Exercise 10.1

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

(a) *trans*-1,3-butadiene,

(b) ethylene,

(c) cyclobutadiene,

(d) cyclopentadienyl radical C_5H_5,

(e) naphthalene,

(f) phenanthrene.

Solution 10.1

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

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

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

Secondly, we mark all carbon atoms as follows.

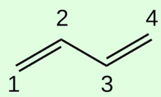


Figure 10.1: The order of carbon atoms in *trans*-1,3-butadiene.

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

Table 10.2: The character of the π-electron atomic orbitals' representation Γ^{AO}.

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

Relevant reduction coefficients are

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

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

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

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

Thus, we arrive at

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

We conclude that there are two basis functions in the irreducible representation Γ^{B_g} and Γ^{A_u}, respectively. Thus, to describe the effect of O_R, two suitable $2\mathrm{p}_z$ atomic orbitals ϕ_i is enough.

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

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

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

For the irreducible representation Γ^{B_g},

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

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 π electrons can be calculated,

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

viz.

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

Next,

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

where

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

Current discriminant is

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

and then two roots are

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

which equal to

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

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

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

which means

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

The sum of squares of coefficients is

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

Thus, we know

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

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,

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

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

Table 10.4: The Hückel MOs in the irreducible representation Γ^{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 Γ^{A_u},

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

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

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

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 Γ^{A_u}, relevant results are listed below.

Table 10.5: The Hückel MOs in the irreducible representation Γ^{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 π-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}
ϕ_1	ϕ_1	ϕ_2	$-\phi_2$	$-\phi_1$

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

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

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

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

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

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

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

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

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

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 π 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 π electrons are localized, in agreement with Hückel's rule which predicts that a π-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 $\mathscr{D}_{4\mathrm{h}}$. However, it has only 4 π-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.

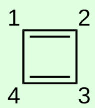


Figure 10.4: The order of carbon atoms in the cyclobutadiene anion.

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

Table 10.8: The character of the π-electron atomic orbitals' representation Γ^{AO}.

$\mathscr{D}_4$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
$\chi^{\mathrm{AO}}(C_i)$	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 ϕ_i under O_R for the cyclobutadiene anion, whose information is recorded below. We only list two ϕ_1 and ϕ_2.

Table 10.9: Transformation of ϕ_i under O_R for the cyclobutadiene anion.

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

For the irreducible representation Γ^{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 π electrons is

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

In another words, its only eigenvalue is $\alpha + 2\beta$, with eigenfunction Φ_1^{π}.

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

Table 10.10: The Hückel MOs in the irreducible representation Γ^{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 Γ^{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 π electrons is

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

In another words, its only eigenvalue is $\alpha - 2\beta$, with eigenfunction Φ_2^{π}.

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

Table 10.11: The Hückel MOs in the irreducible representation Γ^{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 Γ^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 π electrons is

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

It has a two-fold eigenvalue α. 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 α, with two eigenfunctions Φ_3^π and Φ_4^π.

In conclusion, for the irreducible representation Γ^E, relevant results are listed below.

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

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

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	α	E	0.7071	0.0000	-0.7071	0.0000
3	α	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.

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

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 π-electron configuration is $(a_2)^2(e)^4$ and its delocalization energy is -2.000β, 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 $\mathscr{D}_{5\mathrm{h}}$. However, it has only 5 π-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.

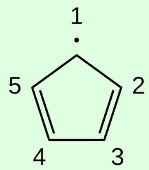


Figure 10.6: The order of carbon atoms in cyclopentadienyl radical.

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

Table 10.15: The character of the π-electron atomic orbitals' representation Γ^{AO}.

$\mathscr{D}_5$	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

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

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

For the irreducible representation Γ^{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 π 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 Γ^{A_2}, relevant results are listed below.

Table 10.16: The Hückel MOs in the irreducible representation Γ^{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 Γ^{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

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

However, they are not mutually orthogonal! We have to orthogonalize ϕ_2' and ϕ_3',

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

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

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

Then, the effective Hamiltonian for π 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 Γ^{E_1}, relevant results are listed below.

Table 10.17: The Hückel MOs in the irreducible representation Γ^{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 Γ^{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

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

However, they are not mutually orthogonal! We have to orthogonalize ϕ_4' and ϕ_5',

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

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

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

and then

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

Then, the effective Hamiltonian for π 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 Γ^{E_2}, relevant results are listed below.

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

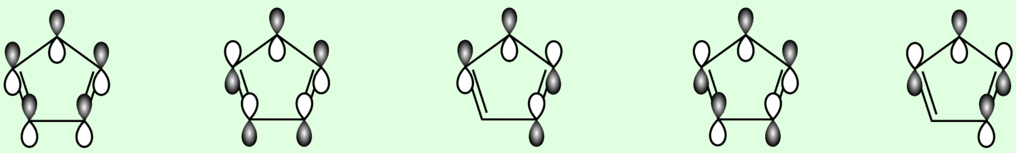
order	eigenvalue	eigenfunction
1	$\alpha - 1.618\beta$	$0.1954\phi_1 + 0.1954\phi_2 - 0.5117\phi_3 + 0.6325\phi_4 - 0.5117\phi_5$
2	$\alpha - 1.618\beta$	$0.6015\phi_1 - 0.6015\phi_2 + 0.3717\phi_3 + 0.0000\phi_4 - 0.3717\phi_5$

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.



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

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 π-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 (0.472β) but also much smaller than benzene (2.000β).

(e) 5555555555555555 naphthalene

Firstly, it is easy find that naphthalene belongs to the point group $\mathscr{D}_{2\mathrm{h}}$, whose character table is shown in Table 10.20.

Table 10.20: The character table for the $\mathscr{D}_{2\mathrm{h}}$ point group.

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

Secondly, we mark all carbon atoms as follows.

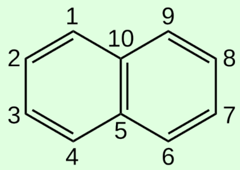


Figure 10.8: The order of carbon atoms in naphthalene.

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

Table 10.21: The character of the π-electron atomic orbitals' representation Γ^{AO}.

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

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

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 $2\mathrm{p}_z$ atomic orbitals ϕ_i is enough.

Table 10.22: Transformation of ϕ_i under O_R for the naphthalene.

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

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

$$\phi_1' = \frac{1}{2}(\phi_1 + \phi_4 - \phi_6 - \phi_9),$$
$$\phi_2' = \frac{1}{2}(\phi_2 + \phi_3 - \phi_7 - \phi_8).$$

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

Then, the effective Hamiltonian for π electrons is

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

Its eigen equation is

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

There are two roots,

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

which equal to

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

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

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

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

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,

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

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}
		- 0.4253	0.2629	0.2629	- 0.4253	0.0000
2	$\alpha + 1.618\beta$	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

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

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

Then, the effective Hamiltonian for π 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,

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

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,

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

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				
1	$\alpha-\beta$	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}
		0.0000	-0.4082	0.4082	0.0000	- 0.4082
2	$\alpha-2.303\beta$	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
3	$\alpha+1.303\beta$	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}
		- 0.3996	-0.1735	0.1735	0.3996	0.3470

For the irreducible representation Γ^{A_u}, the only two basis functions are

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

They can be normalized to

$$\phi_6' = \frac{1}{2}(\phi_1 - \phi_4 + \phi_6 - \phi_9),$$
$$\phi_7' = \frac{1}{2}(\phi_2 - \phi_3 + \phi_7 - \phi_8).$$

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

Then, the effective Hamiltonian for π electrons is

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

Its eigen equation is

$$\det(H_{A_u}' - \varepsilon^\pi S_{A_u}') = \beta^2(x^2 - x - 1) = 0. \tag{10.30}$$

There are two roots,

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

which equal to

$$\varepsilon_6^\pi = \alpha - \frac{\sqrt{5}+1}{2}\beta \approx \alpha - 1.618\beta, \tag{10.32}$$
$$\varepsilon_7^\pi = \alpha + \frac{\sqrt{5}-1}{2}\beta \approx \alpha + 0.618\beta. \tag{10.33}$$

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 Γ^{A_u}, relevant results are listed below.

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

order	eigenvalue	eigenfunction				
1	$\alpha - 1.618\beta$	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
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 π 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,

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

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

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

which means

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

And then,

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

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				
1	$\alpha+\beta$	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}
		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}
		0.3996	-0.1735	-0.1735	0.3996	-0.3470
3	$\alpha+2.303\beta$	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				
1	$\alpha+2.303\beta$	B_{1u}	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
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}
			- 0.2629	-0.4253	- 0.4253	-0.2629	0.0000
3	$\alpha+1.303\beta$	B_{3g}	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}
			- 0.3996	-0.1735	0.1735	0.3996	0.3470
4	$\alpha+\beta$	B_{1u}	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}
			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

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

order	orbital energy	irrep	eigenfunction				
1	$\alpha - 0.618\beta$	B_{2g}	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
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}
			0.0000	-0.4082	0.4082	0.0000	-0.4802
3	$\alpha - 1.303\beta$	B_{1u}	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}
			0.3996	-0.1735	-0.1735	0.3996	-0.3470
4	$\alpha - 1.618\beta$	A_u	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
5	$\alpha - 2.303\beta$	B_{3g}	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

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

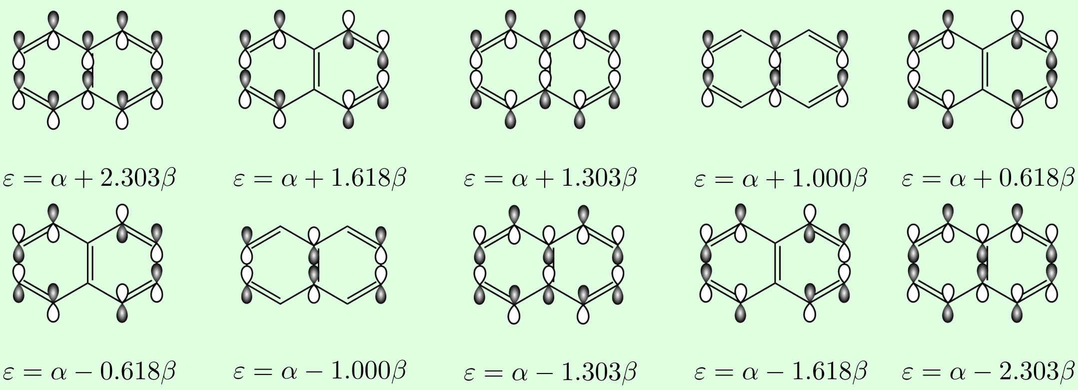
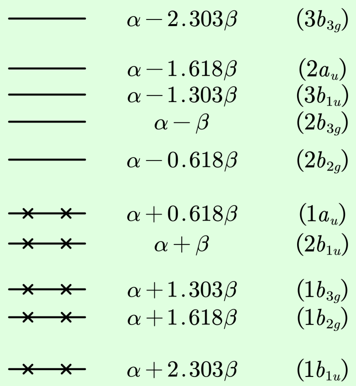


Figure 10.9: Phase diagrams of these Hückel MOs of naphthalene. Black bubbles mean plus phase while white ones mean minus phase. The color is used just for determining relative phase.

In the end, we conclude that for naphthalene, its ground state π-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 (0.472β) and benzene (2.000β).



(f) 66666666666666666 phenanthrene

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

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

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

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

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

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

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