frac{2}{5-\sqrt{5}}} \Phi_4 \quad (10.13)$$

$$= \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}} \phi'_3 + \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}} \phi'_4 \quad (10.14)$$

$$= \frac{1}{2} \sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}} \phi_1 + \frac{1}{2} \sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}} \phi_2 + \frac{1}{2} \sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}} \phi_3 + \frac{1}{2} \sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}} \phi_4 \quad (10.15)$$

$$\approx 0.3717\phi_1 + 0.6015\phi_2 + 0.6015\phi_3 + 0.3717\phi_4. \quad (10.16)$$

Thus, we obtain all results, which are shown as following.

order	orbital energy	irrep	c_1	c_2	c_3	c_4
1	$\alpha + 1.618\beta$	A_u	0.3717	0.6015	0.6015	0.3717
2	$\alpha + 0.618\beta$	B_g	0.6015	0.3717	-0.3717	-0.6015
3	$\alpha - 0.618\beta$	A_u	-0.6015	0.3717	0.3717	-0.6015
4	$\alpha - 1.618\beta$	B_g	-0.3717	0.6015	-0.6015	0.3717

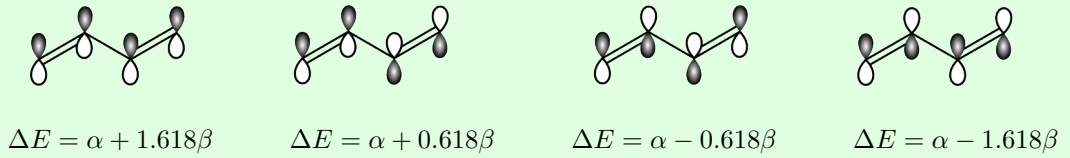


Figure 10.1: aaaaaaa

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\mathcal{D}_2	E	C_{2z}	C_{2y}	C_{2x}
A	1	1	1	1
B_1	1	1	-1	-1
B_2	1	-1	1	-1
B_3	1	-1	-1	1

\mathcal{D}_2	E	C_{2z}	C_{2y}	C_{2x}
$\chi^{\text{AO}}(C_i)$	2	0	0	-2

$$\begin{aligned}
a &= \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^A(R) = \frac{1}{4} [1 \times 2 \times 1 + 1 \times 0 \times 1 + 1 \times 0 \times 1 + 1 \times (-2) \times 1] = 0, \\
b_1 &= \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{B_1}(R) = \frac{1}{4} [1 \times 2 \times 1 + 1 \times 0 \times 1 + 1 \times 0 \times (-1) + 1 \times (-2) \times (-1)] = 1, \\
b_2 &= \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{B_2}(R) = \frac{1}{4} [1 \times 2 \times 1 + 1 \times 0 \times (-1) + 1 \times 0 \times 1 + 1 \times (-2) \times (-1)] = 1, \\
b_3 &= \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{B_3}(R) = \frac{1}{4} [1 \times 2 \times 1 + 1 \times 0 \times (-1) + 1 \times 0 \times (-1) + 1 \times (-2) \times 1] = 0.
\end{aligned}$$

$$\Gamma^{\text{AO}} = \Gamma^{B_1} \oplus \Gamma^{B_2}.$$

\mathcal{D}_2	E	C_{2z}	C_{2y}	C_{2x}
ϕ_1	ϕ_1	ϕ_2	$-\phi_2$	$-\phi_1$

$$\Gamma^{B_1} \phi_1 = \sum_R \chi^{B_1}(R) O_R \phi_1 = (O_E + O_{C_{2z}} - O_{C_{2y}} - O_{C_{2x}}) \phi_1 = \phi_1 + \phi_2 - (-\phi_2) - (-\phi_1) = 2(\phi_1 + \phi_2).$$

$$\phi'_1 = \frac{1}{2}(\phi_1 + \phi_2).$$

$$H^{\text{eff}, \pi} = (\alpha + \beta).$$

$$\Psi^p i_1 = \phi'_1 = \frac{1}{2}(\phi_1 + \phi_2) \quad (10.17)$$

$$\approx 0.7071\phi_1 + 0.7071\phi_2. \quad (10.18)$$

$$\Gamma^{B_2} \phi_1 = \sum_R \chi^{B_2}(R) O_R \phi_1 = (O_E - O_{C_{2z}} + O_{C_{2y}} - O_{C_{2x}}) \phi_1 = \phi_1 - \phi_2 + (-\phi_2) + (-\phi_1) = 2(\phi_1 - \phi_2).$$

$$\phi'_2 = \frac{1}{2}(\phi_1 - \phi_2).$$

$$H^{\text{eff}, \pi} = (\alpha - \beta).$$

$$\Psi^p i_1 = \phi'_1 = \frac{1}{2}(\phi_1 - \phi_2) \quad (10.19)$$

$$\approx 0.7071\phi_1 - 0.7071\phi_2. \quad (10.20)$$

Thus, we obtain all results, which are shown as following.

order	orbital energy	irrep	c_1	c_2
1	$\alpha + \beta$	B_1	0.7071	-0.7071
2	$\alpha - \beta$	B_2	0.7071	-0.7071

(c) This solution is designed for cyclobutadiene anion instead of just cyclobutadiene.

\mathcal{D}_4	E	$2C_4$	C_2	$2C'_2$	$2C''_2$
A_1	1	1	1	1	1
A_1	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	2	0	0

\mathcal{D}_4	E	$2C_4$	C_2	$2C'_2$	$2C''_2$
$\chi^{\text{AO}}(C_i)$	4	0	0	0	-2

$$a_1 = \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{A_1}(R) = \frac{1}{8} [1 \times 4 \times 1 + 2 \times 0 \times 1 + 1 \times 0 \times 1 + 2 \times 0 \times 1 + 2 \times (-2) \times 1] = 0,$$

$$a_2 = \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{A_2}(R) = \frac{1}{8} [1 \times 4 \times 1 + 2 \times 0 \times 1 + 1 \times 0 \times 1 + 2 \times 0 \times (-1) + 2 \times (-2) \times (-1)] = 1,$$

$$b_1 = \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{B_1}(R) = \frac{1}{8} [1 \times 4 \times 1 + 2 \times 0 \times (-1) + 1 \times 0 \times 1 + 2 \times 0 \times 1 + 2 \times (-2) \times (-1)] = 1,$$

$$b_2 = \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{B_2}(R) = \frac{1}{8} [1 \times 4 \times 1 + 2 \times 0 \times (-1) + 1 \times 0 \times 1 + 2 \times 0 \times (-1) + 2 \times (-2) \times 1] = 0,$$

$$e = \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^E(R) = \frac{1}{8} [1 \times 4 \times 2 + 2 \times 0 \times 0 + 1 \times 0 \times (-2) + 2 \times 0 \times 1 + 2 \times (-2) \times 0] = 1.$$

$$\Gamma^{\text{AO}} = \Gamma^{A_2} \oplus \Gamma^{B_1} \oplus \Gamma^E.$$

\mathcal{D}_4	E	C_4	C_2	C_4^3	$C'_{2,1}$	$C'_{2,2}$	$C''_{2,1}$	$C''_{2,2}$
ϕ_1	ϕ_1	ϕ_2	ϕ_3	ϕ_4	$-\phi_2$	$-\phi_4$	$-\phi_3$	$-\phi_1$
ϕ_2	ϕ_2	ϕ_3	ϕ_4	ϕ_1	$-\phi_1$	$-\phi_3$	$-\phi_2$	$-\phi_4$

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\mathcal{D}_5	E	$2C_5$	$2C_5^2$	$5C'_2$
A_1	1	1	1	1
A_2	1	1	1	-1
E_1	2	$2 \cos \alpha$	$2 \cos 2\alpha$	0
E_2	2	$2 \cos 2\alpha$	$2 \cos \alpha$	0

\mathcal{D}_5	E	$2C_5$	$2C_5^2$	$5C'_2$
$\chi^{\text{AO}}(C_i)$	5	0	0	-1

$$a_1 = \frac{1}{10} \sum_R \chi^{\text{AO}}(R) \chi^{A_1}(R) = \frac{1}{10} [1 \times 5 \times 1 + 2 \times 0 \times 1 + 2 \times 0 \times 1 + 5 \times (-1) \times 1] = 0,$$

$$a_2 = \frac{1}{10} \sum_R \chi^{\text{AO}}(R) \chi^{A_2}(R) = \frac{1}{10} [1 \times 5 \times 1 + 2 \times 0 \times 1 + 2 \times 0 \times 1 + 5 \times (-1) \times (-1)] = 1,$$

$$e_1 = \frac{1}{10} \sum_R \chi^{\text{AO}}(R) \chi^{E_1}(R) = \frac{1}{10} [1 \times 5 \times 2 + 2 \times 0 \times 2 \cos \alpha + 2 \times 0 \times 2 \cos 2\alpha + 5 \times (-1) \times 0] = 1,$$

$$e_2 = \frac{1}{10} \sum_R \chi^{\text{AO}}(R) \chi^{E_2}(R) = \frac{1}{10} [1 \times 5 \times 2 + 2 \times 0 \times 2 \cos 2\alpha + 2 \times 0 \times 2 \cos \alpha + 5 \times (-1) \times 0] = 1,$$

$$\Gamma^{\text{AO}} = \Gamma^{A_2} \oplus \Gamma^{E_1} \oplus \Gamma^{E_2}.$$

\mathcal{D}_5	E	C_5^1	C_5^2	C_5^3	C_5^4	$C'_{2,1}$	$C'_{2,2}$	$C'_{2,3}$	$C'_{2,4}$	$C'_{2,5}$
ϕ_1	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	$-\phi_1$	$-\phi_3$	$-\phi_5$	$-\phi_2$	$-\phi_4$
ϕ_2	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_1	$-\phi_5$	$-\phi_2$	$-\phi_4$	$-\phi_1$	$-\phi_3$

(e) 5555555555555555

\mathcal{D}_{2h}	E	C_{2z}	C_{2y}	C_{2x}	i	σ_{xy}	σ_{xz}	σ_{yz}
A_g	1	1	1	1	1	1	1	1
B_{1g}	1	1	-1	-1	1	1	-1	-1
B_{2g}	1	-1	1	-1	1	-1	1	-1
B_{3g}	1	-1	-1	1	1	-1	-1	1
A_u	1	1	1	1	-1	-1	-1	-1
B_{1u}	1	1	-1	-1	-1	-1	1	1
B_{2u}	1	-1	1	-1	-1	1	-1	1
B_{3u}	1	-1	-1	1	-1	1	1	-1

\mathcal{D}_{2h}	E	C_{2z}	C_{2y}	C_{2x}	i	σ_{xy}	σ_{xz}	σ_{yz}
$\chi^{\text{AO}}(C_i)$	10	0	-2	0	0	-10	0	2

$$\begin{aligned}
a_g &= \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{A_g}(R) = \frac{1}{8} [1 \times 10 \times 1 + 1 \times 0 \times 1 + 1 \times (-2) \times 1 + 1 \times 0 \times 1 \\
&\quad + 1 \times 0 \times 1 + 1 \times (-10) \times 1 + 1 \times 0 \times 1 + 1 \times 2 \times 1] = 0, \\
b_{1g} &= \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{B_{1g}}(R) = \frac{1}{8} [1 \times 10 \times 1 + 1 \times 0 \times 1 + 1 \times (-2) \times (-1) + 1 \times 0 \times (-1) \\
&\quad + 1 \times 0 \times 1 + 1 \times (-10) \times 1 + 1 \times 0 \times (-1) + 1 \times 2 \times (-1)] = 0, \\
b_{2g} &= \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{B_{2g}}(R) = \frac{1}{8} [1 \times 10 \times 1 + 1 \times 0 \times (-1) + 1 \times (-2) \times 1 + 1 \times 0 \times (-1) \\
&\quad + 1 \times 0 \times 1 + 1 \times (-10) \times (-1) + 1 \times 0 \times 1 + 1 \times 2 \times (-1)] = 2, \\
b_{3g} &= \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{B_{3g}}(R) = \frac{1}{8} [1 \times 10 \times 1 + 1 \times 0 \times (-1) + 1 \times (-2) \times (-1) + 1 \times 0 \times 1 \\
&\quad + 1 \times 0 \times 1 + 1 \times (-10) \times (-1) + 1 \times 0 \times (-1) + 1 \times 2 \times 1] = 3, \\
a_u &= \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{A_u}(R) = \frac{1}{8} [1 \times 10 \times 1 + 1 \times 0 \times 1 + 1 \times (-2) \times 1 + 1 \times 0 \times 1 \\
&\quad + 1 \times 0 \times (-1) + 1 \times (-10) \times (-1) + 1 \times 0 \times (-1) + 1 \times 2 \times (-1)] = 2, \\
b_{1u} &= \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{B_{1u}}(R) = \frac{1}{8} [1 \times 10 \times 1 + 1 \times 0 \times 1 + 1 \times (-2) \times (-1) + 1 \times 0 \times (-1) \\
&\quad + 1 \times 0 \times (-1) + 1 \times (-10) \times (-1) + 1 \times 0 \times 1 + 1 \times 2 \times 1] = 3, \\
b_{2u} &= \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{B_{2u}}(R) = \frac{1}{8} [1 \times 10 \times 1 + 1 \times 0 \times (-1) + 1 \times (-2) \times 1 + 1 \times 0 \times (-1) \\
&\quad + 1 \times 0 \times (-1) + 1 \times (-10) \times 1 + 1 \times 0 \times (-1) + 1 \times 2 \times 1] = 0, \\
b_{3u} &= \frac{1}{8} \sum_R \chi^{\text{AO}}(R) \chi^{B_{3u}}(R) = \frac{1}{8} [1 \times 10 \times 1 + 1 \times 0 \times (-1) + 1 \times (-2) \times (-1) + 1 \times 0 \times 1 \\
&\quad + 1 \times 0 \times (-1) + 1 \times (-10) \times 1 + 1 \times 0 \times 1 + 1 \times 2 \times (-1)] = 0.
\end{aligned}$$

$$\Gamma^{\text{AO}} = 2\Gamma^{B_{2g}} \oplus 3\Gamma^{B_{3g}} \oplus 2\Gamma^{A_u} \oplus 3\Gamma^{B_{1u}}.$$

\mathcal{D}_5	E	C_{2z}	C_{2y}	C_{2x}	i	σ_{xy}	σ_{xz}	σ_{yz}
ϕ_1	ϕ_1	ϕ_6	$-\phi_9$	$-\phi_4$	$-\phi_6$	$-\phi_1$	ϕ_4	ϕ_9
ϕ_2	ϕ_2	ϕ_7	$-\phi_8$	$-\phi_3$	$-\phi_7$	$-\phi_2$	ϕ_3	ϕ_8
ϕ_5	ϕ_5	ϕ_{10}	$-\phi_5$	$-\phi_{10}$	$-\phi_{10}$	$-\phi_5$	ϕ_{10}	ϕ_5

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\mathcal{D}_5	E	C_2	σ_{xz}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

\mathcal{C}_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\chi^{\text{AO}}(C_i)$	14	0	0	-14

$$a_1 = \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{A_1}(R) = \frac{1}{4} [1 \times 14 \times 1 + 1 \times 0 \times 1 + 1 \times 0 \times 1 + 1 \times (-14) \times 1] = 0,$$

$$a_2 = \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{A_2}(R) = \frac{1}{4} [1 \times 14 \times 1 + 1 \times 0 \times 1 + 1 \times 0 \times (-1) + 1 \times (-14) \times (-1)] = 7,$$

$$b_1 = \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{B_1}(R) = \frac{1}{4} [1 \times 14 \times 1 + 1 \times 0 \times (-1) + 1 \times 0 \times 1 + 1 \times (-14) \times (-1)] = 7,$$

$$b_2 = \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{B_2}(R) = \frac{1}{4} [1 \times 14 \times 1 + 1 \times 0 \times (-1) + 1 \times 0 \times (-1) + 1 \times (-14) \times 1] = 0,$$

$$\Gamma^{\text{AO}} = 7\Gamma^{A_2} \oplus 7\Gamma^{B_1}.$$

\mathcal{C}_{2v}	E	C_2	σ_{xz}	σ_{yz}
ϕ_1	ϕ_1	$-\phi_{10}$	ϕ_{10}	$-\phi_1$
ϕ_2	ϕ_2	$-\phi_9$	ϕ_9	$-\phi_2$
ϕ_3	ϕ_3	$-\phi_8$	ϕ_8	$-\phi_3$
ϕ_4	ϕ_4	$-\phi_7$	ϕ_7	$-\phi_4$
ϕ_5	ϕ_5	$-\phi_6$	ϕ_6	$-\phi_5$
ϕ_{11}	ϕ_{11}	$-\phi_{14}$	ϕ_{14}	$-\phi_{11}$
ϕ_{12}	ϕ_{12}	$-\phi_{13}$	ϕ_{13}	$-\phi_{12}$