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

(a) Firstly, it is easy to find that *trans*-1,3-butadiene belongs to the point group $\mathscr{C}_{2\mathrm{h}}$, whose character table is listed below.

$\mathscr{C}_{2\mathrm{h}}$	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

Secondly, we mark all carbon atoms as follows.

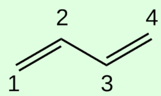

Figure 10.1: The order of carbon atoms in *trans*-1,3-butadiene.

For π-electron atomic orbitals' representation Γ^{AO}, its following characters is listed below.

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

Relevant reduction coefficients are

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

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

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

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

Thus, we arrive at

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

We conclude that there are two basis functions in the irreducible representation Γ^{B_g} and Γ^{A_u}, respectively. Thus, to describe the effect of O_R, two suitable π atomic orbitals ϕ_i is enough.

Thirdly, we inspect the transformation of ϕ_i under O_R for the *trans*-1,3-butadiene, whose information is recorded below. We only list two ϕ_1 and ϕ_2, which is enough in current case.

Table 10.1: Transformation of ϕ_i under O_R for the *trans*-1,3-butadiene.

$\mathscr{C}_{2\mathrm{h}}$	O_E	O_{C_2}	O_i	O_{σ_h}
ϕ_1	ϕ_1	ϕ_4	$-\phi_4$	$-\phi_1$
ϕ_2	ϕ_2	ϕ_3	$-\phi_3$	$-\phi_2$

For the irreducible representation Γ^{B_g},

$$\Gamma^{B_g}\phi_1 = \sum_R \chi^{B_g}(R) O_R \phi_1 = (O_E - O_{C_2} + O_i - O_{\sigma_h})\phi_1 = \phi_1 - \phi_4 + (-\phi_4) - (-\phi_1) = 2(\phi_1 - \phi_4),$$
$$\Gamma^{B_g}\phi_2 = \sum_R \chi^{B_g}(R) O_R \phi_2 = (O_E - O_{C_2} + O_i - O_{\sigma_h})\phi_2 = \phi_2 - \phi_3 + (-\phi_3) - (-\phi_2) = 2(\phi_2 - \phi_3).$$

It is easy to find that they are mutually orthogonal. They can be normalized to

$$\phi_1' = \frac{1}{\sqrt{2}}(\phi_1 - \phi_4),$$
$$\phi_2' = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3).$$

Then, the effective Hamitonian matrix elements for π electrons can be calculated,

$$H_{11}' = \int_{\mathrm{R}^3} \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) H^{\mathrm{eff},\pi} \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) = \frac{1}{2}(\alpha + 0 + 0 + \alpha) = \alpha,$$
$$H_{12}' = \int_{\mathrm{R}^3} \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) H^{\mathrm{eff},\pi} \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) = \frac{1}{2}(\beta - 0 - 0 + \beta) = \beta,$$
$$H_{22}' = \int_{\mathrm{R}^3} \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) H^{\mathrm{eff},\pi} \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) = \frac{1}{2}(\alpha - \beta - \beta + \alpha) = \alpha - \beta,$$

viz.

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

Next,

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

where

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

Current discriminant is

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

and then two roots are

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

which equal to

$$\varepsilon_1 = \alpha - x_1\beta = \alpha - \frac{1 + \sqrt{5}}{2}\beta \approx \alpha - 1.618\beta, \tag{10.1}$$
$$\varepsilon_2 = \alpha - x_2\beta = \alpha - \frac{1 - \sqrt{5}}{2}\beta = \alpha + \frac{\sqrt{5} - 1}{2}\beta \approx \alpha + 0.618\beta. \tag{10.2}$$

For $H_{B_g}' - \varepsilon_1^\pi S_{B_g}'$, its reduced row echelon form is

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

which means

$$\Phi_1 = -\frac{\sqrt{5} - 1}{2}\phi_1' + \phi_2'.$$

The sum of squares of coefficients is

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

Thus, we know

$$\begin{aligned}\Phi_1^\pi &= \sqrt{\frac{2}{5-\sqrt{5}}}\Phi_1 = -\frac{\sqrt{5}-1}{2}\phi_1' + \phi_2' = -\sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}\phi_1' + \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}\phi_2' \\ &= -\frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_1 + \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_2 - \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_3 + \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_4 \\ &\approx -0.3717\phi_1 + 0.6015\phi_2 - 0.6015\phi_3 + 0.3717\phi_4. \end{aligned} \tag{10.3}$$

Similarly, the reduced row echelon form of $H'_{B_g} - \varepsilon_2^\pi S'_{B_g}$ is

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

which means

$$\Phi_2 = \frac{\sqrt{5}+1}{2}\phi_1' + \phi_2'.$$

And then,

$$\begin{aligned}\Phi_2^\pi &= \sqrt{\frac{2}{5+\sqrt{5}}}\Phi_2 = \frac{\sqrt{5}+1}{2}\phi_1' + \phi_2' = \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}\phi_1' + \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}\phi_2' \\ &= \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_1 + \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_2 - \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_3 - \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_4 \\ &\approx 0.6015\phi_1 + 0.3717\phi_2 - 0.3717\phi_3 - 0.6015\phi_4. \end{aligned} \tag{10.4}$$

In conclusion, for the irreducible representation Γ^{B_g}, relevant results are listed below.

order	eigenvalue	eigenfunction
1	$\alpha - 1.618\beta$	$0.3717\phi_1 - 0.6015\phi_2 + 0.6015\phi_3 - 0.3717\phi_4$
2	$\alpha + 0.618\beta$	$0.6015\phi_1 + 0.3717\phi_2 - 0.3717\phi_3 - 0.6015\phi_4$

$$\Gamma^{A_u}\phi_1 = \sum_R \chi^{A_u}(R) O_R \phi_1 = (O_E + O_{C_2} - O_i - O_{\sigma_h})\phi_1 = \phi_1 + \phi_4 - (-\phi_4) - (-\phi_1) = 2(\phi_1 + \phi_4),$$
$$\Gamma^{A_u}\phi_2 = \sum_R \chi^{A_u}(R) O_R \phi_2 = (O_E + O_{C_2} - O_i - O_{\sigma_h})\phi_2 = \phi_2 + \phi_3 - (-\phi_3) - (-\phi_2) = 2(\phi_2 + \phi_3).$$

$$\phi_3' = \frac{1}{\sqrt{2}}(\phi_1 + \phi_4),$$
$$\phi_4' = \frac{1}{\sqrt{2}}(\phi_2 + \phi_3).$$

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

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

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

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

$$\varepsilon_3 = \alpha - x_3\beta = \alpha - \frac{-1+\sqrt{5}}{2}\beta \approx \alpha - 0.618\beta,$$
$$\varepsilon_4 = \alpha - x_4\beta = \alpha - \frac{-1-\sqrt{5}}{2}\beta = \alpha + \frac{\sqrt{5}+1}{2}\beta \approx \alpha + 1.618\beta.$$

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

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

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

$$\Phi_3^\pi = \sqrt{\frac{2}{5+\sqrt{5}}}\Phi_3 \tag{10.5}$$
$$= -\sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}\phi'_3 + \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}\phi'_4 \tag{10.6}$$
$$= -\frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_1 + \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_2 + \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_3 - \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_4 \tag{10.7}$$
$$\approx -0.6015\phi_1 + 0.3717\phi_2 + 0.3717\phi_3 - 0.6015\phi_4. \tag{10.8}$$

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

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

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

$$\Phi_4^\pi = \sqrt{\frac{2}{5-\sqrt{5}}}\Phi_4 \tag{10.9}$$
$$= \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}\phi'_3 + \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}\phi'_4 \tag{10.10}$$
$$= \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_1 + \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_2 + \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_3 + \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_4 \tag{10.11}$$
$$\approx 0.3717\phi_1 + 0.6015\phi_2 + 0.6015\phi_3 + 0.3717\phi_4. \tag{10.12}$$

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

$\Delta E = \alpha + 1.618\beta$ $\Delta E = \alpha + 0.618\beta$ $\Delta E = \alpha - 0.618\beta$ $\Delta E = \alpha - 1.618\beta$

Figure 10.2: aaaaaaa

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$\mathscr{D}_2$	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

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

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

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

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

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

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

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

$$\begin{aligned}
\Psi^p i_1 = \phi_1' &= \frac{1}{2}(\phi_1 + \phi_2) && (10.13)\\
&\approx 0.7071\phi_1 + 0.7071\phi_2. && (10.14)
\end{aligned}$$

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

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

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

$$\begin{aligned}
\Psi^p i_1 = \phi_1' &= \frac{1}{2}(\phi_1 - \phi_2) && (10.15)\\
&\approx 0.7071\phi_1 - 0.7071\phi_2. && (10.16)
\end{aligned}$$

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.

$\mathscr{D}_4$	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

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

$$a_1 = \frac{1}{8}\sum_R \chi^{\text{AO}}(R)\chi^{A_1}(R) = \frac{1}{8}\left[1\times 4\times 1 + 2\times 0\times 1 + 1\times 0\times 1 + 2\times 0\times 1 + 2\times(-2)\times 1\right] = 0,$$
$$a_2 = \frac{1}{8}\sum_R \chi^{\text{AO}}(R)\chi^{A_2}(R) = \frac{1}{8}\left[1\times 4\times 1 + 2\times 0\times 1 + 1\times 0\times 1 + 2\times 0\times(-1) + 2\times(-2)\times(-1)\right] = 1,$$
$$b_1 = \frac{1}{8}\sum_R \chi^{\text{AO}}(R)\chi^{B_1}(R) = \frac{1}{8}\left[1\times 4\times 1 + 2\times 0\times(-1) + 1\times 0\times 1 + 2\times 0\times 1 + 2\times(-2)\times(-1)\right] = 1,$$
$$b_2 = \frac{1}{8}\sum_R \chi^{\text{AO}}(R)\chi^{B_2}(R) = \frac{1}{8}\left[1\times 4\times 1 + 2\times 0\times(-1) + 1\times 0\times 1 + 2\times 0\times(-1) + 2\times(-2)\times 1\right] = 0,$$
$$e = \frac{1}{8}\sum_R \chi^{\text{AO}}(R)\chi^{E}(R) = \frac{1}{8}\left[1\times 4\times 2 + 2\times 0\times 0 + 1\times 0\times(-2) + 2\times 0\times 1 + 2\times(-2)\times 0\right] = 1.$$

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

$\mathscr{D}_4$	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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$\mathscr{D}_5$	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

$\mathscr{D}_5$	E	$2C_5$	$2C_5^2$	$5C_2'$
$\chi^{\text{AO}}(C_i)$	5	0	0	-1

$$a_1 = \frac{1}{10}\sum_R \chi^{\text{AO}}(R)\chi^{A_1}(R) = \frac{1}{10}\left[1\times 5\times 1 + 2\times 0\times 1 + 2\times 0\times 1 + 5\times(-1)\times 1\right] = 0,$$
$$a_2 = \frac{1}{10}\sum_R \chi^{\text{AO}}(R)\chi^{A_2}(R) = \frac{1}{10}\left[1\times 5\times 1 + 2\times 0\times 1 + 2\times 0\times 1 + 5\times(-1)\times(-1)\right] = 1,$$
$$e_1 = \frac{1}{10}\sum_R \chi^{\text{AO}}(R)\chi^{E_1}(R) = \frac{1}{10}\left[1\times 5\times 2 + 2\times 0\times 2\cos\alpha + 2\times 0\times 2\cos 2\alpha + 5\times(-1)\times 0\right] = 1,$$
$$e_2 = \frac{1}{10}\sum_R \chi^{\text{AO}}(R)\chi^{E_2}(R) = \frac{1}{10}\left[1\times 5\times 2 + 2\times 0\times 2\cos 2\alpha + 2\times 0\times 2\cos\alpha + 5\times(-1)\times 0\right] = 1,$$

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

$\mathscr{D}_5$	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

$\mathscr{D}_{2\mathrm{h}}$	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

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

$$\begin{aligned}
a_g &= \frac{1}{8}\sum_R \chi^{\mathrm{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 \\
&\qquad + 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^{\mathrm{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) \\
&\qquad + 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^{\mathrm{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) \\
&\qquad + 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^{\mathrm{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 \\
&\qquad + 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^{\mathrm{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 \\
&\qquad + 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^{\mathrm{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) \\
&\qquad + 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^{\mathrm{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) \\
&\qquad + 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^{\mathrm{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 \\
&\qquad + 1\times 0\times(-1) + 1\times(-10)\times 1 + 1\times 0\times 1 + 1\times 2\times(-1)] = 0.
\end{aligned}$$

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

$\mathscr{D}_5$	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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$\mathscr{D}_5$	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

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

$$
\begin{aligned}
a_1 &= \frac{1}{4}\sum_R \chi^{\mathrm{AO}}(R)\chi^{A_1}(R) = \frac{1}{4}\left[1\times 14\times 1 + 1\times 0\times 1 + 1\times 0\times 1 + 1\times(-14)\times 1\right] = 0,\\
a_2 &= \frac{1}{4}\sum_R \chi^{\mathrm{AO}}(R)\chi^{A_2}(R) = \frac{1}{4}\left[1\times 14\times 1 + 1\times 0\times 1 + 1\times 0\times(-1) + 1\times(-14)\times(-1)\right] = 7,\\
b_1 &= \frac{1}{4}\sum_R \chi^{\mathrm{AO}}(R)\chi^{B_1}(R) = \frac{1}{4}\left[1\times 14\times 1 + 1\times 0\times(-1) + 1\times 0\times 1 + 1\times(-14)\times(-1)\right] = 7,\\
b_2 &= \frac{1}{4}\sum_R \chi^{\mathrm{AO}}(R)\chi^{B_2}(R) = \frac{1}{4}\left[1\times 14\times 1 + 1\times 0\times(-1) + 1\times 0\times(-1) + 1\times(-14)\times 1\right] = 0,
\end{aligned}
$$

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

$\mathscr{C}_{2\mathrm{v}}$	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}	$-\phi_{12}$