**Exercise 10.1**

For the following molecules, determine the point group and the symmetry of the MOs for the $\pi$-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 $\mathscr{C}_{2h}$, whose character table is listed below.

Table 10.1: The character table for the $\mathscr{C}_{2h}$ point group.

| $\mathscr{C}_{2h}$ | $E$ | $C_2$ | $i$ | $\sigma_h$ |
|---|---|---|---|---|
| $A_g$ | 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.

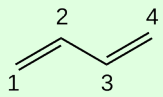


Figure 10.1: The order of carbon atoms in *trans*-1,3-butadiene.

For $\pi$-electron atomic orbitals' representation $\Gamma^{\mathrm{AO}}$, its following characters is listed below.

Table 10.2: The character of the $\pi$-electron atomic orbitals' representation $\Gamma^{\mathrm{AO}}$.

| $\mathscr{C}_{2h}$ | $E$ | $C_2$ | $i$ | $\sigma_h$ |
|---|---|---|---|---|
| $\chi^{\mathrm{AO}}(C_i)$ | 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 $\Gamma^{B_g}$ and $\Gamma^{A_u}$, respectively. Thus, to describe the effect of $O_R$, two suitable $2p_z$ atomic orbitals $\phi_i$ is enough.

Thirdly, we inspect the transformation of $\phi_i$ under $O_R$ for the *trans*-1,3-butadiene, whose information is recorded below. We only list two $\phi_1$ and $\phi_2$, which is enough in current case.

Table 10.3: Transformation of $\phi_i$ under $O_R$ for the *trans*-1,3-butadiene.

| $\mathscr{C}_{2h}$ | $O_E$ | $O_{C_2}$ | $O_i$ | $O_{\sigma_h}$ |
|---|---|---|---|---|
| $\phi_1$ | $\phi_1$ | $\phi_4$ | $-\phi_4$ | $-\phi_1$ |
| $\phi_2$ | $\phi_2$ | $\phi_3$ | $-\phi_3$ | $-\phi_2$ |

For the irreducible representation $\Gamma^{B_g}$,

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

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 $\pi$ 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 $\Gamma^{B_g}$, relevant results are listed below.

Table 10.4: The Hückel MOs in the irreducible representation $\Gamma^{B_g}$ of *trans*-1,3-butadiene.

| 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 | $\alpha + 0.618\beta$ | $0.6015\phi_1 + 0.3717\phi_2 - 0.3717\phi_3 - 0.6015\phi_4$ |

In the same way, for the irreducible representation $\Gamma^{A_u}$,

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

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

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

Then, the effective Hamiltonian can be constructed, viz.

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

Next,

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

Current discriminant is

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

and then two roots are

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

which equal to

$$\varepsilon_3 = \alpha - x_3\beta = \alpha - \frac{-1+\sqrt{5}}{2}\beta \approx \alpha - 0.618\beta, \tag{10.5}$$

$$\varepsilon_4 = \alpha - x_4\beta = \alpha - \frac{-1-\sqrt{5}}{2}\beta = \alpha + \frac{\sqrt{5}+1}{2}\beta \approx \alpha + 1.618\beta. \tag{10.6}$$

For $H'_{A_u} - \varepsilon_3^{\pi} S'_{A_u}$, its reduced row echelon form is

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

which means

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

Thus,

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

For $H'_{A_u} - \varepsilon_4^{\pi} S'_{A_u}$, its reduced row echelon form is

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

which means

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

Thus,

$$\begin{aligned} \Phi_4^{\pi} &= \sqrt{\frac{2}{5-\sqrt{5}}}\Phi_4 = \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}\phi'_3 + \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}\phi'_4 \\ &= \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_1 + \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_2 + \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{\sqrt{5}}}\phi_3 + \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{\sqrt{5}}}\phi_4 \\ &\approx 0.3717\phi_1 + 0.6015\phi_2 + 0.6015\phi_3 + 0.3717\phi_4. \end{aligned} \tag{10.8}$$

In conclusion, for the irreducible representation $\Gamma^{A_u}$, relevant results are listed below.

Table 10.5: The Hückel MOs in the irreducible representation $\Gamma^{A_u}$ of *trans*-1,3-butadiene.

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

Now, we have obtained all results, which are shown as following.

Table 10.6: The Hückel MOs in all irreducible representations of *trans*-1,3-butadiene.

| 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 |

Besides, their phase diagrams have been painted in Fig 10.2. They obey the rule that the less nodal planes are, the lower orbital energy is.

$\varepsilon = \alpha + 1.618\beta$ $\varepsilon = \alpha + 0.618\beta$ $\varepsilon = \alpha - 0.618\beta$ $\varepsilon = \alpha - 1.618\beta$

Figure 10.2: Phase diagrams of these Hückel MOs of *trans*-1,3-butadiene. Black bubbles mean plus phase while white ones mean minus phase. The color is used just for determining relative phase.

In the end, we conclude that for *trans*-1,3-butadiene, its ground state $\pi$-electron configuration is $(a_u)^2(b_g)^2$ and its delocalization energy is $2 \times (1.618\beta + 0.618\beta) - 4\beta = 0.472\beta$.

(b) 22222222222222222

| $\mathscr{D}_2$ | $E$ | $C_{2z}$ | $C_{2y}$ | $C_{2x}$ |
|---|---|---|---|---|
| $A$ | 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 |

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

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

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

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

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

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

$$\Psi^p i_1 = \phi_1' = \frac{1}{2}(\phi_1 + \phi_2) \tag{10.9}$$
$$\approx 0.7071\phi_1 + 0.7071\phi_2. \tag{10.10}$$

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

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

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

$$\Psi^p i_1 = \phi_1' = \frac{1}{2}(\phi_1 - \phi_2) \tag{10.11}$$

$$\approx 0.7071\phi_1 - 0.7071\phi_2. \tag{10.12}$$

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 |

$\varepsilon = \alpha + \beta$ $\varepsilon = \alpha - \beta$

Figure 10.3: Phase diagrams of these Hückel MOs. Black bubbles mean plus phase while white ones mean minus phase. The color is used just for determining relative phase.

(c) This solution is designed for cyclobutadiene anion instead of just cyclobutadiene which is the prototypical antiaromatic hydrocarbon with 4 $\pi$ electrons. Its rectangular structure is the result of a pseudo-(or second order) Jahn–Teller effect, which distorts the molecule and lowers its symmetry, converting the triplet to a singlet ground state. This distortion indicates that the $\pi$ electrons are localized, in agreement with Hückel's rule which predicts that a $\pi$-system of 4 electrons is not aromatic. This information is excerpted from https://en.wikipedia.org/wiki/Cyclobutadiene.

Firstly, it is easy find that cyclobutadiene anion belongs to the point group $\mathscr{D}_{4h}$. However, it has only 4 $\pi$-electrons. Just $\mathscr{D}_4$ is good enough and its character table is shown in Table 10.7.

Table 10.7: The character table for the $\mathscr{D}_4$ point group.

| $\mathscr{D}_4$ | $E$ | $2C_4$ | $C_2$ | $2C_2'$ | $2C_2''$ |
|---|---|---|---|---|---|
| $A_1$ | 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 |

Secondly, we mark all carbon atoms as follows.

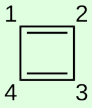


Figure 10.4: The order of carbon atoms in the cyclobutadiene anion.

For $\pi$-electron atomic orbitals' representation $\Gamma^{\text{AO}}$, its following characters is listed below.

Table 10.8: The character of the $\pi$-electron atomic orbitals' representation $\Gamma^{\text{AO}}$.

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

Relevant reduction coefficients are

$$a_1 = 0, \quad a_2 = 1, \quad b_1 = 1, \quad b_2 = 0, \quad e = 1.$$

Then, we arrive at

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

Thus, to describe the effect of $O_R$, two suitable $2\mathrm{p}_z$ atomic orbitals is enough.

Thirdly, we inspect the transformation of $\phi_i$ under $O_R$ for the cyclobutadiene anion, whose information is recorded below. We only list two $\phi_1$ and $\phi_2$.

Table 10.9: Transformation of $\phi_i$ under $O_R$ for the cyclobutadiene anion.

| $\mathscr{D}_4$ | $E$ | $C_4$ | $C_2$ | $C_4^3$ | $C'_{2,1}$ | $C'_{2,2}$ | $C''_{2,1}$ | $C''_{2,2}$ |
|---|---|---|---|---|---|---|---|---|
| $\phi_1$ | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $-\phi_2$ | $-\phi_4$ | $-\phi_3$ | $-\phi_1$ |
| $\phi_2$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\phi_1$ | $-\phi_1$ | $-\phi_3$ | $-\phi_2$ | $-\phi_4$ |

For the irreducible representation $\Gamma^{A_2}$, the only basis function is

$$\begin{aligned} P^{A_2}\phi_1 &= \sum_R \chi^{A_2}(R) O_R \phi_1 = (O_E + O_{C_4} + O_{C_2} + O_{C_4^3} - \sum_{k=1}^{2} O_{C'_{2,k}} - \sum_{k=1}^{2} O_{C''_{2,k}})\phi_1 \\ &= 2(\phi_1 + \phi_2 + \phi_3 + \phi_4). \end{aligned}$$

It can be normalized to

$$\Phi_1^{\pi} = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4). \tag{10.13}$$

Then, the effective Hamiltonian for $\pi$ electrons is

$$H' = (\alpha + 2\beta).$$

In another words, its only eigenvalue is $\alpha + 2\beta$, with eigenfunction $\Phi_1^{\pi}$.

In conclusion, for the irreducible representation $\Gamma^{A_2}$, relevant results are listed below.

Table 10.10: The Hückel MOs in the irreducible representation $\Gamma^{A_2}$ of cyclobutadiene anion.

| order | eigenvalue | eigenfunction |
|---|---|---|
| 1 | $\alpha + 2\beta$ | $0.5000\phi_1 + 0.5000\phi_2 + 0.5000\phi_3 + 0.5000\phi_4$ |

For the irreducible representation $\Gamma^{B_1}$, the only basis function is

$$P^{B_1}\phi_1 = \sum_R \chi^{B_1}(R) O_R \phi_1 = 2(\phi_1 - \phi_2 + \phi_3 - \phi_4).$$

It can be normalized to

$$\Phi_2^{\pi} = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4). \tag{10.14}$$

Then, the effective Hamiltonian for $\pi$ electrons is

$$H' = (\alpha - 2\beta).$$

In another words, its only eigenvalue is $\alpha - 2\beta$, with eigenfunction $\Phi_2^{\pi}$.

In conclusion, for the irreducible representation $\Gamma^{B_1}$, relevant results are listed below.

Table 10.11: The Hückel MOs in the irreducible representation $\Gamma^{B_1}$ of cyclobutadiene anion.

| order | eigenvalue | eigenfunction |
|---|---|---|
| 1 | $\alpha - 2\beta$ | $0.5000\phi_1 - 0.5000\phi_2 + 0.5000\phi_3 - 0.5000\phi_4$ |

For the irreducible representation $\Gamma^E$, the only two basis functions are

$$P^E\phi_1 = \sum_R \chi^E(R) O_R \phi_1 = 2(\phi_1 - \phi_3),$$
$$P^E\phi_2 = \sum_R \chi^E(R) O_R \phi_2 = 2(\phi_2 - \phi_4).$$

They can be normalized to

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

Then, the effective Hamiltonian for $\pi$ electrons is

$$H' = \begin{pmatrix} \alpha & 0 \\ 0 & \alpha \end{pmatrix}.$$

It has a two-fold eigenvalue $\alpha$. Thus, corresponding eigenfunctions can be

$$\Phi_3^\pi = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3), \tag{10.15}$$
$$\Phi_4^\pi = \frac{1}{\sqrt{2}}(\phi_2 - \phi_4). \tag{10.16}$$

In another words, its only eigenvalue is $\alpha$, with two eigenfunctions $\Phi_3^\pi$ and $\Phi_4^\pi$.
In conclusion, for the irreducible representation $\Gamma^E$, relevant results are listed below.

Table 10.12: The Hückel MOs in the irreducible representation $\Gamma^E$ of cyclobutadiene anion.

| order | eigenvalue | eigenfunction |
|---|---|---|
| 1 | $\alpha$ | $0.7071\phi_1 - 0.7071\phi_3$ |
| 2 | $\alpha$ | $0.7071\phi_2 - 0.7071\phi_4$ |

Now, we have obtained all results, which are shown as following.

Table 10.13: The Hückel MOs in all irreducible representations of cyclobutadiene anion.

| order | orbital energy | irrep | $c_1$ | $c_2$ | $c_3$ | $c_4$ |
|---|---|---|---|---|---|---|
| 1 | $\alpha + 2.000\beta$ | $A_2$ | 0.5000 | 0.5000 | 0.5000 | 0.5000 |
| 2 | $\alpha$ | $E$ | 0.7071 | 0.0000 | -0.7071 | 0.0000 |
| 3 | $\alpha$ | $E$ | 0.0000 | 0.7071 | 0.0000 | -0.7071 |
| 4 | $\alpha - 2.000\beta$ | $B_1$ | 0.5000 | -0.5000 | 0.5000 | -0.5000 |

Besides, their phase diagrams have been painted in Fig 10.5.

$\varepsilon = \alpha + 2.000\beta$ $\varepsilon = \alpha + 0.000\beta$ $\varepsilon = \alpha + 0.000\beta$ $\varepsilon = \alpha - 2.000\beta$

Figure 10.5: Phase diagrams of these Hückel MOs of cyclobutadiene anion. Black bubbles mean plus phase while white ones mean minus phase. The color is used just for determining relative phase.

In the end, we conclude that for cyclobutadiene anion, its ground state $\pi$-electron configuration is $(a_2)^2(e)^4$ and its delocalization energy is $-2.000\beta$, which means that cyclobutadiene anion needs other stable structures to stabilize itself.

(d) Firstly, it is easy find that cyclopentadienyl radical belongs to the point group $\mathscr{D}_{5h}$. However, it has only 5 $\pi$-electrons. Just $\mathscr{D}_5$ is good enough and its character table is shown in Table 10.7.

Table 10.14: The character table for the $\mathscr{D}_5$ point group. Here, $\gamma = \frac{2\pi}{5}$.

| $\mathscr{D}_5$ | $E$ | $2C_5$ | $2C_5^2$ | $5C_2'$ |
|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | 1 | -1 |
| $E_1$ | 2 | $2\cos\gamma$ | $2\cos 2\gamma$ | 0 |
| $E_2$ | 2 | $2\cos 2\gamma$ | $2\cos\gamma$ | 0 |

Secondly, we mark all carbon atoms as follows.

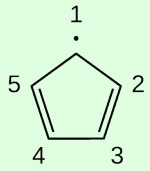


Figure 10.6: The order of carbon atoms in cyclopentadienyl radical.

For $\pi$-electron atomic orbitals' representation $\Gamma^{\mathrm{AO}}$, its following characters is listed below.

Table 10.15: The character of the $\pi$-electron atomic orbitals' representation $\Gamma^{\mathrm{AO}}$.

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

Relevant reduction coefficients are

$$a_1 = 0, \quad a_2 = 1, \quad e_1 = 1, \quad e_2 = 1,$$

which equal to

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

| $\mathscr{D}_5$ | $E$ | $C_5^1$ | $C_5^2$ | $C_5^3$ | $C_5^4$ | $C_{2,1}'$ | $C_{2,2}'$ | $C_{2,3}'$ | $C_{2,4}'$ | $C_{2,5}'$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\phi_1$ | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\phi_5$ | $-\phi_1$ | $-\phi_3$ | $-\phi_5$ | $-\phi_2$ | $-\phi_4$ |
| $\phi_2$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\phi_5$ | $\phi_1$ | $-\phi_5$ | $-\phi_2$ | $-\phi_4$ | $-\phi_1$ | $-\phi_3$ |

For the irreducible representation $\Gamma^{A_2}$, the only basis function is

$$P^{A_2}\phi_1 = \sum_R \chi^{A_2}(R) O_R \phi_1 = 2(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5).$$

It can be normalized to

$$\phi_1' = \frac{1}{\sqrt{5}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5). \tag{10.17}$$

Then, the effective Hamiltonian for $\pi$ electrons is

$$H' = (\alpha + 2\beta).$$

In another words, its only eigenvalue is $\alpha + 2\beta$, with eigenfunction $\Phi_1^\pi = \phi_1'$.

In conclusion, for the irreducible representation $\Gamma^{A_2}$, relevant results are listed below.

Table 10.16: The Hückel MOs in the irreducible representation $\Gamma^{A_2}$ of cyclopentadienyl radical.

| order | eigenvalue | eigenfunction |
|---|---|---|
| 1 | $\alpha + 2\beta$ | $0.4472\phi_1 + 0.4472\phi_2 + 0.4472\phi_3 + 0.4472\phi_4 + 0.4472\phi_5$ |

For the irreducible representation $\Gamma^{E_1}$, the only two basis functions are

$$P^{E_1}\phi_1 = \sum_R \chi^{E_1}(R) O_R \phi_1 = 2\phi_1 + \frac{\sqrt{5}-1}{2}(\phi_2 + \phi_5) - \frac{\sqrt{5}+1}{2}(\phi_3 + \phi_4).$$

$$P^{E_1}\phi_2 = \sum_R \chi^{E_1}(R) O_R \phi_2 = 2\phi_1 + \frac{\sqrt{5}-1}{2}(\phi_1 + \phi_3) - \frac{\sqrt{5}+1}{2}(\phi_4 + \phi_5).$$

They can be normalized to

$$\phi_2' = \sqrt{\frac{1}{10}} P^{E_1}\phi_1 = \sqrt{\frac{2}{5}}\phi_1 + \frac{\sqrt{5}-1}{2\sqrt{10}}(\phi_2+\phi_5) - \frac{\sqrt{5}+1}{2\sqrt{10}}(\phi_3+\phi_4),$$
$$\phi_3' = \sqrt{\frac{1}{10}} P^{E_1}\phi_1 = \sqrt{\frac{2}{5}}\phi_2 + \frac{\sqrt{5}-1}{2\sqrt{10}}(\phi_1+\phi_3) - \frac{\sqrt{5}+1}{2\sqrt{10}}(\phi_4+\phi_5).$$

However, they are not mutually orthogonal! We have to orthogonalize $\phi_2'$ and $\phi_3'$.

$$\phi_2' + \phi_3' = \sqrt{\frac{2}{5}}\left[\frac{3+\sqrt{5}}{4}(\phi_1+\phi_2) - \frac{1}{2}(\phi_3+\phi_5) - \frac{\sqrt{5}-1}{2}\Phi_4\right],$$
$$\phi_2' - \phi_3' = \sqrt{\frac{2}{5}}\left[\frac{5-\sqrt{5}}{4}(\phi_1-\phi_2) - \frac{\sqrt{5}}{2}(\phi_3-\phi_5)\right].$$

Then, the effective Hamiltonian for $\pi$ electrons is

$$H' = (\alpha + 2\beta).$$

In another words, its only eigenvalue is $\alpha + 2\beta$, with eigenfunction $\Phi_1^\pi = \phi_1'$.

In conclusion, for the irreducible representation $\Gamma^{A_2}$, relevant results are listed below.

Table 10.17: The Hückel MOs in the irreducible representation $\Gamma^{A_2}$ of cyclopentadienyl radical.

| order | eigenvalue | eigenfunction |
|---|---|---|
| 1 | $\alpha + 2\beta$ | $0.4472\phi_1 + 0.4472\phi_2 + 0.4472\phi_3 + 0.4472\phi_4 + 0.4472\phi_5$ |

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| $\mathscr{D}_{2h}$ | $E$ | $C_{2z}$ | $C_{2y}$ | $C_{2x}$ | $i$ | $\sigma_{xy}$ | $\sigma_{xz}$ | $\sigma_{yz}$ |
|---|---|---|---|---|---|---|---|---|
| $A_g$ | 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 |

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

$$a_g = \frac{1}{8}\sum_R \chi^{\mathrm{AO}}(R)\chi^{A_g}(R) = \frac{1}{8}[1\times 10\times 1 + 1\times 0\times 1 + 1\times(-2)\times 1 + 1\times 0\times 1 + 1\times 0\times 1 + 1\times(-10)\times 1 + 1\times 0\times 1 + 1\times 2\times 1] = 0,$$

$$b_{1g} = \frac{1}{8}\sum_R \chi^{\mathrm{AO}}(R)\chi^{B_{1g}}(R) = \frac{1}{8}[1\times 10\times 1 + 1\times 0\times 1 + 1\times(-2)\times(-1) + 1\times 0\times(-1) + 1\times 0\times 1 + 1\times(-10)\times 1 + 1\times 0\times(-1) + 1\times 2\times(-1)] = 0,$$

$$b_{2g} = \frac{1}{8}\sum_R \chi^{\mathrm{AO}}(R)\chi^{B_{2g}}(R) = \frac{1}{8}[1\times 10\times 1 + 1\times 0\times(-1) + 1\times(-2)\times 1 + 1\times 0\times(-1) + 1\times 0\times 1 + 1\times(-10)\times(-1) + 1\times 0\times 1 + 1\times 2\times(-1)] = 2,$$

$$b_{3g} = \frac{1}{8}\sum_R \chi^{\mathrm{AO}}(R)\chi^{B_{3g}}(R) = \frac{1}{8}[1\times 10\times 1 + 1\times 0\times(-1) + 1\times(-2)\times(-1) + 1\times 0\times 1 + 1\times 0\times 1 + 1\times(-10)\times(-1) + 1\times 0\times(-1) + 1\times 2\times 1] = 3,$$

$$a_u = \frac{1}{8}\sum_R \chi^{\mathrm{AO}}(R)\chi^{A_u}(R) = \frac{1}{8}[1\times 10\times 1 + 1\times 0\times 1 + 1\times(-2)\times 1 + 1\times 0\times 1 + 1\times 0\times(-1) + 1\times(-10)\times(-1) + 1\times 0\times(-1) + 1\times 2\times(-1)] = 2,$$

$$b_{1u} = \frac{1}{8}\sum_R \chi^{\mathrm{AO}}(R)\chi^{B_{1u}}(R) = \frac{1}{8}[1\times 10\times 1 + 1\times 0\times 1 + 1\times(-2)\times(-1) + 1\times 0\times(-1) + 1\times 0\times(-1) + 1\times(-10)\times(-1) + 1\times 0\times 1 + 1\times 2\times 1] = 3,$$

$$b_{2u} = \frac{1}{8}\sum_R \chi^{\mathrm{AO}}(R)\chi^{B_{2u}}(R) = \frac{1}{8}[1\times 10\times 1 + 1\times 0\times(-1) + 1\times(-2)\times 1 + 1\times 0\times(-1) + 1\times 0\times(-1) + 1\times(-10)\times 1 + 1\times 0\times(-1) + 1\times 2\times 1] = 0,$$

$$b_{3u} = \frac{1}{8}\sum_R \chi^{\mathrm{AO}}(R)\chi^{B_{3u}}(R) = \frac{1}{8}[1\times 10\times 1 + 1\times 0\times(-1) + 1\times(-2)\times(-1) + 1\times 0\times 1 + 1\times 0\times(-1) + 1\times(-10)\times 1 + 1\times 0\times 1 + 1\times 2\times(-1)] = 0.$$

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

| $\mathscr{D}_5$ | $E$ | $C_{2z}$ | $C_{2y}$ | $C_{2x}$ | $i$ | $\sigma_{xy}$ | $\sigma_{xz}$ | $\sigma_{yz}$ |
|---|---|---|---|---|---|---|---|---|
| $\phi_1$ | $\phi_1$ | $\phi_6$ | $-\phi_9$ | $-\phi_4$ | $-\phi_6$ | $-\phi_1$ | $\phi_4$ | $\phi_9$ |
| $\phi_2$ | $\phi_2$ | $\phi_7$ | $-\phi_8$ | $-\phi_3$ | $-\phi_7$ | $-\phi_2$ | $\phi_3$ | $\phi_8$ |
| $\phi_5$ | $\phi_5$ | $\phi_{10}$ | $-\phi_5$ | $-\phi_{10}$ | $-\phi_{10}$ | $-\phi_5$ | $\phi_{10}$ | $\phi_5$ |

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| $\mathscr{D}_5$ | $E$ | $C_2$ | $\sigma_{xz}$ | $\sigma_{yz}$ |
|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | -1 | -1 |
| $B_1$ | 1 | -1 | 1 | -1 |
| $B_2$ | 1 | -1 | -1 | 1 |

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

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

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

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

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

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

| $\mathscr{C}_{2\mathrm{v}}$ | $E$ | $C_2$ | $\sigma_{xz}$ | $\sigma_{yz}$ |
|---|---|---|---|---|
| $\phi_1$ | $\phi_1$ | $-\phi_{10}$ | $\phi_{10}$ | $-\phi_1$ |
| $\phi_2$ | $\phi_2$ | $-\phi_9$ | $\phi_9$ | $-\phi_2$ |
| $\phi_3$ | $\phi_3$ | $-\phi_8$ | $\phi_8$ | $-\phi_3$ |
| $\phi_4$ | $\phi_4$ | $-\phi_7$ | $\phi_7$ | $-\phi_4$ |
| $\phi_5$ | $\phi_5$ | $-\phi_6$ | $\phi_6$ | $-\phi_5$ |
| $\phi_{11}$ | $\phi_{11}$ | $-\phi_{14}$ | $\phi_{14}$ | $-\phi_{11}$ |
| $\phi_{12}$ | $\phi_{12}$ | $-\phi_{13}$ | $\phi_{13}$ | $-\phi_{12}$ |