

### 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  $\mathcal{C}_{2h}$ , whose character table is listed below.

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

$\mathcal{C}_{2h}$	$E$	$C_2$	$i$	$\sigma_h$
$A_g$	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.

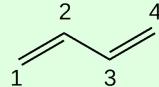


Figure 10.1: The label of carbon atoms in *trans*-1,3-butadiene.

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

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

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

Relevant reduction coefficients are

$$\begin{aligned} a_g &= \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{A_g}(R) = \frac{1}{4} [1 \times 4 \times 1 + 1 \times 0 \times 1 + 1 \times 0 \times 1 + 1 \times (-4) \times 1] = 0, \\ b_g &= \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{B_g}(R) = \frac{1}{4} [1 \times 4 \times 1 + 1 \times 0 \times (-1) + 1 \times 0 \times 1 + 1 \times (-4) \times (-1)] = 2, \\ a_u &= \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{A_u}(R) = \frac{1}{4} [1 \times 4 \times 1 + 1 \times 0 \times 1 + 1 \times 0 \times (-1) + 1 \times (-4) \times (-1)] = 2, \\ b_u &= \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{B_u}(R) = \frac{1}{4} [1 \times 4 \times 1 + 1 \times 0 \times (-1) + 1 \times 0 \times (-1) + 1 \times (-4) \times 1] = 0. \end{aligned}$$

Thus, we arrive at

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

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.

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

Fourthly, it's time to discuss situations in different irreducible representation.

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

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

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

$$\begin{aligned} \phi'_1 &= \frac{1}{\sqrt{2}}(\phi_1 - \phi_4), \\ \phi'_2 &= \frac{1}{\sqrt{2}}(\phi_2 - \phi_3). \end{aligned}$$

Then, the effective Hamitonian matrix elements for  $\pi$  electrons can be calculated,

$$\begin{aligned} H'_{11} &= \int_{\mathbb{R}^3} \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) H^{\text{eff}, \pi} \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) = \frac{1}{2}(\alpha + 0 + 0 + \alpha) = \alpha, \\ H'_{12} &= \int_{\mathbb{R}^3} \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) H^{\text{eff}, \pi} \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) = \frac{1}{2}(\beta - 0 - 0 + \beta) = \beta, \\ H'_{22} &= \int_{\mathbb{R}^3} \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) H^{\text{eff}, \pi} \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) = \frac{1}{2}(\alpha - \beta - \beta + \alpha) = \alpha - \beta, \end{aligned}$$

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

$$\varepsilon_1 = \alpha - x_1 \beta = \alpha - \frac{1 + \sqrt{5}}{2} \beta \approx \alpha - 1.618\beta, \quad (10.1)$$

$$\varepsilon_2 = \alpha - x_2 \beta = \alpha - \frac{1 - \sqrt{5}}{2} \beta = \alpha + \frac{\sqrt{5} - 1}{2} \beta \approx \alpha + 0.618\beta. \quad (10.2)$$

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

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

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

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

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

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,

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

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,

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

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.

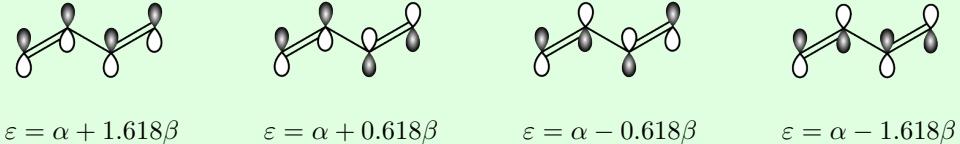


Figure 10.2: Phase diagrams of these Hückel MOs of *trans*-1,3-butadiene. Black bubbles mean plus phase while white ones mean minus phase. The color is used just for determining relative phase.

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) bbbbbbbbbb

$\mathcal{D}_2$	$E$	$C_{2z}$	$C_{2y}$	$C_{2x}$
$A$	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

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

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

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

$$b_3 = \frac{1}{4} \sum_R \chi^{\text{AO}}(R) \chi^{B_3}(R) = \frac{1}{4} [1 \times 2 \times 1 + 1 \times 0 \times (-1) + 1 \times 0 \times (-1) + 1 \times (-2) \times 1] = 0.$$

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

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

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

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

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

$$\Psi^p i_1 = \phi'_1 = \frac{1}{2}(\phi_1 + \phi_2) \quad (10.9)$$

$$\approx 0.7071\phi_1 + 0.7071\phi_2. \quad (10.10)$$

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

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

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

$$\Psi^p i_1 = \phi'_1 = \frac{1}{2}(\phi_1 - \phi_2) \quad (10.11)$$

$$\approx 0.7071\phi_1 - 0.7071\phi_2. \quad (10.12)$$

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



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

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  $D_{4h}$ . However, it has only  $4\pi$ -electrons. Just  $D_4$  is good enough and its character table is shown in Table 10.7.

Table 10.7: The character table for the  $D_4$  point group.

$D_4$	$E$	$2C_4$	$C_2$	$2C'_2$	$2C''_2$
$A_1$	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.

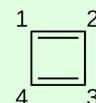


Figure 10.4: The order of carbon atoms in the cyclobutadiene anion.

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  $\Gamma^{\text{AO}}$ .

$D_4$	$E$	$2C_4$	$C_2$	$2C'_2$	$2C''_2$
$\chi^{\text{AO}}(C_i)$	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

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

Thus, to describe the effect of  $O_R$ , two suitable  $2p_z$  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.

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

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

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

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

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

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

$$\Phi_3^\pi = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3), \quad (10.15)$$

$$\Phi_4^\pi = \frac{1}{\sqrt{2}}(\phi_2 - \phi_4). \quad (10.16)$$

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.

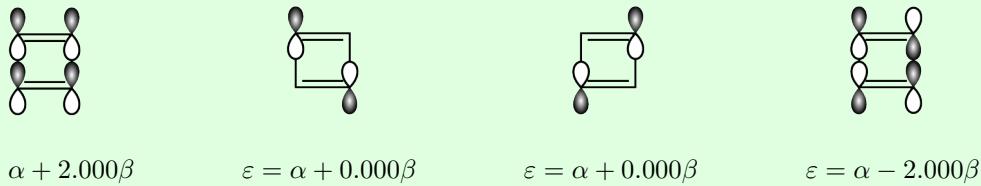


Figure 10.5: Phase diagrams of these Hückel MOs of cyclobutadiene anion. Black bubbles mean plus phase while white ones mean minus phase. The color is used just for determining relative phase.

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  $D_{5h}$ . However, it has only 5  $\pi$ -electrons. Just  $D_5$  is good enough and its character table is shown in Table 10.7.

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

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

Secondly, we mark all carbon atoms as follows.

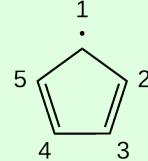


Figure 10.6: The order of carbon atoms in cyclopentadienyl radical.

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

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

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

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

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

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

$$\phi'_1 = \frac{1}{\sqrt{5}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5). \quad (10.17)$$

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

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

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

They can be normalized to

$$\begin{aligned}\phi'_2 &= \sqrt{\frac{1}{10}} P^{E_1} \phi_1 = \sqrt{\frac{2}{5}} \phi_1 + \frac{\sqrt{5}-1}{2\sqrt{10}} (\phi_2 + \phi_5) - \frac{\sqrt{5}+1}{2\sqrt{10}} (\phi_3 + \phi_4) \\ &= \sqrt{\frac{2}{5}} [\phi_1 + \phi_2 \cos \gamma + \phi_3 \cos 2\gamma + \phi_4 \cos 2\gamma + \phi_5 \cos \gamma], \\ \phi'_3 &= \sqrt{\frac{1}{10}} P^{E_1} \phi_2 = \sqrt{\frac{2}{5}} \phi_2 + \frac{\sqrt{5}-1}{2\sqrt{10}} (\phi_1 + \phi_3) - \frac{\sqrt{5}+1}{2\sqrt{10}} (\phi_4 + \phi_5) \\ &= \sqrt{\frac{2}{5}} [\phi_1 \cos \gamma + \phi_2 + \phi_3 \cos \gamma + \phi_4 \cos 2\gamma + \phi_5 \cos 2\gamma].\end{aligned}$$

However, they are not mutually orthogonal! We have to orthogonalize  $\phi'_2$  and  $\phi'_3$ ,

$$\begin{aligned}\phi'_2 + \phi'_3 &= \sqrt{\frac{2}{5}} [(\phi_1 + \phi_2)(1 + \cos \gamma) + (\phi_3 + \phi_5)(\cos \gamma + \cos 2\gamma) + 2\phi_4 \cos 2\gamma] \\ &= \sqrt{\frac{2}{5}} \left[ \frac{3 + \sqrt{5}}{4} (\phi_1 + \phi_2) - \frac{1}{2} (\phi_3 + \phi_5) - \frac{\sqrt{5} + 1}{2} \Phi_4 \right], \\ \phi'_2 - \phi'_3 &= \sqrt{\frac{2}{5}} [(\phi_1 - \phi_2)(1 - \cos \gamma) + (\phi_3 - \phi_5)(\cos 2\gamma - \cos \gamma)] \\ &= \sqrt{\frac{2}{5}} \left[ \frac{5 - \sqrt{5}}{4} (\phi_1 - \phi_2) - \frac{\sqrt{5}}{2} (\phi_3 - \phi_5) \right].\end{aligned}$$

and then normalize them. Their sum of squares of coefficients are

$$\begin{aligned}\sum_{k=1}^5 c_{2,k}^2 &= \frac{3 + \sqrt{5}}{2}, \\ \sum_{k=1}^5 c_{3,k}^2 &= \frac{5 - \sqrt{5}}{2},\end{aligned}$$

and then

$$\begin{aligned}\phi''_2 &= \sqrt{\frac{2}{3 + \sqrt{5}}} [\phi'_2 + \phi'_3] = \frac{2}{\sqrt{5(3 + \sqrt{5})}} \left[ \frac{3 + \sqrt{5}}{4} (\phi_1 + \phi_2) - \frac{1}{2} (\phi_3 + \phi_5) - \frac{\sqrt{5} + 1}{2} \Phi_4 \right] \\ &= \frac{\sqrt{3 + \sqrt{5}}}{2\sqrt{5}} (\phi_1 + \phi_2) - \frac{1}{\sqrt{5(3 + \sqrt{5})}} (\phi_3 + \phi_5) - \frac{1 + \sqrt{5}}{\sqrt{5(3 + \sqrt{5})}} \phi_4 \\ &\approx 0.5117\phi_1 + 0.5117\phi_2 - 0.1954\phi_3 - 0.6325\phi_4 - 0.1954\phi_5, \\ \phi''_3 &= \sqrt{\frac{2}{5 - \sqrt{5}}} [\phi'_2 - \phi'_3] = \frac{2}{\sqrt{5(5 - \sqrt{5})}} \left[ \frac{5 - \sqrt{5}}{4} (\phi_1 - \phi_2) - \frac{\sqrt{5}}{2} (\phi_3 - \phi_5) \right] \\ &= \frac{\sqrt{5 - \sqrt{5}}}{2\sqrt{5}} (\phi_1 - \phi_2) - \frac{1}{\sqrt{5 - \sqrt{5}}} (\phi_3 - \phi_5) \\ &\approx 0.3717\phi_1 - 0.3717\phi_2 - 0.6015\phi_3 + 0.6015\phi_5.\end{aligned}$$

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

$$H' = \begin{pmatrix} \alpha + \frac{\sqrt{5}-1}{2}\beta & 0 \\ 0 & \alpha + \frac{\sqrt{5}-1}{2}\beta \end{pmatrix} \approx \begin{pmatrix} \alpha + 0.618\beta & 0 \\ 0 & \alpha + 0.618\beta \end{pmatrix},$$

In another words, it has only one two-fold eigenvalue  $\alpha + \frac{\sqrt{5}-1}{2}\beta \approx \alpha + 0.618\beta$ , with two mutually orthogonal eigenfunctions  $\Phi_2^\pi = \phi''_2$ ,  $\Phi_3^\pi = \phi''_3$ .

In conclusion, for the irreducible representation  $\Gamma^{E_1}$ , relevant results are listed below.

Table 10.17: The Hückel MOs in the irreducible representation  $\Gamma^{E_1}$  of cyclopentadienyl radical.

order	eigenvalue	eigenfunction
1	$\alpha + 0.618\beta$	$0.5117\phi_1 + 0.5117\phi_2 - 0.1954\phi_3 - 0.6325\phi_4 - 0.1954\phi_5$
2	$\alpha + 0.618\beta$	$0.3717\phi_1 - 0.3717\phi_2 - 0.6015\phi_3 + 0.0000\phi_4 + 0.6015\phi_5$

For the irreducible representation  $\Gamma^{E_2}$ , the only two basis functions are

$$P^{E_2}\phi_1 = \sum_R \chi^{E_2}(R) O_R \phi_1 = 2\phi_1 - \frac{\sqrt{5}+1}{2}(\phi_2 + \phi_5) + \frac{\sqrt{5}-1}{2}(\phi_3 + \phi_4).$$

$$P^{E_2}\phi_2 = \sum_R \chi^{E_2}(R) O_R \phi_2 = 2\phi_2 - \frac{\sqrt{5}+1}{2}(\phi_1 + \phi_3) + \frac{\sqrt{5}-1}{2}(\phi_4 + \phi_5).$$

They can be normalized to

$$\begin{aligned} \phi'_4 &= \sqrt{\frac{1}{10}} P^{E_1} \phi_1 = \sqrt{\frac{2}{5}} \phi_1 - \frac{\sqrt{5}+1}{2\sqrt{10}} (\phi_2 + \phi_5) + \frac{\sqrt{5}-1}{2\sqrt{10}} (\phi_3 + \phi_4) \\ &= \sqrt{\frac{2}{5}} [\phi_1 + \phi_2 \cos 2\gamma + \phi_3 \cos \gamma + \phi_4 \cos \gamma + \phi_5 \cos 2\gamma], \\ \phi'_5 &= \sqrt{\frac{1}{10}} P^{E_1} \phi_2 = \sqrt{\frac{2}{5}} \phi_2 - \frac{\sqrt{5}+1}{2\sqrt{10}} (\phi_1 + \phi_3) - \frac{\sqrt{5}-1}{2\sqrt{10}} (\phi_4 + \phi_5) \\ &= \sqrt{\frac{2}{5}} [\phi_1 \cos 2\gamma + \phi_2 + \phi_3 \cos 2\gamma + \phi_4 \cos \gamma + \phi_5 \cos \gamma]. \end{aligned}$$

However, they are not mutually orthogonal! We have to orthogonalize  $\phi'_4$  and  $\phi'_5$ ,

$$\begin{aligned} \phi'_4 + \phi'_5 &= \sqrt{\frac{2}{5}} [(\phi_1 + \phi_2)(1 + \cos 2\gamma) + (\phi_3 + \phi_5)(\cos \gamma + \cos 2\gamma) + 2\phi_4 \cos \gamma] \\ &= \sqrt{\frac{2}{5}} \left[ \frac{3 - \sqrt{5}}{4} (\phi_1 + \phi_2) - \frac{1}{2} (\phi_3 + \phi_5) + \frac{\sqrt{5} - 1}{2} \Phi_4 \right], \\ \phi'_4 - \phi'_5 &= \sqrt{\frac{2}{5}} [(\phi_1 - \phi_2)(1 - \cos 2\gamma) + (\phi_3 - \phi_5)(\cos \gamma - \cos 2\gamma)] \\ &= \sqrt{\frac{2}{5}} \left[ \frac{5 + \sqrt{5}}{4} (\phi_1 - \phi_2) + \frac{\sqrt{5}}{2} (\phi_3 - \phi_5) \right]. \end{aligned}$$

and then normalize them. Their sum of squares of coefficients are

$$\begin{aligned} \sum_{k=1}^5 c_{4,k}^2 &= \frac{3 - \sqrt{5}}{2}, \\ \sum_{k=1}^5 c_{5,k}^2 &= \frac{5 + \sqrt{5}}{2}, \end{aligned}$$

and then

$$\begin{aligned} \phi''_4 &= \sqrt{\frac{2}{3 - \sqrt{5}}} [\phi'_4 + \phi'_5] = \frac{2}{\sqrt{5(3 - \sqrt{5})}} \left[ \frac{3 - \sqrt{5}}{4} (\phi_1 + \phi_2) - \frac{1}{2} (\phi_3 + \phi_5) + \frac{\sqrt{5} - 1}{2} \Phi_4 \right] \\ &= \frac{\sqrt{3 - \sqrt{5}}}{2\sqrt{5}} (\phi_1 + \phi_2) - \frac{1}{\sqrt{5(3 - \sqrt{5})}} (\phi_3 + \phi_5) + \frac{\sqrt{5} - 1}{\sqrt{5(3 - \sqrt{5})}} \phi_4 \\ &\approx 0.1954\phi_1 + 0.1954\phi_2 - 0.5117\phi_3 + 0.6325\phi_4 - 0.5117\phi_5, \\ \phi''_5 &= \sqrt{\frac{2}{5 + \sqrt{5}}} [\phi'_4 - \phi'_5] = \frac{2}{\sqrt{5(5 + \sqrt{5})}} \left[ \frac{5 + \sqrt{5}}{4} (\phi_1 - \phi_2) + \frac{\sqrt{5}}{2} (\phi_3 - \phi_5) \right] \end{aligned}$$

$$\begin{aligned}
&= \frac{\sqrt{5} + \sqrt{5}}{2\sqrt{5}}(\phi_1 - \phi_2) + \frac{1}{\sqrt{5} + \sqrt{5}}(\phi_3 - \phi_5) \\
&\approx 0.6015\phi_1 - 0.6015\phi_2 + 0.3717\phi_3 - 0.3717\phi_5.
\end{aligned}$$

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

$$H' = \begin{pmatrix} \alpha - \frac{\sqrt{5}+1}{2}\beta & 0 \\ 0 & \alpha - \frac{\sqrt{5}+1}{2}\beta \end{pmatrix} \approx \begin{pmatrix} \alpha - 1.618\beta & 0 \\ 0 & \alpha - 1.618\beta \end{pmatrix},$$

In another words, it has only one two-fold eigenvalue  $\alpha + \frac{\sqrt{5}-1}{2}\beta \approx \alpha - 1.618\beta$ , with two mutually orthogonal eigenfunctions  $\Phi_4^\pi = \phi_4'', \Phi_5^\pi = \phi_5''$ .

In conclusion, for the irreducible representation  $\Gamma^{E_2}$ , relevant results are listed below.

Table 10.18: The Hückel MOs in the irreducible representation  $\Gamma^{E_2}$  of cyclopentadienyl radical.

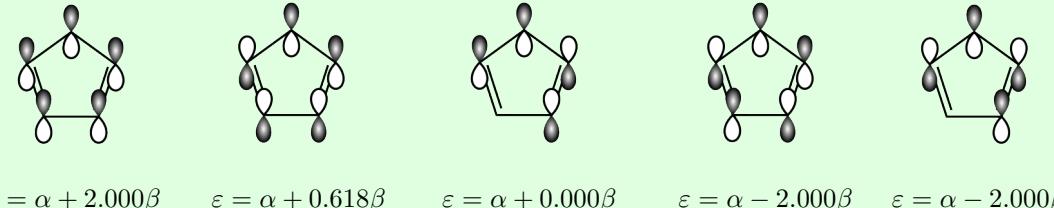
order	eigenvalue	eigenfunction
1	$\alpha - 1.618\beta$	$0.1954\phi_1 + 0.1954\phi_2 - 0.5117\phi_3 + 0.6325\phi_4 - 0.5117\phi_5$
2	$\alpha - 1.618\beta$	$0.6015\phi_1 - 0.6015\phi_2 + 0.3717\phi_3 + 0.0000\phi_4 - 0.3717\phi_5$

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

Table 10.19: The Hückel MOs in all irreducible representations of cyclopentadienyl radical.

order	orbital energy	irrep	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
1	$\alpha + 2.000\beta$	$A_2$	0.4472	0.4472	0.4472	0.4472	0.4472
2	$\alpha + 0.618\beta$	$E_1$	0.5117	0.5117	-0.1954	-0.6325	-0.1954
3	$\alpha + 0.618\beta$	$E_1$	0.3717	-0.3717	-0.6015	0.0000	0.6015
4	$\alpha - 1.618\beta$	$E_2$	0.1954	0.1954	-0.5117	0.6325	-0.5117
5	$\alpha - 1.618\beta$	$E_2$	0.6015	-0.6015	0.3717	0.0000	-0.3717

Besides, their phase diagrams have been painted in Fig 10.7.



$$\varepsilon = \alpha + 2.000\beta \quad \varepsilon = \alpha + 0.618\beta \quad \varepsilon = \alpha + 0.000\beta \quad \varepsilon = \alpha - 2.000\beta \quad \varepsilon = \alpha - 2.000\beta$$

Figure 10.7: Phase diagrams of these Hückel MOs of cyclopentadienyl radical. 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 cyclopentadienyl radical, its ground state  $\pi$ -electron configuration is  $(a_2)^2(e_1)^3$  and its delocalization energy is  $2 \times 2.000\beta + 3 \times 0.618\beta - 5 \times 1.000\beta = 0.854\beta$ , much larger than *trans*-1,3-butadiene ( $0.472\beta$ ) but also much smaller than benzene ( $2.000\beta$ ).

- (e) Firstly, it is easy find that naphthalene belongs to the point group  $D_{2h}$ , whose character table is shown in Table 10.20.

Table 10.20: The character table for the  $D_{2h}$  point group.

$D_{2h}$	$E$	$C_{2z}$	$C_{2y}$	$C_{2x}$	$i$	$\sigma_{xy}$	$\sigma_{xz}$	$\sigma_{yz}$
$A_g$	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

Secondly, we mark all carbon atoms as follows.

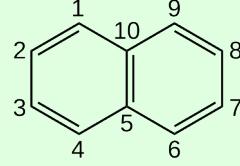


Figure 10.8: The order of carbon atoms in naphthalene.

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

Table 10.21: The character of the  $\pi$ -electron atomic orbitals' representation  $\Gamma^{\text{AO}}$ .

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

Relevant reduction coefficients are

$$a_g = 0, \quad b_{1g} = 0, \quad b_{2g} = 2, \quad b_{3g} = 3, \quad a_u = 2, \quad b_{1u} = 3, \quad b_{2u} = 0, \quad b_{3u} = 0.$$

Thus, we arrive at

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

We conclude that there are three basis functions in the irreducible representation  $\Gamma^{B_{3g}}$  and  $\Gamma^{B_{1u}}$ , respectively. Thus, to describe the effect of  $O_R$ , three suitable  $2p_z$  atomic orbitals  $\phi_i$  is enough.

Table 10.22: Transformation of  $\phi_i$  under  $O_R$  for the naphthalene.

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

For the irreducible representation  $\Gamma^{B_{2g}}$ , the only two basis functions are

$$P^{B_{2g}}\phi_1 = \sum_R \chi^{B_{2g}}(R)O_R\phi_1 = 2(\phi_1 + \phi_4 - \phi_6 - \phi_9),$$

$$P^{B_{2g}}\phi_2 = \sum_R \chi^{B_{2g}}(R)O_R\phi_2 = 2(\phi_2 + \phi_3 - \phi_7 - \phi_8).$$

They can be normalized to

$$\begin{aligned}\phi'_1 &= \frac{1}{2}(\phi_1 + \phi_4 - \phi_6 - \phi_9), \\ \phi'_2 &= \frac{1}{2}(\phi_2 + \phi_3 - \phi_7 - \phi_8).\end{aligned}$$

Besides, it is easy to find that they are mutually orthogonal.

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

$$H'_{B_{2g}} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha + \beta \end{pmatrix}.$$

Its eigen equation is

$$\det(H'_{B_{2g}} - \varepsilon^\pi S'_{B_{2g}}) = \beta^2(x^2 + x - 1) = 0. \quad (10.18)$$

There are two roots,

$$x_1 = \frac{-1 + \sqrt{5}}{2}, \quad x_2 = \frac{-1 - \sqrt{5}}{2}, \quad (10.19)$$

which equal to

$$\varepsilon_1^\pi = \alpha - \frac{\sqrt{5} - 1}{2}\beta, \quad (10.20)$$

$$\varepsilon_2^\pi = \alpha + \frac{\sqrt{5}+1}{2}\beta. \quad (10.21)$$

For  $H'_{B_{2g}} - \varepsilon_1^\pi S'_{B_{2g}}$ , 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

$$\sum_i c_i^2 = \frac{5+\sqrt{5}}{2},$$

Thus, we know

$$\begin{aligned} \Phi_1^\pi &= \sqrt{\frac{2}{5+\sqrt{5}}}\Phi_1 = \sqrt{\frac{2}{5+\sqrt{5}}}\left[\frac{\sqrt{5}+1}{2}\phi'_1 - \phi'_2\right] = \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}\phi'_1 - \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}\phi'_2 \\ &= \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}(\phi_1 + \phi_4 - \phi_6 - \phi_9) - \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}(\phi_2 + \phi_3 - \phi_7 - \phi_8) \\ &\approx 0.4253\phi_1 - 0.2629\phi_2 - 0.2629\phi_3 + 0.4253\phi_4 - 0.4253\phi_6 + 0.2629\phi_7 + 0.2629\phi_8 - 0.4253\phi_9. \end{aligned} \quad (10.22)$$

Similarly, the reduced row echelon form of  $H'_{B_{2g}} - \varepsilon_2^\pi S'_{B_{2g}}$  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,

$$\begin{aligned} \Phi_2^\pi &= \sqrt{\frac{2}{5-\sqrt{5}}}\Phi_2 = \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}\phi'_1 + \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}\phi'_2 \\ &= \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}(\phi_1 + \phi_4 - \phi_6 - \phi_9) + \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}(\phi_2 + \phi_3 - \phi_7 - \phi_8) \\ &\approx 0.2629\phi_1 + 0.4253\phi_2 + 0.4253\phi_3 + 0.2629\phi_4 - 0.2629\phi_6 - 0.4253\phi_7 - 0.4253\phi_8 - 0.2629\phi_9. \end{aligned} \quad (10.23)$$

In conclusion, for the irreducible representation  $\Gamma^{B_{2g}}$ , relevant results are listed below.

Table 10.23: The Hückel MOs in the irreducible representation  $\Gamma^{B_{2g}}$  of naphthalene.

order	eigenvalue	eigenfunction				
1	$\alpha - 0.618\beta$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
		0.4253	- 0.2629	- 0.2629	0.4253	0.0000
		$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
2	$\alpha + 1.618\beta$	- 0.4253	0.2629	0.2629	- 0.4253	0.0000
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
		0.2629	0.4253	0.4253	0.2629	0.0000
		$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
		- 0.2629	- 0.4253	- 0.4253	- 0.2629	0.0000

For the irreducible representation  $\Gamma^{B_{3g}}$ , the only three basis functions are

$$\begin{aligned} P^{B_{3g}}\phi_1 &= \sum_R \chi^{B_{3g}}(R) O_R \phi_1 = 2(\phi_1 - \phi_4 - \phi_6 + \phi_9), \\ P^{B_{3g}}\phi_2 &= \sum_R \chi^{B_{3g}}(R) O_R \phi_2 = 2(\phi_2 - \phi_3 - \phi_7 + \phi_8), \\ P^{B_{3g}}\phi_5 &= \sum_R \chi^{B_{3g}}(R) O_R \phi_5 = 4(\phi_5 - \phi_{10}). \end{aligned}$$

They can be normalized to

$$\begin{aligned} \phi'_3 &= \frac{1}{2}(\phi_1 - \phi_4 - \phi_6 + \phi_9), \\ \phi'_4 &= \frac{1}{2}(\phi_2 - \phi_3 - \phi_7 + \phi_8), \\ \phi'_5 &= \frac{1}{\sqrt{2}}(\phi_5 - \phi_{10}). \end{aligned}$$

Besides, it is easy to find that they are mutually orthogonal.

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

$$H'_{B_{3g}} = \begin{pmatrix} \alpha & \beta & -\sqrt{2}\beta \\ \beta & \alpha - \beta & 0 \\ -\sqrt{2}\beta & 0 & \alpha - \beta \end{pmatrix}.$$

Its eigen equation is

$$\det(H'_{B_{2g}} - \varepsilon^\pi S'_{B_{2g}}) = \beta^3(x - 1)(x^2 - x - 3) = 0.$$

There are three roots,

$$x_3 = 1, \quad x_4 = \frac{1 + \sqrt{13}}{2}, \quad x_2 = \frac{1 - \sqrt{13}}{2},$$

which equal to

$$\varepsilon_3^\pi = \alpha - \beta, \tag{10.24}$$

$$\varepsilon_4^\pi = \alpha - \frac{1 + \sqrt{13}}{2}\beta \approx \alpha - 2.303\beta, \tag{10.25}$$

$$\varepsilon_5^\pi = \alpha + \frac{\sqrt{13} - 1}{2}\beta \approx \alpha + 1.303\beta. \tag{10.26}$$

For  $H'_{B_{3g}} - \varepsilon_3^\pi S'_{B_{3g}}$ , its reduced row echelon form is

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

which means

$$\Phi_3 = \sqrt{2}\phi'_4 + \phi'_5.$$

The sum of squares of coefficients is

$$\sum_i c_{3,i}^2 = 3,$$

Thus, we know

$$\begin{aligned} \Phi_3^\pi &= \sqrt{\frac{2}{3}}\phi'_4 + \sqrt{\frac{1}{3}}\phi'_5 \\ &= \sqrt{\frac{1}{6}}(\phi_2 - \phi_3 + \phi_5 - \phi_7 + \phi_8 - \phi_{10}) \\ &\approx 0.4082\phi_2 - 0.4082\phi_3 + 0.4082\phi_5 - 0.4082\phi_7 + 0.4082\phi_8 - 0.4082\phi_{10}. \end{aligned} \tag{10.27}$$

Similarly, the reduced row echelon form of  $H'_{B_{3g}} - \varepsilon_4^\pi S'_{B_{3g}}$  is

$$\begin{pmatrix} 1 & 0 & -\frac{\sqrt{13}-1}{2\sqrt{2}} \\ 0 & 1 & \frac{1}{\sqrt{2}} \\ 0 & 0 & 0 \end{pmatrix},$$

which means

$$\Phi_4 = \frac{\sqrt{13}-1}{2\sqrt{2}}\phi'_3 - \frac{1}{\sqrt{2}}\phi'_4 + \phi'_5.$$

The sum of squares of coefficients is

$$\sum_i c_{4,i}^2 = \frac{13 - \sqrt{13}}{4}.$$

And then,

$$\begin{aligned} \Phi_4^\pi &= \frac{2}{\sqrt{13} - \sqrt{13}}\Phi_4 = \sqrt{\frac{\sqrt{13}-1}{2\sqrt{13}}}\phi'_3 - \sqrt{\frac{\sqrt{13}+1}{6\sqrt{13}}}\phi'_4 + \sqrt{\frac{\sqrt{13}+1}{3\sqrt{13}}}\phi'_5 \\ &= \frac{1}{2}\sqrt{\frac{\sqrt{13}-1}{2\sqrt{13}}}(\phi_1 - \phi_4 - \phi_6 + \phi_9) - \frac{1}{2}\sqrt{\frac{\sqrt{13}+1}{6\sqrt{13}}}(\phi_2 - \phi_3 - \phi_7 + \phi_8) + \sqrt{\frac{\sqrt{13}+1}{6\sqrt{13}}}(\phi_5 - \phi_{10}) \\ &\approx 0.3006\phi_1 - 0.2307\phi_2 + 0.2307\phi_3 - 0.3006\phi_4 + 0.4614\phi_5 \\ &\quad - 0.3006\phi_6 + 0.2307\phi_7 - 0.2307\phi_8 + 0.3006\phi_9 - 0.4614\phi_{10}. \end{aligned} \tag{10.28}$$

Similarly, the reduced row echelon form of  $H'_{B_{3g}} - \varepsilon_5^\pi S'_{B_{3g}}$  is

$$\begin{pmatrix} 1 & 0 & \frac{1+\sqrt{13}}{2\sqrt{2}} \\ 0 & 1 & \frac{1}{\sqrt{2}} \\ 0 & 0 & 0 \end{pmatrix},$$

which means

$$\Phi_5 = \frac{\sqrt{13}+1}{2\sqrt{2}}\phi'_3 + \frac{1}{\sqrt{2}}\phi'_4 - \phi'_5.$$

The sum of squares of coefficients is

$$\sum_i c_{5,i}^2 = \frac{13 + \sqrt{13}}{4}.$$

And then,

$$\begin{aligned} \Phi_5^\pi &= \frac{2}{\sqrt{13} + \sqrt{13}}\Phi_5 = \sqrt{\frac{\sqrt{13}+1}{2\sqrt{13}}}\phi'_3 + \sqrt{\frac{\sqrt{13}-1}{6\sqrt{13}}}\phi'_4 - \sqrt{\frac{\sqrt{13}-1}{3\sqrt{13}}}\phi'_5 \\ &= \frac{1}{2}\sqrt{\frac{\sqrt{13}+1}{2\sqrt{13}}}(\phi_1 - \phi_4 - \phi_6 + \phi_9) + \frac{1}{2}\sqrt{\frac{\sqrt{13}-1}{6\sqrt{13}}}(\phi_2 - \phi_3 - \phi_7 + \phi_8) - \sqrt{\frac{\sqrt{13}-1}{6\sqrt{13}}}(\phi_5 - \phi_{10}) \\ &\approx 0.3996\phi_1 + 0.1735\phi_2 - 0.1735\phi_3 - 0.3996\phi_4 - 0.3470\phi_5 \\ &\quad - 0.3996\phi_6 - 0.1735\phi_7 + 0.1735\phi_8 + 0.3996\phi_9 + 0.3470\phi_{10}. \end{aligned} \tag{10.29}$$

In conclusion, for the irreducible representation  $\Gamma^{B_{3g}}$ , relevant results are listed below.

Table 10.24: The Hückel MOs in the irreducible representation  $\Gamma^{B_{3g}}$  of naphthalene.

order	eigenvalue	eigenfunction				
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
1	$\alpha - \beta$	0.0000	0.4082	-0.4082	0.0000	0.4082
		$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
2	$\alpha - 2.303\beta$	0.0000	-0.4082	0.4082	0.0000	-0.4082
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
3	$\alpha + 1.303\beta$	0.3006	-0.2307	0.2307	-0.3006	0.4614
		$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
3	$\alpha + 1.303\beta$	-0.3006	0.2307	-0.2307	0.3006	-0.4614
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
3	$\alpha + 1.303\beta$	0.3996	0.1735	-0.1735	-0.3996	-0.3470
		$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
		-0.3996	-0.1735	0.1735	0.3996	0.3470

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

$$\begin{aligned} P^{A_u} \phi_1 &= \sum_R \chi^{A_u}(R) O_R \phi_1 = 2(\phi_1 - \phi_4 + \phi_6 - \phi_9), \\ P^{A_u} \phi_2 &= \sum_R \chi^{A_u}(R) O_R \phi_2 = 2(\phi_2 - \phi_3 + \phi_7 - \phi_8). \end{aligned}$$

They can be normalized to

$$\begin{aligned} \phi'_6 &= \frac{1}{2}(\phi_1 - \phi_4 + \phi_6 - \phi_9), \\ \phi'_7 &= \frac{1}{2}(\phi_2 - \phi_3 + \phi_7 - \phi_8). \end{aligned}$$

Besides, it is easy to find that they are mutually orthogonal.

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

$$H'_{B_{2g}} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha - \beta \end{pmatrix}.$$

Its eigen equation is

$$\det(H'_{A_u} - \varepsilon^\pi S'_{A_u}) = \beta^2(x^2 - x - 1) = 0. \quad (10.30)$$

There are two roots,

$$x_6 = \frac{1 + \sqrt{5}}{2}, \quad x_7 = \frac{1 - \sqrt{5}}{2}, \quad (10.31)$$

which equal to

$$\varepsilon_6^\pi = \alpha - \frac{\sqrt{5} + 1}{2}\beta \approx \alpha - 1.618\beta, \quad (10.32)$$

$$\varepsilon_7^\pi = \alpha + \frac{\sqrt{5} - 1}{2}\beta \approx \alpha + 0.618\beta. \quad (10.33)$$

For  $H'_{A_u} - \varepsilon_6^\pi S'_{A_u}$ , its reduced row echelon form is

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

which means

$$\Phi_6 = \frac{\sqrt{5} - 1}{2}\phi'_6 - \phi'_7.$$

The sum of squares of coefficients is

$$\sum_i c_{6,i}^2 = \frac{5 - \sqrt{5}}{2},$$

Thus, we know

$$\begin{aligned}
\Phi_6^\pi &= \sqrt{\frac{2}{5-\sqrt{5}}}\Phi_6 = \sqrt{\frac{2}{5-\sqrt{5}}}\left[\frac{\sqrt{5}-1}{2}\phi'_6 - \phi'_7\right] = \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}\phi'_6 - \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}\phi'_7 \\
&= \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}(\phi_1 - \phi_4 + \phi_6 - \phi_9) - \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}(\phi_2 - \phi_3 + \phi_7 - \phi_8) \\
&\approx 0.2629\phi_1 - 0.4253\phi_2 + 0.4253\phi_3 - 0.2629\phi_4 + 0.2629\phi_6 - 0.4253\phi_7 + 0.4253\phi_8 - 0.2629\phi_9.
\end{aligned} \tag{10.34}$$

Similarly, the reduced row echelon form of  $H'_{A_u} - \varepsilon_7^\pi S'_{A_u}$  is

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

which means

$$\Phi_7 = \frac{\sqrt{5}+1}{2}\phi'_6 + \phi'_7.$$

And then,

$$\begin{aligned}
\Phi_7^\pi &= \sqrt{\frac{2}{5+\sqrt{5}}}\Phi_7 = \sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}\phi'_6 + \sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}\phi'_7 \\
&= \frac{1}{2}\sqrt{\frac{\sqrt{5}+1}{2\sqrt{5}}}(\phi_1 - \phi_4 + \phi_6 - \phi_9) + \frac{1}{2}\sqrt{\frac{\sqrt{5}-1}{2\sqrt{5}}}(\phi_2 - \phi_3 + \phi_7 - \phi_8) \\
&\approx 0.4253\phi_1 + 0.2629\phi_2 - 0.2629\phi_3 - 0.4253\phi_4 + 0.4253\phi_6 + 0.2629\phi_7 - 0.2629\phi_8 - 0.4253\phi_9.
\end{aligned} \tag{10.35}$$

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

Table 10.25: The Hückel MOs in the irreducible representation  $\Gamma^{A_u}$  of naphthalene.

order	eigenvalue	eigenfunction				
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
1	$\alpha - 1.618\beta$	0.2629	-0.4253	0.4253	-0.2629	0.0000
		$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
		0.2629	-0.4253	0.4253	-0.2629	0.0000
2	$\alpha + 0.618\beta$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
		0.4253	0.2629	-0.2629	-0.4253	0.0000
		$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
		0.4253	0.2629	-0.2629	-0.4253	0.0000

For the irreducible representation  $\Gamma^{B_{1u}}$ , the only three basis functions are

$$\begin{aligned}
P^{B_{1u}}\phi_1 &= \sum_R \chi^{B_{1u}}(R)O_R\phi_1 = 2(\phi_1 + \phi_4 + \phi_6 + \phi_9), \\
P^{B_{1u}}\phi_2 &= \sum_R \chi^{B_{1u}}(R)O_R\phi_2 = 2(\phi_2 + \phi_3 + \phi_7 + \phi_8), \\
P^{B_{1u}}\phi_5 &= \sum_R \chi^{B_{1u}}(R)O_R\phi_5 = 4(\phi_5 + \phi_{10}).
\end{aligned}$$

They can be normalized to

$$\begin{aligned}
\phi'_8 &= \frac{1}{2}(\phi_1 + \phi_4 + \phi_6 + \phi_9), \\
\phi'_9 &= \frac{1}{2}(\phi_2 + \phi_3 + \phi_7 + \phi_8), \\
\phi'_{10} &= \frac{1}{\sqrt{2}}(\phi_5 + \phi_{10}).
\end{aligned}$$

Besides, it is easy to find that they are mutually orthogonal.

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

$$H'_{B_{1u}} = \begin{pmatrix} \alpha & \beta & \sqrt{2}\beta \\ \beta & \alpha + \beta & 0 \\ \sqrt{2}\beta & 0 & \alpha + \beta \end{pmatrix}.$$

Its eigen equation is

$$\det(H'_{B_{1u}} - \varepsilon^\pi S'_{B_{1u}}) = \beta^3(x+1)(x^2+x-3) = 0.$$

There are three roots,

$$x_8 = -1, \quad x_9 = \frac{-1 + \sqrt{13}}{2}, \quad x_{10} = \frac{-1 - \sqrt{13}}{2},$$

which equal to

$$\varepsilon_8^\pi = \alpha + \beta, \tag{10.36}$$

$$\varepsilon_9^\pi = \alpha - \frac{\sqrt{13}-1}{2}\beta \approx \alpha - 1.303\beta, \tag{10.37}$$

$$\varepsilon_{10}^\pi = \alpha + \frac{\sqrt{13}+1}{2}\beta \approx \alpha + 2.303\beta. \tag{10.38}$$

For  $H'_{B_{1u}} - \varepsilon_8^\pi S'_{B_{1u}}$ , its reduced row echelon form is

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

which means

$$\Phi_8 = \sqrt{2}\phi'_9 - \phi'_{10}.$$

Thus, we know

$$\begin{aligned} \Phi_8^\pi &= \sqrt{\frac{1}{3}}\Phi_8 = \sqrt{\frac{2}{3}}\phi'_9 + \sqrt{\frac{1}{3}}\phi'_{10} = \sqrt{\frac{1}{6}}(\phi_2 + \phi_3 + \phi_5 + \phi_7 + \phi_8 + \phi_{10}) \\ &\approx 0.4082\phi_2 + 0.4082\phi_3 + 0.4082\phi_5 + 0.4082\phi_7 + 0.4082\phi_8 + 0.4082\phi_{10}. \end{aligned} \tag{10.39}$$

Similarly, the reduced row echelon form of  $H'_{B_{3g}} - \varepsilon_4^\pi S'_{B_{3g}}$  is

$$\begin{pmatrix} 1 & 0 & \frac{1+\sqrt{13}}{2\sqrt{2}} \\ 0 & 1 & -\frac{1}{\sqrt{2}} \\ 0 & 0 & 0 \end{pmatrix},$$

which means

$$\Phi_9 = \frac{\sqrt{13}+1}{2\sqrt{2}}\phi'_8 - \frac{1}{\sqrt{2}}\phi'_9 - \phi'_{10}.$$

And then,

$$\begin{aligned} \Phi_9^\pi &= \frac{2}{\sqrt{13} + \sqrt{13}}\Phi_4 = \sqrt{\frac{\sqrt{13}+1}{2\sqrt{13}}}\phi'_8 - \sqrt{\frac{\sqrt{13}-1}{6\sqrt{13}}}\phi'_9 - \sqrt{\frac{\sqrt{13}-1}{3\sqrt{13}}}\phi'_{10} \\ &= \frac{1}{2}\sqrt{\frac{\sqrt{13}+1}{2\sqrt{13}}}(\phi_1 + \phi_4 + \phi_6 + \phi_9) - \frac{1}{2}\sqrt{\frac{\sqrt{13}-1}{6\sqrt{13}}}(\phi_2 + \phi_3 + \phi_7 + \phi_8) - \sqrt{\frac{\sqrt{13}-1}{6\sqrt{13}}}(\phi_5 + \phi_{10}) \\ &\approx 0.3996\phi_1 - 0.1735\phi_2 - 0.1735\phi_3 + 0.3996\phi_4 - 0.3470\phi_5 \\ &\quad + 0.3996\phi_6 - 0.1735\phi_7 - 0.1735\phi_8 + 0.3996\phi_9 - 0.3470\phi_{10}. \end{aligned} \tag{10.40}$$

Similarly, the reduced row echelon form of  $H'_{B_{1u}} - \varepsilon_{10}^\pi S'_{B_{1u}}$  is

$$\begin{pmatrix} 1 & 0 & -\frac{-1+\sqrt{13}}{2\sqrt{2}} \\ 0 & 1 & -\frac{\sqrt{2}}{\sqrt{2}} \\ 0 & 0 & 0 \end{pmatrix},$$

which means

$$\Phi_{10} = \frac{\sqrt{13}-1}{2\sqrt{2}}\phi'_8 + \frac{1}{\sqrt{2}}\phi'_9 + \phi'_{10}.$$

And then,

$$\begin{aligned} \Phi_{10}^\pi &= \frac{2}{\sqrt{13-\sqrt{13}}} \Phi_{10} = \sqrt{\frac{\sqrt{13}-1}{2\sqrt{13}}} \phi'_8 + \sqrt{\frac{\sqrt{13}+1}{6\sqrt{13}}} \phi'_9 + \sqrt{\frac{\sqrt{13}+1}{3\sqrt{13}}} \phi'_{10} \\ &= \frac{1}{2} \sqrt{\frac{\sqrt{13}-1}{2\sqrt{13}}} (\phi_1 + \phi_4 + \phi_6 + \phi_9) + \frac{1}{2} \sqrt{\frac{\sqrt{13}+1}{6\sqrt{13}}} (\phi_2 + \phi_3 + \phi_7 + \phi_8) \\ &\quad + \sqrt{\frac{\sqrt{13}+1}{6\sqrt{13}}} (\phi_5 + \phi_{10}) \\ &\approx 0.3006\phi_1 + 0.2307\phi_2 + 0.2307\phi_3 + 0.3006\phi_4 + 0.4614\phi_5 \\ &\quad + 0.3006\phi_6 + 0.2307\phi_7 + 0.2307\phi_8 + 0.3006\phi_9 + 0.4614\phi_{10}. \end{aligned} \quad (10.41)$$

In conclusion, for the irreducible representation  $\Gamma^{B_{1u}}$ , relevant results are listed below.

Table 10.26: The Hückel MOs in the irreducible representation  $\Gamma^{B_{1u}}$  of naphthalene.

order	eigenvalue	eigenfunction				
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
1	$\alpha + \beta$	0.0000	0.4082	0.4082	0.0000	0.4082
		$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
		0.0000	0.4082	0.4082	0.0000	0.4082
2	$\alpha - 1.303\beta$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
		0.3996	-0.1735	-0.1735	0.3996	-0.3470
		$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
3	$\alpha + 2.303\beta$	0.3996	-0.1735	-0.1735	0.3996	-0.3470
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
		0.3006	0.2307	0.2307	0.3006	0.4614
		$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
		0.3006	0.2307	0.2307	0.3006	0.4614

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

Table 10.27: The occupied Hückel MOs in all irreducible representations of naphthalene.

order	orbital energy	irrep	eigenfunction				
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
1	$\alpha + 2.303\beta$	$B_{1u}$	0.3006	0.2307	0.2307	0.3006	0.4614
			$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
			0.3006	0.2307	0.2307	0.3006	0.4614
2	$\alpha + 1.618\beta$	$B_{2g}$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
			0.2629	0.4253	0.4253	0.2629	0.0000
			$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
3	$\alpha + 1.303\beta$	$B_{3g}$	-0.2629	-0.4253	-0.4253	-0.2629	0.0000
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
			0.3996	0.1735	-0.1735	-0.3996	-0.3470
4	$\alpha + \beta$	$B_{1u}$	$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
			0.0000	0.4082	0.4082	0.0000	0.4082
			0.0000	0.4082	0.4082	0.0000	0.4082
5	$\alpha + 0.618\beta$	$A_u$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
			0.4253	0.2629	-0.2629	-0.4253	0.0000
			$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
			0.4253	0.2629	-0.2629	-0.4253	0.0000

Table 10.28: The unoccupied Hückel MOs in all irreducible representations of naphthalene.

order	orbital energy	irrep	eigenfunction				
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
1	$\alpha - 0.618\beta$	$B_{2g}$	0.4253	-0.2629	-0.2629	0.4253	0.0000
			$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
			-0.4253	0.2629	0.2629	-0.4253	0.0000
2	$\alpha - \beta$	$B_{3g}$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
			0.0000	0.4082	-0.4082	0.0000	0.4082
			$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
3	$\alpha - 1.303\beta$	$B_{1u}$	0.0000	-0.4082	0.4082	0.0000	-0.4802
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
			0.3996	-0.1735	-0.1735	0.3996	-0.3470
4	$\alpha - 1.618\beta$	$A_u$	$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
			0.3996	-0.1735	-0.1735	0.3996	-0.3470
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
5	$\alpha - 2.303\beta$	$B_{3g}$	0.2629	-0.4253	0.4253	-0.2629	0.0000
			$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$
			0.2629	-0.4253	0.4253	-0.2629	0.0000

Besides, their phase diagrams have been painted in Fig 10.9.

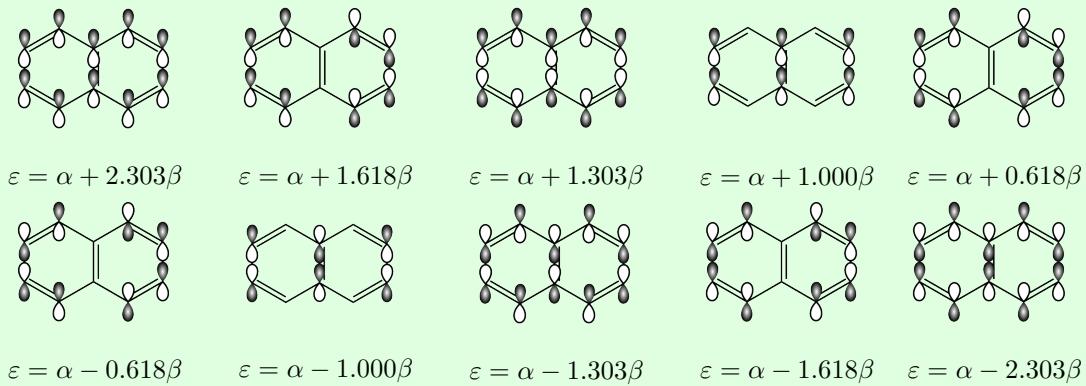


Figure 10.9: Phase diagrams of these Hückel MOs of naphthalene. Black bubbles mean plus phase while white ones mean minus phase. The color is used just for determining relative phase.

In the end, we conclude that for naphthalene, its ground state  $\pi$ -electron configuration is  $(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^2$  and its delocalization energy is  $2 \times 2.303\beta + 2 \times 1.618\beta + 2 \times 1.313\beta + 2 \times 1.000\beta + 2 \times 0.618\beta - 10 \times 1.000\beta = 3.684\beta$ , much larger than the sum of that of *trans*-1,3-butadiene ( $0.472\beta$ ) and benzene ( $2.000\beta$ ).

—	$\alpha - 2.303\beta$	$(3b_{3g})$
—	$\alpha - 1.618\beta$	$(2a_u)$
—	$\alpha - 1.303\beta$	$(3b_{1u})$
—	$\alpha - \beta$	$(2b_{3g})$
—	$\alpha - 0.618\beta$	$(2b_{2g})$
—*	$\alpha + 0.618\beta$	$(1a_u)$
—*	$\alpha + \beta$	$(2b_{1u})$
—*	$\alpha + 1.303\beta$	$(1b_{3g})$
—*	$\alpha + 1.618\beta$	$(1b_{2g})$
—*	$\alpha + 2.303\beta$	$(1b_{1u})$

- (f) Firstly, it is easy to find that phenanthrene belongs to the point group  $C_{2h}$ , whose character table is listed below.

Table 10.29: The character table for the  $C_{2h}$  point group.

$C_{2h}$	$E$	$C_2$	$i$	$\sigma_h$
$A_g$	1	1	1	1
$B_g$	1	-1	1	-1
$A_u$	1	1	-1	-1
$B_u$	1	-1	-1	1

Besides, its all nontrivial symmetry elements are shown in Fig 10.10.

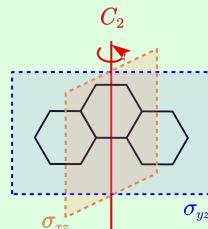


Figure 10.10: All nontrivial symmetry elements of phenanthrene.

Secondly, we mark all carbon atoms as shown in Fig 10.11.

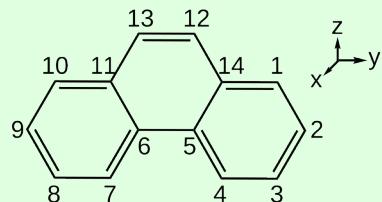


Figure 10.11: The label of carbon atoms in phenanthrene.

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

Table 10.30: The character of the  $\pi$ -electron atomic orbitals' representation  $\Gamma^{AO}$ .

	$E$	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$\chi^{AO}(C_i)$	14	0	0	-14

Relevant reduction coefficients are

$$a_1 = 0, \quad a_2 = 7, \quad b_1 = 7, \quad b_2 = 0.$$

Thus, we obtain

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

We conclude that there are seven basis functions in the irreducible representation  $\Gamma^{A_2}$  and  $\Gamma^{B_1}$ , respectively. Thus, to describe the effect of  $O_R$ , seven suitable  $2p_z$  atomic orbitals  $\phi_i$  is enough.

Thirdly, we inspect the transformation of  $\phi_i$  under  $O_R$  for the phenanthrene, whose information is recorded below. We have to list up to seven  $2p_z$  functions in current case.

Table 10.31: Transformation of  $\phi_i$  under  $O_R$  for the phenanthrene.

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

Fourthly, it's time to discuss situations in different irreducible representation.

For the irreducible representation  $\Gamma^{A_2}$ ,

$$\begin{aligned} P^{A_2}\phi_1 &= \sum_R \chi^{A_2}(R)O_R\phi_1 = 2(\phi_1 - \phi_{10}), \\ P^{A_2}\phi_2 &= \sum_R \chi^{A_2}(R)O_R\phi_2 = 2(\phi_2 - \phi_9), \\ P^{A_2}\phi_3 &= \sum_R \chi^{A_2}(R)O_R\phi_3 = 2(\phi_3 - \phi_8), \\ P^{A_2}\phi_4 &= \sum_R \chi^{A_2}(R)O_R\phi_4 = 2(\phi_4 - \phi_7), \\ P^{A_2}\phi_5 &= \sum_R \chi^{A_2}(R)O_R\phi_5 = 2(\phi_5 - \phi_6), \\ P^{A_2}\phi_6 &= \sum_R \chi^{A_2}(R)O_R\phi_6 = 2(\phi_{11} - \phi_{14}), \\ P^{A_2}\phi_7 &= \sum_R \chi^{A_2}(R)O_R\phi_7 = 2(\phi_{12} - \phi_{13}). \end{aligned}$$

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

$$\begin{aligned} \phi'_1 &= \frac{1}{\sqrt{2}}(\phi_1 - \phi_{10}), \\ \phi'_2 &= \frac{1}{\sqrt{2}}(\phi_2 - \phi_9), \\ \phi'_3 &= \frac{1}{\sqrt{2}}(\phi_3 - \phi_8), \\ \phi'_4 &= \frac{1}{\sqrt{2}}(\phi_4 - \phi_7), \\ \phi'_5 &= \frac{1}{\sqrt{2}}(\phi_5 - \phi_6), \\ \phi'_6 &= \frac{1}{\sqrt{2}}(\phi_{11} - \phi_{14}), \\ \phi'_7 &= \frac{1}{\sqrt{2}}(\phi_{12} - \phi_{13}). \end{aligned}$$

Then, the effective Hamitonian matrix elements for  $\pi$  electrons can be calculated,

$$H'_{A_2} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & -\beta & 0 \\ \beta & \alpha & \beta & 0 & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & 0 & \beta & \alpha - \beta & -\beta & 0 \\ -\beta & 0 & 0 & 0 & -\beta & \alpha & \beta \\ 0 & 0 & 0 & 0 & 0 & \beta & \alpha - \beta \end{pmatrix}$$

Next,

$$\det(H'_{A_2} - \varepsilon^\pi S'_{A_2}) = \beta^7(x^7 - 2x^6 - 6x^5 + 11x^4 + 9x^3 - 15x^2 - 4x + 5) = 0,$$

where

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

Obviously, it is hard to solve this equation analytically. We have to apply numerical solution. The polynomial function  $y = x^7 - 2x^6 - 6x^5 + 11x^4 + 9x^3 - 15x^2 - 4x + 5$  in the closed interval  $[-2.5, 2.5]$  can be plotted as shown in Fig 10.12.

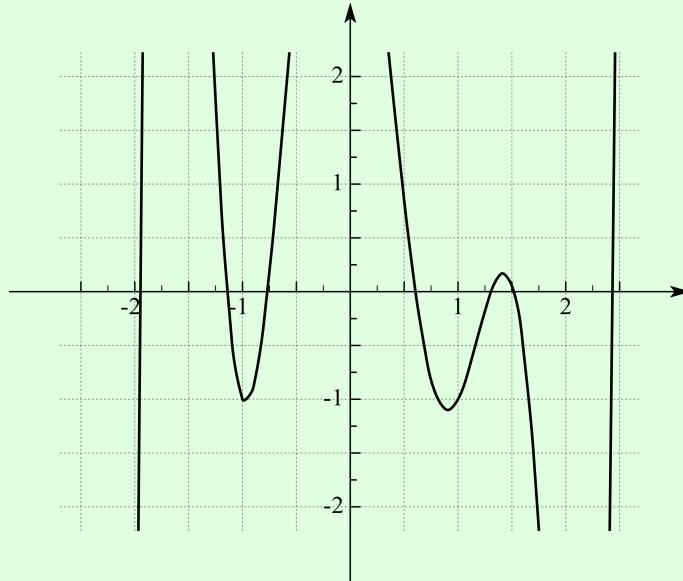


Figure 10.12: The diagram of function  $y = x^7 - 2x^6 - 6x^5 + 11x^4 + 9x^3 - 15x^2 - 4x + 5$  in the closed interval  $[-2.5, 2.5]$ .

There are seven roots,

$$x_1 \approx -1.95063, \quad x_2 \approx -1.14238, \quad x_3 \approx -0.769052, \quad x_4 \approx 0.605225, \\ x_5 \approx 1.30580, \quad x_6 \approx 1.51627, \quad x_7 \approx 2.43476.$$

which equal to

$$\varepsilon_1 = \alpha - x_1\beta \approx \alpha + 1.95063\beta, \tag{10.42}$$

$$\varepsilon_2 = \alpha - x_2\beta \approx \alpha + 1.14238\beta, \tag{10.43}$$

$$\varepsilon_3 = \alpha - x_3\beta \approx \alpha + 0.769052\beta, \tag{10.44}$$

$$\varepsilon_4 = \alpha - x_4\beta \approx \alpha - 0.605225\beta, \tag{10.45}$$

$$\varepsilon_5 = \alpha - x_5\beta \approx \alpha - 1.30580\beta, \tag{10.46}$$

$$\varepsilon_6 = \alpha - x_6\beta \approx \alpha - 1.51627\beta, \tag{10.47}$$

$$\varepsilon_7 = \alpha - x_7\beta \approx \alpha - 2.43476\beta. \tag{10.48}$$

For  $H'_{B_2} - \varepsilon_1^\pi S'_{B_2}$ , its reduced row echelon form is

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 2.991107 \\ 0 & 1 & 0 & 0 & 0 & 0 & 2.884044 \\ 0 & 0 & 1 & 0 & 0 & 0 & 2.634595 \\ 0 & 0 & 0 & 1 & 0 & 0 & 2.255077 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1.764225 \\ 0 & 0 & 0 & 0 & 0 & 1 & -2.950499 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

which means

$$\Phi_1 = 2.991107\phi'_1 + 2.884044\phi'_2 + 2.634595\phi'_3 + 2.255077\phi'_4 + 1.764225\phi'_5 - 2.950499\phi'_6 - 1.000000\phi'_7.$$

The sum of squares of coefficients is

$$\sum_{i=1}^7 c_{1,i}^2 = 42.1088.$$

Thus, we know

$$\begin{aligned} \Phi_1^\pi &= \frac{1}{\sqrt{\sum_{i=1}^7 c_{1,i}^2}} \Phi_1 \approx 0.154104 \Phi_1 \\ &\approx 0.46094\phi'_1 + 0.44444\phi'_2 + 0.40600\phi'_3 + 0.34752\phi'_4 + 0.27187\phi'_5 - 0.45468\phi'_6 - 0.15410\phi'_7 \\ &\approx 0.32594\phi_1 + 0.31427\phi_2 + 0.28709\phi_3 + 0.24573\phi_4 + 0.19224\phi_5 \\ &\quad - 0.19224\phi_6 - 0.24573\phi_7 - 0.28709\phi_8 - 0.31427\phi_9 - 0.32594\phi_{10} \\ &\quad - 0.32151\phi_{11} - 0.10897\phi_{12} + 0.10897\phi_{13} + 0.32151\phi_{14}. \end{aligned} \tag{10.49}$$

Similarly, we can obtain other eigenvalues and their eigenfunctions. Their intermediate and final results are listed.

- $\varepsilon_2 \approx \alpha + 1.14238\beta$

The original eigenfunction is

$$\Phi_2 = 1.19554\phi'_1 - 0.77669\phi'_2 - 2.08281\phi'_3 - 1.60267\phi'_4 + 0.25195\phi'_5 - 2.14244\phi'_6 - 1.00000\phi'_7.$$

The sum of coefficients is

$$\sum_i c_{2,i}^2 = 14.5927.$$

The normalized eigenfunction is

$$\begin{aligned} \Phi_2^\pi &\approx 0.261777 \Phi_2 \\ &\approx 0.31296\phi'_1 - 0.20332\phi'_2 - 0.54523\phi'_3 - 0.41954\phi'_4 + 0.06596\phi'_5 - 0.56084\phi'_6 - 0.26178\phi'_7 \\ &\approx 0.22130\phi_1 - 0.14377\phi_2 - 0.38544\phi_3 - 0.29666\phi_4 + 0.04664\phi_5 \\ &\quad - 0.04664\phi_6 + 0.29666\phi_7 + 0.38544\phi_8 + 0.14377\phi_9 - 0.22130\phi_{10} \\ &\quad - 0.39658\phi_{11} - 0.18510\phi_{12} + 0.18510\phi_{13} + 0.39658\phi_{14}. \end{aligned} \tag{10.50}$$

- $\varepsilon_3 \approx \alpha + 0.769052\beta$

The original eigenfunction is

$$\Phi_3 = 2.70354\phi'_1 + 3.84820\phi'_2 + 0.25592\phi'_3 - 3.65138\phi'_4 - 3.06402\phi'_5 + 1.76903\phi'_6 + 1.00000\phi'_7.$$

The sum of coefficients is

$$\sum_i c_{3,i}^2 = 49.0335.$$

The normalized eigenfunction is

$$\Phi_3^\pi \approx 0.142808 \Phi_3$$

$$\begin{aligned}
&\approx 0.38609\phi'_1 + 0.54955\phi'_2 + 0.03655\phi'_3 - 0.52145\phi'_4 - 0.43757\phi'_5 + 0.25263\phi'_6 + 0.14281\phi'_7 \\
&\approx 0.27301\phi_1 + 0.38858\phi_2 + 0.02584\phi_3 - 0.36872\phi_4 - 0.30941\phi_5 \\
&\quad + 0.30941\phi_6 + 0.36872\phi_7 - 0.02584\phi_8 - 0.38858\phi_9 - 0.27301\phi_{10} \\
&\quad + 0.17864\phi_{11} + 0.10098\phi_{12} - 0.10098\phi_{13} - 0.17864\phi_{14}.
\end{aligned} \tag{10.51}$$

- $\varepsilon_4 \approx \alpha - 0.605225\beta$

$$\Phi_4 = 0.81967\phi'_1 - 0.10131\phi'_2 - 0.75836\phi'_3 + 0.56029\phi'_4 + 0.41926\phi'_5 + 0.39478\phi'_6 + 1.00000\phi'_7.$$

$$\sum_i c_{4,i}^2 = 2.90277.$$

$$\begin{aligned}
\Phi_4^\pi &\approx 0.586940\Phi_4 \\
&\approx 0.48110\phi'_1 - 0.05946\phi'_2 - 0.44511\phi'_3 + 0.32885\phi'_4 + 0.24608\phi'_5 + 0.23171\phi'_6 + 0.58694\phi'_7 \\
&\approx 0.34019\phi_1 - 0.04205\phi_2 - 0.31474\phi_3 + 0.23253\phi_4 + 0.17400\phi_5 \\
&\quad - 0.17400\phi_6 - 0.23253\phi_7 + 0.31474\phi_8 + 0.04205\phi_9 - 0.34019\phi_{10} \\
&\quad + 0.16384\phi_{11} + 0.41503\phi_{12} - 0.41503\phi_{13} - 0.16384\phi_{14}.
\end{aligned} \tag{10.52}$$

- $\varepsilon_5 \approx \alpha - 1.30580\beta$

The original eigenfunction is

$$\Phi_5 = 3.45516\phi'_1 - 4.20593\phi'_2 + 2.03694\phi'_3 + 1.54608\phi'_4 - 4.05582\phi'_5 + 0.30582\phi'_6 - 1.00000\phi'_7.$$

The sum of coefficients is

$$\sum_i c_{5,i}^2 = 53.7106.$$

The normalized eigenfunction is

$$\begin{aligned}
\Phi_5^\pi &\approx 0.136449\Phi_5 \\
&\approx 0.47145\phi'_1 - 0.57389\phi'_2 + 0.27794\phi'_3 + 0.21096\phi'_4 - 0.55341\phi'_5 + 0.04173\phi'_6 - 0.13644\phi'_7 \\
&\approx 0.33337\phi_1 - 0.40580\phi_2 + 0.19653\phi_3 + 0.14917\phi_4 - 0.39132\phi_5 \\
&\quad + 0.39132\phi_6 - 0.14917\phi_7 - 0.19653\phi_8 + 0.40580\phi_9 - 0.33337\phi_{10} \\
&\quad + 0.02951\phi_{11} - 0.09648\phi_{12} + 0.09648\phi_{13} - 0.02951\phi_{14}.
\end{aligned} \tag{10.53}$$

- $\varepsilon_6 \approx \alpha - 1.51627\beta$

The original eigenfunction is

$$\Phi_6 = 0.04360\phi'_1 + 0.45017\phi'_2 - 0.72618\phi'_3 + 0.65091\phi'_4 - 0.26078\phi'_5 + 0.51628\phi'_6 - 1.00000\phi'_7.$$

The sum of coefficients is

$$\sum_i c_{6,i}^2 = 2.49013.$$

The normalized eigenfunction is

$$\begin{aligned}
\Phi_6^\pi &\approx 0.633708\Phi_6 \\
&\approx 0.02763\phi'_1 + 0.28528\phi'_2 - 0.46018\phi'_3 + 0.41249\phi'_4 - 0.16526\phi'_5 + 0.32717\phi'_6 - 0.63371\phi'_7 \\
&\approx 0.01954\phi_1 + 0.20172\phi_2 - 0.32540\phi_3 + 0.29167\phi_4 - 0.11686\phi_5 \\
&\quad + 0.11686\phi_6 - 0.29167\phi_7 + 0.32540\phi_8 - 0.20172\phi_9 - 0.01954\phi_{10} \\
&\quad + 0.23134\phi_{11} - 0.44810\phi_{12} + 0.44810\phi_{13} - 0.23134\phi_{14}.
\end{aligned} \tag{10.54}$$

- $\varepsilon_7 \approx \alpha - 2.43476\beta$

The original eigenfunction is

$$\Phi_7 = 0.83768\phi'_1 - 0.60476\phi'_2 + 0.63476\phi'_3 - 0.94073\phi'_4 + 1.65569\phi'_5 + 1.43479\phi'_6 - 1.00000\phi'_7.$$

The sum of coefficients is

$$\sum_i c_{7,i}^2 = 8.15527.$$

The normalized eigenfunction is

$$\begin{aligned}\Phi_7^\pi &\approx 0.350171\Phi_7 \\ &\approx 0.29333\phi'_1 - 0.21177\phi'_2 + 0.22228\phi'_3 - 0.32942\phi'_4 + 0.57978\phi'_5 + 0.50242\phi'_6 - 0.35017\phi'_7 \\ &\approx 0.20742\phi_1 - 0.14974\phi_2 + 0.15717\phi_3 - 0.23293\phi_4 + 0.40996\phi_5 \\ &\quad - 0.40996\phi_6 + 0.23293\phi_7 - 0.15717\phi_8 + 0.14974\phi_9 - 0.20742\phi_{10} \\ &\quad + 0.35527\phi_{11} - 0.24761\phi_{12} + 0.24761\phi_{13} - 0.35527\phi_{14}. \end{aligned} \tag{10.55}$$

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

Table 10.32: The Hückel MOs in the irreducible representation  $\Gamma^{A_2}$  of phenanthrene.

order	eigenvalue	eigenfunction						
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
1	$\alpha + 1.951\beta$	0.3259	0.3143	0.2871	0.2457	0.1922	-0.1922	-0.2457
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
		-0.2871	-0.3143	-0.3259	-0.3215	-0.1090	0.1090	0.3215
2	$\alpha + 1.142\beta$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.2213	-0.1438	-0.3855	-0.2967	0.0466	-0.0466	0.2967
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
3	$\alpha + 0.769\beta$	0.3855	0.1438	-0.2213	-0.3966	-0.1851	0.1851	0.3966
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.2730	0.3886	0.0258	-0.3687	-0.3094	0.3094	0.3687
4	$\alpha - 0.605\beta$	$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
		-0.0258	-0.3886	-0.2730	0.1786	0.1010	-0.1010	-0.1786
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
5	$\alpha - 1.306\beta$	0.3402	-0.0420	-0.3147	0.2325	0.1740	-0.1740	-0.2325
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
		0.3147	0.0420	-0.3402	0.1638	0.4150	-0.4150	-0.1638
6	$\alpha - 1.516\beta$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.3334	-0.4058	0.1965	0.1492	-0.3913	0.3913	-0.1492
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
7	$\alpha - 2.435\beta$	-0.1965	0.4058	-0.3334	0.0295	-0.0965	0.0965	-0.0295
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.0195	0.2017	-0.3254	0.2917	-0.1169	0.1169	-0.2917
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
		0.3254	-0.2017	-0.0195	0.2313	-0.4481	0.4481	-0.2313
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.2074	-0.1497	0.1572	-0.2329	0.4100	-0.4100	0.2329
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
		-0.1572	0.1497	-0.2074	0.3553	-0.2476	0.2476	-0.3553

For the irreducible representation  $\Gamma^{B_1}$ ,

$$\begin{aligned}P^{B_1}\phi_1 &= \sum_R \chi^{B_1}(R)O_R\phi_1 = 2(\phi_1 + \phi_{10}), \\ P^{B_1}\phi_2 &= \sum_R \chi^{B_1}(R)O_R\phi_2 = 2(\phi_2 + \phi_9), \\ P^{B_1}\phi_3 &= \sum_R \chi^{B_1}(R)O_R\phi_3 = 2(\phi_3 + \phi_8), \\ P^{B_1}\phi_4 &= \sum_R \chi^{B_1}(R)O_R\phi_4 = 2(\phi_4 + \phi_7), \\ P^{B_1}\phi_5 &= \sum_R \chi^{B_1}(R)O_R\phi_5 = 2(\phi_5 + \phi_6),\end{aligned}$$

$$P^{B_1}\phi_6 = \sum_R \chi^{B_1}(R) O_R \phi_6 = 2(\phi_{11} + \phi_{14}),$$

$$P^{B_1}\phi_7 = \sum_R \chi^{B_1}(R) O_R \phi_7 = 2(\phi_{12} + \phi_{13}).$$

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

$$\phi'_8 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_{10}),$$

$$\phi'_9 = \frac{1}{\sqrt{2}}(\phi_2 + \phi_9),$$

$$\phi'_{10} = \frac{1}{\sqrt{2}}(\phi_3 + \phi_8),$$

$$\phi'_{11} = \frac{1}{\sqrt{2}}(\phi_4 + \phi_7),$$

$$\phi'_{12} = \frac{1}{\sqrt{2}}(\phi_5 + \phi_6),$$

$$\phi'_{13} = \frac{1}{\sqrt{2}}(\phi_{11} + \phi_{14}),$$

$$\phi'_{14} = \frac{1}{\sqrt{2}}(\phi_{12} + \phi_{13}).$$

Then, the effective Hamitonian matrix elements for  $\pi$  electrons can be calculated,

$$H'_{B_1} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta & 0 \\ \beta & \alpha & \beta & 0 & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & 0 & \beta & \alpha + \beta & \beta & 0 \\ \beta & 0 & 0 & 0 & \beta & \alpha & \beta \\ 0 & 0 & 0 & 0 & 0 & \beta & \alpha + \beta \end{pmatrix}$$

Next,

$$\det(H'_{B_1} - \varepsilon^\pi S'_{B_1}) = \beta^7(x^7 + 2x^6 - 6x^5 - 11x^4 + 9x^3 + 15x^2 - 4x - 5) = 0.$$

We also apply numerical approach to solve  $x^7 + 2x^6 - 6x^5 - 11x^4 + 9x^3 + 15x^2 - 4x - 5 = 0$ . The function  $y = x^7 + 2x^6 - 6x^5 - 11x^4 + 9x^3 + 15x^2 - 4x - 5$  in the closed interval  $[-2.5, 2.5]$  is plotted as shown in Fig 10.13.

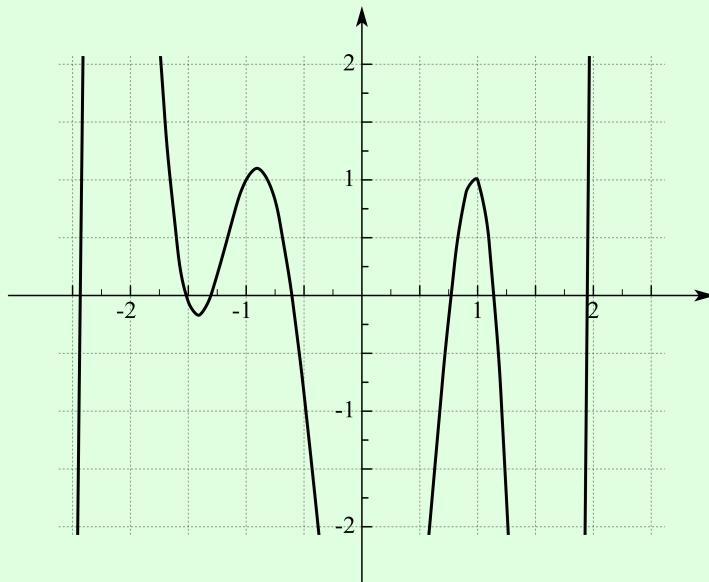


Figure 10.13: The diagram of function  $y = x^7 + 2x^6 - 6x^5 - 11x^4 + 9x^3 + 15x^2 - 4x - 5$  in range  $[-2.5, 2.5]$ .

There are also seven roots,

$$\begin{aligned} x_8 &\approx -2.43476, & x_9 &\approx -1.51627, & x_{10} &\approx -1.30580, & x_{11} &\approx -0.605225, \\ x_{12} &\approx 0.769052, & x_{13} &\approx 1.14238, & x_{14} &\approx 1.95063. \end{aligned}$$

which equal to

$$\varepsilon_8 \approx \alpha + 2.43476\beta, \quad (10.56)$$

$$\varepsilon_9 \approx \alpha + 1.51627\beta, \quad (10.57)$$

$$\varepsilon_{10} \approx \alpha + 1.30580\beta, \quad (10.58)$$

$$\varepsilon_{11} \approx \alpha + 0.605225\beta, \quad (10.59)$$

$$\varepsilon_{12} \approx \alpha - 0.769052\beta, \quad (10.60)$$

$$\varepsilon_{13} \approx \alpha - 1.14238\beta, \quad (10.61)$$

$$\varepsilon_{14} \approx \alpha - 1.95063\beta. \quad (10.62)$$

And then, their eigenfunctions can be solved. Intermediate and final results are listed below, too.

- $\varepsilon_8 \approx \alpha + 2.43476\beta$

The original eigenfunction is

$$\Phi_8 = 0.83768\phi'_8 + 0.60476\phi'_9 + 0.63476\phi'_{10} + 0.94073\phi'_{11} + 1.65569\phi'_{12} + 1.43479\phi'_{13} + 1.00000\phi'_{14}.$$

The sum of coefficients is

$$\sum_i c_{8,i}^2 = 8.15527.$$

The normalized eigenfunction is

$$\begin{aligned} \Phi_8^\pi &\approx 0.350171\Phi_8 \\ &\approx 0.29333\phi'_8 + 0.21177\phi'_9 + 0.22228\phi'_{10} + 0.32942\phi'_{11} + 0.57978\phi'_{12} \\ &\quad + 0.50242\phi'_{13} + 0.35017\phi'_{14} \\ &\approx 0.20742\phi_1 + 0.14974\phi_2 + 0.15717\phi_3 + 0.23293\phi_4 + 0.40996\phi_5 \\ &\quad + 0.40996\phi_6 + 0.23293\phi_7 + 0.15717\phi_8 + 0.14974\phi_9 + 0.20742\phi_{10} \\ &\quad + 0.35527\phi_{11} + 0.24761\phi_{12} + 0.24761\phi_{13} + 0.35527\phi_{14}. \end{aligned} \quad (10.63)$$

- $\varepsilon_9 \approx \alpha + 1.51627\beta$

The original eigenfunction is

$$\Phi_9 = 0.04360\phi'_8 - 0.45017\phi'_9 - 0.72618\phi'_{10} - 0.65091\phi'_{11} - 0.26078\phi'_{12} + 0.51628\phi'_{13} + 1.00000\phi'_{14}.$$

The sum of coefficients is

$$\sum_i c_{9,i}^2 = 2.49013.$$

The normalized eigenfunction is

$$\begin{aligned} \Phi_9^\pi &\approx 0.633708\Phi_9 \\ &\approx 0.02763\phi'_8 - 0.28528\phi'_9 - 0.46018\phi'_{10} - 0.41249\phi'_{11} - 0.16526\phi'_{12} \\ &\quad + 0.32717\phi'_{13} + 0.63371\phi'_{14} \\ &\approx 0.01954\phi_1 - 0.20172\phi_2 - 0.32540\phi_3 - 0.29167\phi_4 - 0.11686\phi_5 \\ &\quad - 0.11686\phi_6 - 0.29167\phi_7 - 0.32540\phi_8 - 0.20172\phi_9 + 0.01954\phi_{10} \\ &\quad + 0.23134\phi_{11} + 0.44810\phi_{12} + 0.44810\phi_{13} + 0.23134\phi_{14}. \end{aligned} \quad (10.64)$$

- $\varepsilon_{10} \approx \alpha + 1.30580\beta$

The original eigenfunction is

$$\Phi_{10} = 3.45516\phi'_8 + 4.20593\phi'_9 + 2.03694\phi'_{10} - 1.54608\phi'_{11} - 4.05582\phi'_{12} + 0.30582\phi'_{13} + 1.00000\phi'_{14}.$$

The sum of coefficients is

$$\sum_i c_{10,i}^2 = 53.7106.$$

The normalized eigenfunction is

$$\begin{aligned}\Phi_{10}^\pi &\approx 0.13645\Phi_{10} \\ &\approx 0.47145\phi'_8 + 0.57389\phi'_9 + 0.27794\phi'_{10} - 0.21096\phi'_{11} - 0.55341\phi'_{12} \\ &\quad + 0.04173\phi'_{13} + 0.13644\phi'_{14} \\ &\approx 0.33337\phi_1 + 0.40580\phi_2 + 0.19653\phi_3 - 0.14917\phi_4 - 0.39132\phi_5 \\ &\quad - 0.39132\phi_6 - 0.14917\phi_7 + 0.19653\phi_8 + 0.40580\phi_9 + 0.33337\phi_{10} \\ &\quad + 0.02951\phi_{11} + 0.09648\phi_{12} + 0.09648\phi_{13} + 0.02951\phi_{14}. \end{aligned} \tag{10.65}$$

- $\varepsilon_{11} \approx \alpha + 0.605225\beta$

The original eigenfunction is

$$\Phi_{11} = 0.81967\phi'_8 + 0.10131\phi'_9 - 0.75836\phi'_{10} - 0.56029\phi'_{11} + 0.41926\phi'_{12} + 0.39478\phi'_{13} - 1.00000\phi'_{14}.$$

The sum of coefficients is

$$\sum_i c_{11,i}^2 = 2.90277.$$

The normalized eigenfunction is

$$\begin{aligned}\Phi_{11}^\pi &\approx 0.586940\Phi_{11} \\ &\approx 0.48110\phi'_8 + 0.05946\phi'_9 - 0.44511\phi'_{10} - 0.32885\phi'_{11} + 0.24608\phi'_{12} \\ &\quad + 0.23171\phi'_{13} - 0.58694\phi'_{14} \\ &\approx 0.34019\phi_1 - 0.04205\phi_2 - 0.31474\phi_3 + 0.23253\phi_4 + 0.17400\phi_5 \\ &\quad + 0.17400\phi_6 + 0.23253\phi_7 - 0.31474\phi_8 - 0.04205\phi_9 + 0.34019\phi_{10} \\ &\quad + 0.16384\phi_{11} - 0.41503\phi_{12} - 0.41503\phi_{13} + 0.16384\phi_{14}. \end{aligned} \tag{10.66}$$

- $\varepsilon_{12} \approx \alpha - 0.769052\beta$

The original eigenfunction is

$$\Phi_{12} = 2.70354\phi'_8 - 3.84820\phi'_9 + 0.25592\phi'_{10} + 3.65138\phi'_{11} - 3.06402\phi'_{12} + 1.76903\phi'_{13} - 1.00000\phi'_{14}.$$

The sum of coefficients is

$$\sum_i c_{12,i}^2 = 49.0335.$$

The normalized eigenfunction is

$$\begin{aligned}\Phi_{12}^\pi &\approx 0.142808\Phi_{12} \\ &\approx 0.38609\phi'_8 - 0.54955\phi'_9 + 0.03655\phi'_{10} + 0.52145\phi'_{11} - 0.43757\phi'_{12} \\ &\quad + 0.25263\phi'_{13} - 0.14281\phi'_{14} \\ &\approx 0.27301\phi_1 - 0.38858\phi_2 + 0.02584\phi_3 + 0.36872\phi_4 - 0.30941\phi_5 \\ &\quad - 0.30941\phi_6 + 0.36872\phi_7 + 0.02584\phi_8 - 0.38858\phi_9 + 0.27301\phi_{10} \\ &\quad + 0.17864\phi_{11} - 0.10098\phi_{12} - 0.10098\phi_{13} + 0.17864\phi_{14}. \end{aligned} \tag{10.67}$$

- $\varepsilon_{13} \approx \alpha - 1.14238\beta$

The original eigenfunction is

$$\Phi_{13} = 1.19554\phi'_8 + 0.77669\phi'_9 - 2.08281\phi'_{10} + 1.60267\phi'_{11} + 0.25195\phi'_{12} - 2.14244\phi'_{13} + 1.00000\phi'_{14}.$$

The sum of coefficients is

$$\sum_i c_{13,i}^2 = 14.5927.$$

The normalized eigenfunction is

$$\begin{aligned}
\Phi_{13}^\pi &\approx 0.261777\Phi_{13} \\
&\approx 0.31296\phi'_8 + 0.20332\phi'_9 - 0.54523\phi'_{10} + 0.41954\phi'_{11} + 0.06596\phi'_{12} \\
&\quad - 0.56084\phi'_{13} + 0.26178\phi'_{14} \\
&\approx 0.22130\phi_1 + 0.14377\phi_2 - 0.38554\phi_3 + 0.29666\phi_4 + 0.04664\phi_5 \\
&\quad + 0.04664\phi_6 + 0.29666\phi_7 - 0.38554\phi_8 + 0.14377\phi_9 + 0.22130\phi_{10} \\
&\quad - 0.39658\phi_{11} + 0.18510\phi_{12} + 0.18510\phi_{13} - 0.39658\phi_{14}.
\end{aligned} \tag{10.68}$$

- $\varepsilon_{14} \approx \alpha - 1.95063\beta$

The original eigenfunction is

$$\Phi_{14} = 2.99111\phi'_8 - 2.88404\phi'_9 + 2.63460\phi'_{10} - 2.25508\phi'_{11} + 1.76423\phi'_{12} - 2.95050\phi'_{13} + 1.00000\phi'_{14}.$$

The sum of coefficients is

$$\sum_i c_{14,i}^2 = 42.1088$$

The normalized eigenfunction is

$$\begin{aligned}
\Phi_{14}^\pi &\approx 0.154104\Phi_{14} \\
&\approx 0.46094\phi'_8 - 0.44444\phi'_9 + 0.40600\phi'_{10} - 0.34752\phi'_{11} + 0.27187\phi'_{12} \\
&\quad - 0.45468\phi'_{13} + 0.15410\phi'_{14} \\
&\approx 0.32594\phi_1 - 0.31427\phi_2 + 0.28709\phi_3 - 0.24573\phi_4 + 0.19224\phi_5 \\
&\quad + 0.19224\phi_6 - 0.24573\phi_7 + 0.28709\phi_8 - 0.31427\phi_9 + 0.32594\phi_{10} \\
&\quad - 0.32151\phi_{11} + 0.10897\phi_{12} + 0.10897\phi_{13} - 0.32151\phi_{14}.
\end{aligned} \tag{10.69}$$

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

Table 10.33: The Hückel MOs in the irreducible representation  $\Gamma^{B_1}$  of phenanthrene.

order	eigenvalue	eigenfunction						
1	$\alpha + 2.435\beta$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.2074	0.1497	0.1572	0.2329	0.4100	0.4100	0.2329
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
2	$\alpha + 1.516\beta$	0.1572	0.1497	0.2074	0.3553	0.2476	0.2476	0.3553
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.0195	-0.2017	-0.3254	-0.2917	-0.1169	-0.1169	-0.2917
3	$\alpha + 1.306\beta$	$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
		-0.3254	-0.2017	0.0195	0.2313	0.4481	0.4481	0.2313
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
4	$\alpha + 0.605\beta$	0.3334	0.4058	0.1965	-0.1492	-0.3913	-0.3913	-0.1492
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
		0.1965	0.4058	0.3334	0.0295	0.0965	0.0965	0.0295
5	$\alpha - 0.769\beta$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.3402	-0.0420	-0.3147	0.2325	0.1740	0.1740	0.2325
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
6	$\alpha - 1.142\beta$	-0.3147	-0.0420	0.3402	0.1638	-0.4150	-0.4150	0.1638
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.2730	-0.3886	0.0258	0.3687	-0.3094	-0.3094	0.3687
7	$\alpha - 1.951\beta$	$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
		0.0258	-0.3886	0.2730	0.1786	-0.1010	-0.1010	0.1786
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.2213	0.1438	-0.3855	0.2967	0.0466	0.0466	0.2967
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
		-0.3855	0.1438	0.2213	-0.3966	0.1851	0.1851	-0.3966
		$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
		0.3259	-0.3143	0.2871	-0.2457	0.1922	0.1922	-0.2457
		$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
		0.2871	-0.3143	0.3259	-0.3215	0.1090	0.1090	-0.3215

Now, we have obtained all results, which are shown in Table 10.34

Table 10.34: The occupied Hückel MOs in all irreducible representations of phenanthrene.

order	orbital energy	irrep	eigenfunction						
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
1	$\alpha + 2.435\beta$	$B_1$	0.2074	0.1497	0.1572	0.2329	0.4100	0.4100	0.2329
			$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
			0.1572	0.1497	0.2074	0.3553	0.2476	0.2476	0.3553
2	$\alpha + 1.951\beta$	$A_2$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
			0.3259	0.3143	0.2871	0.2457	0.1922	-0.1922	-0.2457
			$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
3	$\alpha + 1.516\beta$	$B_1$	-0.2871	-0.3143	-0.3259	-0.3215	-0.1090	0.1090	0.3215
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
			0.0195	-0.2017	-0.3254	-0.2917	-0.1169	-0.1169	-0.2917
4	$\alpha + 1.306\beta$	$B_1$	$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
			-0.3254	-0.2017	0.0195	0.2313	0.4481	0.4481	0.2313
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
5	$\alpha + 1.142\beta$	$A_2$	0.3334	0.4058	0.1965	-0.1492	-0.3913	-0.3913	-0.1492
			$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
			0.1965	0.4058	0.3334	0.0295	0.0965	0.0965	0.0295
6	$\alpha + 0.769\beta$	$A_2$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
			0.2213	-0.1438	-0.3855	-0.2967	0.0466	-0.0466	0.2967
			$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
7	$\alpha + 0.605\beta$	$B_1$	0.3855	0.1438	-0.2213	-0.3966	-0.1851	0.1851	0.3966
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
			0.2730	0.3886	0.0258	-0.3687	-0.3094	0.3094	0.3687
8	$\alpha - 0.605\beta$	$A_2$	$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
			-0.0258	-0.3886	-0.2730	0.1786	0.1010	-0.1010	-0.1786
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
9	$\alpha - 0.769\beta$	$B_1$	0.3402	-0.0420	-0.3147	0.2325	0.1740	0.1740	0.2325
			$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
			-0.3147	-0.0420	0.3402	0.1638	-0.4150	-0.4150	0.1638
10	$\alpha - 1.142\beta$	$B_1$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
			0.3402	-0.0420	-0.3147	0.2325	0.1740	-0.1740	-0.2325
			$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
11	$\alpha - 1.306\beta$	$A_2$	0.3147	0.0420	-0.3402	0.1638	0.4150	-0.4150	-0.1638
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
			0.2730	-0.3886	0.0258	0.3687	-0.3094	-0.3094	0.3687
12	$\alpha - 1.516\beta$	$A_2$	$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
			-0.0258	-0.3886	0.2730	0.1786	-0.1010	-0.1010	0.1786
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
13	$\alpha - 1.951\beta$	$B_1$	0.2213	0.1438	-0.3855	0.2967	0.0466	0.0466	0.2967
			$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
			-0.3855	0.1438	0.2213	-0.3966	0.1851	0.1851	-0.3966
14	$\alpha - 2.435\beta$	$A_2$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$
			0.3259	-0.3143	0.2871	-0.2457	0.1922	0.1922	-0.2457
			$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
			0.2871	-0.3143	0.3259	-0.3215	0.1090	0.1090	-0.3215
			$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$

0.2074	-0.1497	0.1572	-0.2329	0.4100	-0.4100	0.2329
$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$
-0.1572	0.1497	-0.2074	0.3553	-0.2476	0.2476	-0.3553

Besides, their phase diagrams have been painted in Fig 10.14.

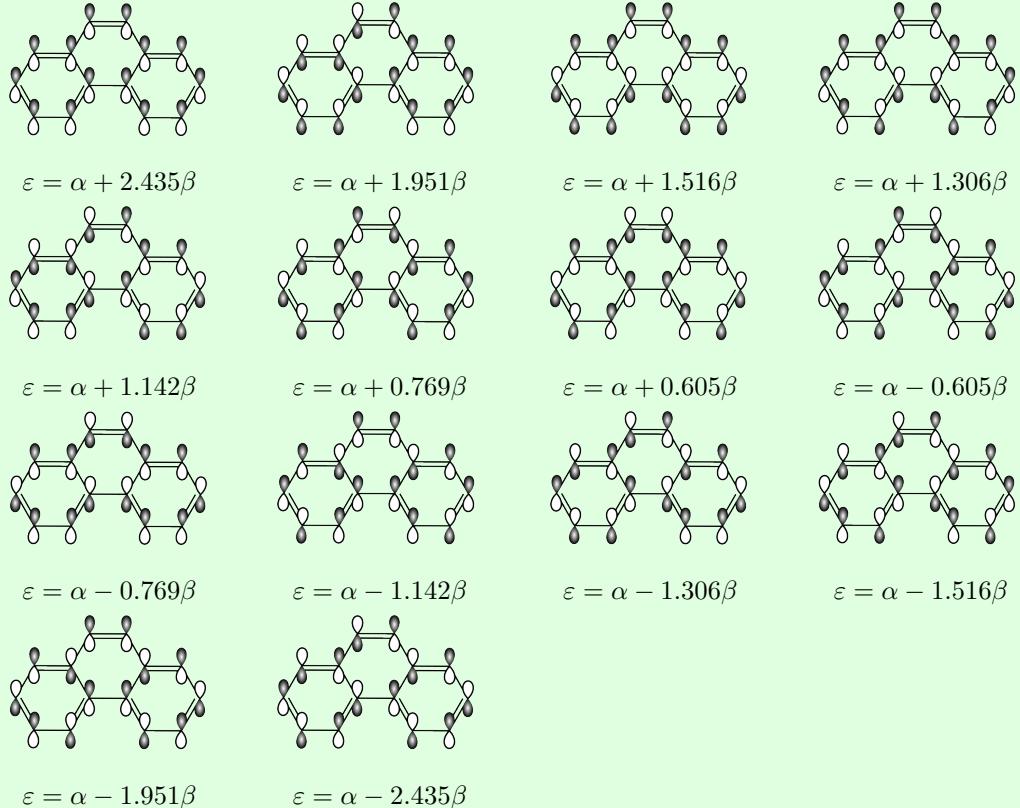


Figure 10.14: Phase diagrams of these Hückel MOs of phenanthrene. Black bubbles mean plus phase while white ones mean minus phase. The color is used just for determining relative phase.

In the end, we conclude that for phenanthrene, its ground state  $\pi$ -electron configuration is  $(1b_1)^2(1a_2)^2(2b_1)^2(3b_1)^2(2a_2)^2(3a_2)^2(4b_1)^2$  and its delocalization energy is  $2 \times 2.435\beta + 2 \times 1.951\beta + 2 \times 1.516\beta + 2 \times 1.306\beta + 2 \times 1.142\beta + 2 \times 0.769\beta + 2 \times 0.605\beta - 14 \times 1.000\beta = 5.448\beta$ , much larger than the sum of that of *trans*-1,3-butadiene ( $0.472\beta$ ) and two benzenes ( $2.000\beta \times 2$ ).

—	$\alpha - 2.435\beta$	$(7a_2)$
—	$\alpha - 1.951\beta$	$(7b_1)$
—	$\alpha - 1.516\beta$	$(6a_2)$
—	$\alpha - 1.306\beta$	$(5a_2)$
—	$\alpha - 1.142\beta$	$(6b_1)$
—	$\alpha - 0.769\beta$	$(5b_1)$
—	$\alpha - 0.605\beta$	$(4a_2)$
—*	$\alpha + 0.605\beta$	$(4b_1)$
—*	$\alpha + 0.769\beta$	$(3a_2)$
—*	$\alpha + 1.142\beta$	$(2a_2)$
—*	$\alpha + 1.306\beta$	$(3b_1)$
—*	$\alpha + 1.516\beta$	$(2b_1)$
—*	$\alpha + 1.951\beta$	$(1a_2)$
—*	$\alpha + 2.435\beta$	$(1b_1)$