# Hückel Theory

2.1 Foundation of the Hückel MO Method

Hückel molecular orbital theory is one of the simplest methods to determine the energy of π electrons in conjugated organic molecules. This approach neglects the σ electrons and makes several simplifications in the treatment of the π electrons.

> ■ **Example 2.1.1 | ethylene, 2 electrons / 2 orbitals.**
> The simplest problem that can be solved with the Hückel method is the ethylene molecule. For each carbon we describe the electrons in the C $2p_z$ using one basis function (χ_1 and χ_2)
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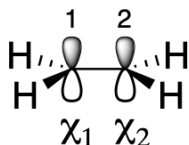
> ■ **Example 2.1.2 | benzene, 6 electrons / 6 orbitals.**
> In the case of benzene, the Hückel method only describes electrons in the C $2p_z$ responsible for π bonding
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>
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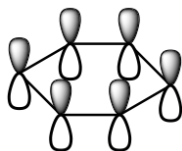
In the Hückel method electrons occupy molecular orbitals (MOs), $\psi_i(\mathbf{r})$, that are written as a linear combination of atomic orbitals (LCAO). The i-th molecular orbital $\psi_i(\mathbf{r})$ is written as

$$\psi_i(\mathbf{r}) = \sum_{\mu}^{N} \chi_\mu(\mathbf{r}) C_{\mu i}, \qquad (2.1)$$

where:

- N is the number of atomic orbitals (AOs) = number of molecular orbitals (MOs) = number of atoms that share p_z orbitals

- the functions $\chi_\mu(\mathbf{r}) : \mathbb{R}^3 \to \mathbb{R}$ are atomic p_z orbitals (also called basis functions)

- $\mathbf{r} = (x, y, z)$ is the electron coordinate (we will neglect spin for now)

- the matrix $\mathbf{C}$ with elements $(\mathbf{C})_{\mu i} = C_{\mu i}$ gives the coefficient of the μ-th AO in the i-th MO. In other words, read the coefficient of ψ_i from the i-th column of the matrix $\mathbf{C}$.

■ **Example 2.1.3**
The MOs of ethylene are written as $\psi_i(r) = \chi_1(r)C_{1i} + \chi_2(r)C_{2i}$.   ■

Hückel theory postulates that the MOs satisfy the following Schrödinger equation:

$$\hat{h}(1)\psi_i(1) = \epsilon_i \psi_i(1), \tag{2.2}$$

where

- $\hat{h}(1)$ is an effective one-electron Hamiltonian

- ϵ_i is energy of the i-th MO

- $(1) = (x_1, y_1, z_1)$ collects the space coordinate of an electron

The Hückel one-electron Hamiltonian is expressed as

$$\hat{h}(1) = \hat{T}(1) + \hat{V}(1), \tag{2.3}$$

where $\hat{T}(1)$ is the kinetic energy operator

$$\hat{T}(1) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right), \tag{2.4}$$

and $\hat{V}(1)$ is an "effective" potential energy for an electron. In Hückel we do not assume that $\hat{V}(1)$ is known. All the integrals that enter in the theory are parameters that are adjusted to match experiment.

It is convenient to introduce the following integrals in the AO basis:

$$h_{\mu\mu} = \langle \chi_\mu | \hat{h} | \chi_\mu \rangle = \int d\mathbf{r}\, \chi_\mu^*\hat{h}(\mathbf{r})\chi_\mu(\mathbf{r}) \quad \text{(Coulomb integral of AO } \mu) \tag{2.5}$$

$$h_{\mu\nu} = \langle \chi_\mu | \hat{h} | \chi_\nu \rangle = \int d\mathbf{r}\, \chi_\mu^*(\mathbf{r})\hat{h}\chi_\nu(\mathbf{r}) \quad \text{(Resonance integral between AOs } \mu \text{ and } \nu)$$
$$\tag{2.6}$$

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle = \int d\mathbf{r}\, \chi_\mu^*(\mathbf{r})\chi_\nu(\mathbf{r})d\mathbf{r} \quad \text{(Overlap integral between AOs } \mu \text{ and } \nu) \tag{2.7}$$

2.2   Determination of the MO coefficients

To determine the MO orbitals we insert the definition $|\psi_i\rangle = \sum_\mu^N |\chi_\mu\rangle C_{\mu i}$ into the Schrödinger equation [Eq. (2.2)]

$$\hat{h}(1) \sum_\mu^N |\chi_\mu\rangle C_{\mu i} = \epsilon_i \sum_\mu^N |\chi_\mu\rangle C_{\mu i}, \tag{2.8}$$

Multiply by $\langle \chi_\nu |$ from the left. The left hand side becomes:

$$\langle \chi_\nu | \hat{h}(1) \sum_\mu^N |\chi_\mu\rangle C_{\mu i} = \sum_\mu^N \langle \chi_\nu | \hat{h}(1) | \chi_\mu \rangle C_{\mu i} = \sum_\mu^N h_{\nu\mu} C_{\mu i} \tag{2.9}$$

The right hand side is:

$$\langle \chi_\nu | \, \epsilon_i \sum_\mu^N |\chi_\mu\rangle \, C_{\mu i} = \sum_\mu^N \langle \chi_\nu | \chi_\mu \rangle \, C_{\mu i} \epsilon_i = \sum_\mu^N S_{\nu\mu} C_{\mu i} \epsilon_i \tag{2.10}$$

Therefore we have:

$$\sum_\mu^N h_{\nu\mu} C_{\mu i} = \sum_\mu^N S_{\nu\mu} C_{\mu i} \epsilon_i, \tag{2.11}$$

which in matrix notation reads:

$$\begin{pmatrix} h_{11} & h_{12} & \ldots & h_{1N} \\ h_{21} & h_{22} & \ldots & h_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ h_{N1} & h_{N2} & \ldots & h_{NN} \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{Ni} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & \ldots & S_{1N} \\ S_{21} & S_{22} & \ldots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \ldots & S_{NN} \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{Ni} \end{pmatrix} \epsilon_i, \tag{2.12}$$

or more compactly:

$$\mathbf{H}\mathbf{c}_i = \mathbf{S}\mathbf{c}_i \epsilon_i, \tag{2.13}$$

where $\mathbf{c}_i$ is the column matrix

$$\mathbf{c}_i = \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{Ni} \end{pmatrix}. \tag{2.14}$$

If we combine all the columns together into the matrix $\mathbf{C} = (\mathbf{c}_1, \mathbf{c}_2, \ldots, \mathbf{c}_N)$, we can write Eq. (2.13) as

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon, \tag{2.15}$$

where the matrix ϵ contains all the orbital energies in the diagonal elements

$$\epsilon = \begin{pmatrix} \epsilon_1 & 0 & \ldots & 0 \\ 0 & \epsilon_2 & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \ldots & \epsilon_N \end{pmatrix} \tag{2.16}$$

Problem 2.2.1 Convince yourself that Eq. 2.15 is correct.

The Hückel method for conjugated hydrocarbons further **assumes**:

- $h_{\mu\mu} = \alpha < 0$ (same for all carbon atoms), where α is the energy of an electron in AO $\chi_\mu \approx -I_\mu$ (ionization energy)

- $h_{\mu\nu} = \begin{cases} \beta < 0 & \text{if } \mu \text{ and } \nu \text{ are on adjacent atoms} \\ 0 & \text{otherwise} \end{cases}$

  $|\beta|$ measures the strength of interaction between AOs μ and ν and it is a negative quantity.

- That we neglect the overlap of atomic orbitals. This means that atomic orbitals are normalized ($\langle \chi_\mu | \chi_\mu \rangle = 1$) and orthogonal ($\langle \chi_\mu | \chi_\nu \rangle = 0$ if $\mu \neq \nu$). This implies that the overlap matrix $\mathbf{S}$ is the identity matrix, that is, $S_{\mu\nu} = \delta_{\mu\nu} = \begin{cases} 1 & \text{if } \mu = \nu \\ 0 & \text{if } \mu \neq \nu \end{cases}$.

2.3   The Hückel Method in Practice

■ **Example 2.3.1 | Ethylene.**
The Hamiltonian in the Hückel approximation is:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \tag{2.17}$$

The Schrödinger equation reads:

$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} \epsilon_i \tag{2.18}$$

Simplify and rearrange:

$$\begin{pmatrix} \alpha - \epsilon_i & \beta \\ \beta & \alpha - \epsilon_i \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} = 0 \tag{2.19}$$

This equation has non-trivial solutions A trivial solution to a linear system $\mathbf{Ax} = \mathbf{0}$ is the solution $\mathbf{x} = \mathbf{0}$. In this example the trivial solution is $\begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$ only if the determinant of the secular matrix is equal to zero:
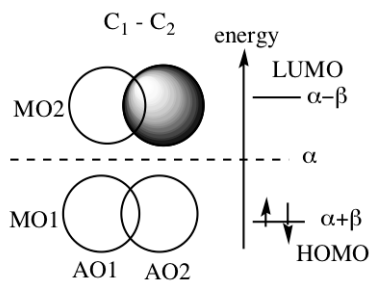
$$\begin{vmatrix} \alpha - \epsilon_i & \beta \\ \beta & \alpha - \epsilon_i \end{vmatrix} = 0 \Rightarrow \beta^2 \begin{vmatrix} \frac{\alpha - \epsilon_i}{\beta} & 1 \\ 1 & \frac{\alpha - \epsilon_i}{\beta} \end{vmatrix} = 0 \tag{2.20}$$

Introduce the reduced variable $\frac{\alpha - \epsilon_i}{\beta} = -\lambda$ and evaluate the secular determinant:

$$\begin{vmatrix} \frac{\alpha - \epsilon_i}{\beta} & 1 \\ 1 & \frac{\alpha - \epsilon_i}{\beta} \end{vmatrix} = \begin{vmatrix} -\lambda & 1 \\ 1 & -\lambda \end{vmatrix} = \lambda^2 - 1 = 0, \tag{2.21}$$
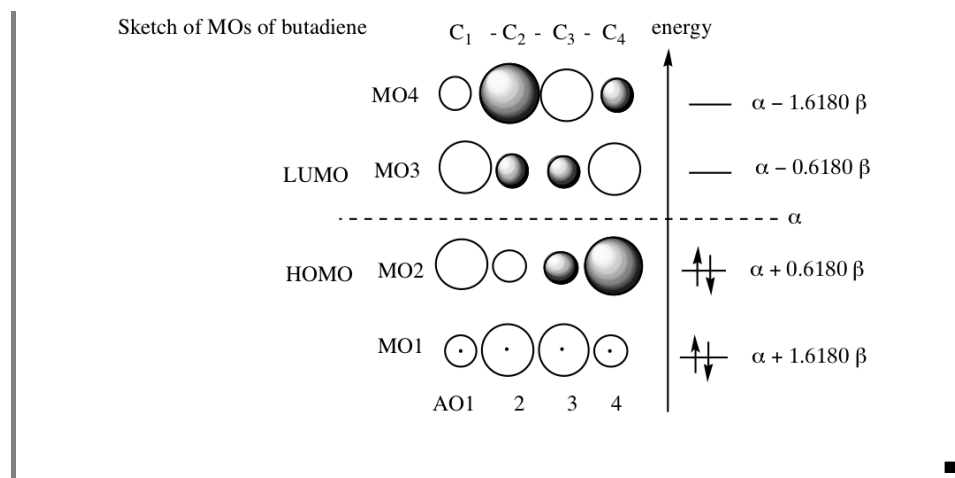
from this equation we obtain the eigenvalues:

$$\lambda^2 = \left(\frac{\alpha - \epsilon_i}{\beta} \right)^2 = 1 \Rightarrow \frac{\alpha - \epsilon_i}{\beta} = \pm 1 \Rightarrow \epsilon_i = \alpha \pm \beta \tag{2.22}$$

■

■ **Example 2.3.2 | Butadiene.**
Note that cis-butadiene and trans-butadiene are the same in Hückel MOs.

Sketch of MOs of butadiene C_1 - C_2 - C_3 - C_4 energy

MO4 $\alpha - 1.6180\,\beta$

LUMO   MO3 $\alpha - 0.6180\,\beta$

α

HOMO   MO2 $\alpha + 0.6180\,\beta$

MO1 $\alpha + 1.6180\,\beta$

AO1   2   3   4

■

■ **Example 2.3.3 | Benzene.**
The Hamiltonian in the Hückel approximation is:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & & & & \beta \\ \beta & \alpha & \beta & & & \\ & \beta & \alpha & \beta & & \\ & & \beta & \alpha & \beta & \\ & & & \beta & \alpha & \beta \\ \beta & & & & \beta & \alpha \end{pmatrix} \tag{2.23}$$

■

You only need the "connectivity" of a molecule to write down the Hückel Hamiltonian.

Problem 2.3.1 Write down the Hückel Hamiltonian for:

1. butadiene

2. naphthalene

3. azulene

In the Hückel method, the energy is given by the sum of the orbital energies (ϵ_i) of all the occupied orbitals

$$E = \sum_i \epsilon_i n_i, \tag{2.24}$$

where n_i is the occupation number of the orbital i. This quantity can be 0, 1, or 2

$$n_i \in \{0, 1, 2\}. \tag{2.25}$$

Note that some times the eigenvalues are also expressed in the following form

$$\epsilon_i = \alpha + \lambda_i \beta, \tag{2.26}$$

in terms of the reduced variable λ_i.

2.4   Heteroatoms

For hydrocarbons containing heteroatoms we introduce atom-specific and bond-specific matrix elements.

■ **Example 2.4.1 | Acrolein.**

In the case of acrolein we define modified Hückel parameters:

- $\alpha_O = \alpha + 2\beta$ (O is more electronegative than C)
- $\beta_{CO} = \sqrt{2}\beta$ (C = O π bond is shorter and stronger than C=C)
- $\alpha_{C'} = \alpha + 0.2\beta$ (C of CO is slightly more electronegative due to C→O charge transfer)
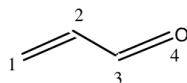
The Hückel Hamiltonian for acrolein is

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & & \\ \beta & \alpha & \beta & \\ & \beta & \alpha + 0.2\beta & \sqrt{2}\beta \\ & & \sqrt{2}\beta & \alpha + 2\beta \end{pmatrix}. \tag{2.27}$$

■

Table 2.1: Recommended values of the parameters for heteroatoms in the Hückel method

Diagonal elements			Off-diagonal elements		
Coulomb Integrals $\alpha_X = \alpha_C + l_X \beta_{CC}$			Resonance Integrals $\beta_{XY} = k_{XY} \beta_{CC}$		
atom X	# of π electrons	l_X	atom X-Y	# of π electrons	k_{XY}
= C –	(1)	0.0	C–C	(1-1)	1.0
= N –	(1)	0.5	C = N	(1-1)	1.1
- N:<	(2)	0.8	C $\equiv$ N	(1-1)	1.3
- O -	(1)	1.1	C–N:	(1-2)	0.9
- O:	(2)	1.5	C = O	(1-1)	1.2
- F:	(2)	2.0	C–O:	(1-2)	0.7
- Cl:	(2)	1.7	C = S	(1-1)	1.0
- Br:	(2)	1.3	C–S:	(1-2)	0.5
- I:	(2)	1.15	C–F	(1-2)	0.95
= S	(1)	0.3	C–Cl	(1-2)	0.7
- S:	(2)	1.0	C–I	(1-2)	0.5
			N = N	(1-1)	1.2
			N–O	(2-1)	1.1
Hyperconjugated methyl group (CH$_3$)					
C	(1)	−0.1	C $\equiv$ H$_3$	(1-1)	2.5
H$_3$	(1)	−0.5	C–CH$_3$	(1-1)	0.6

Larger l_X, more electronegative the atom X. Larger k_{XY}, stronger the bond XY.

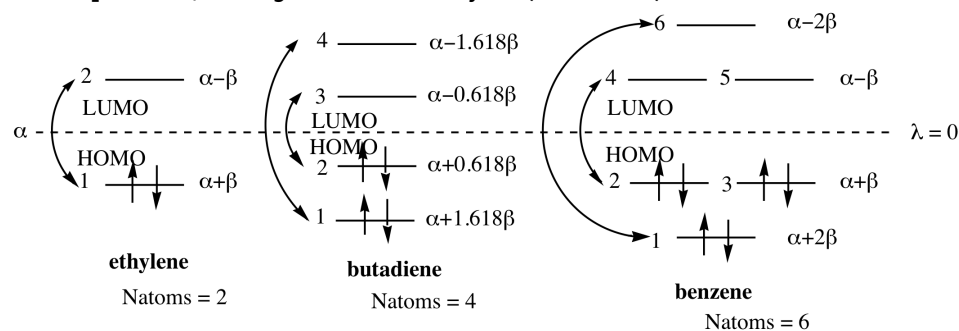## 2.5   Pairing Theorem for Alternant Hydrocarbons (AHs)

For alternant hydrocarbons (hydrocarbons without odd-membered rings), MO energies are paired, which means that they are symmetric with respect to the energy α[1]

$$\epsilon_i = \alpha + \lambda_i \beta, \tag{2.28}$$
$$\epsilon_{N-i+1} = \alpha - \lambda_i \beta. \tag{2.29}$$

[1] Recall that $\frac{\alpha - \epsilon_i}{\beta} = -\lambda_i$.

■ **Example 2.5.1 | Pairing theorem for ethylene, butadiene, and benzene.**

ethylene
Natoms = 2

butadiene
Natoms = 4

benzene
Natoms = 6

■

An interesting implication is that alternant hydrocarbons with an odd number of carbons have an orbital with $\lambda_i = 0$, that is $\epsilon_i = \alpha$. To see this consider the case $N = 2k + 1$ and consider the level $i = k + 1$. In this case the energy ϵ_{k+1} is equal to that of $\epsilon_{N-(k+1)+1}$, from which we obtain

$$\epsilon_{k+1} = \epsilon_{N-(k+1)+1} \Rightarrow \alpha + \lambda_i\beta = \alpha - \lambda_i\beta \Rightarrow \lambda_i = 0. \tag{2.30}$$

■ **Example 2.5.2 | Pairing theorem for the allyl and benzyl radicals (odd alternant).**

allenyl (allyl radical)
Natoms = 3

benzyl radical
Natoms = 7
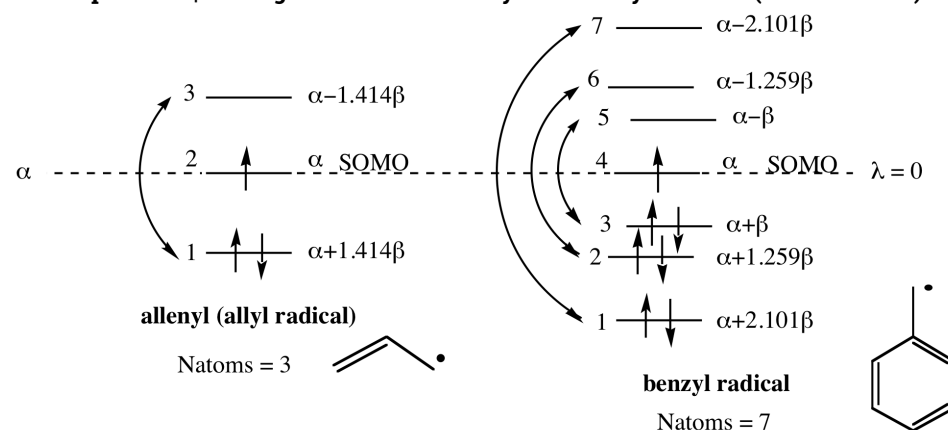
In the allyl radical the second MO (ψ_2, $\epsilon_2 = \alpha$) is paired to itself. In the benzyl radical the fourth MO (ψ_4, $\epsilon_4 = \alpha$) is paired to itself. ■

■ **Example 2.5.3 | Non alternant hydrocarbons.**
In this example, the energies of the cyclopropenyl cation are not paired

For non-AHs, MO energies are not paired.

cyclopropenyl cation

■
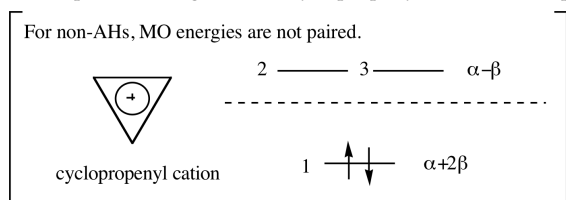
Another consequence of this theorem is that the coefficients of paired orbitals are also paired (MOs ψ_i and ψ_{N-i+1} are paired). This property is best expressed by labeling alternating carbon atoms with a star (*) and the relationship
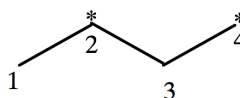
$$C_{\mu,N-i+1} = \quad C_{\mu i} \quad \text{when } \mu = \text{starred atom} \tag{2.31}$$
$$= -C_{\mu i} \quad \text{when } \mu = \text{unstarred atom.} \tag{2.32}$$

• Method of putting * on alternating carbon atoms
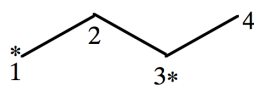
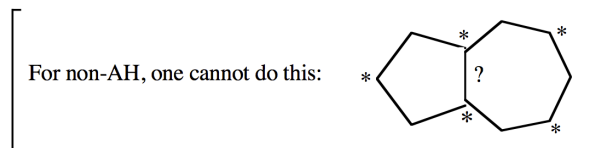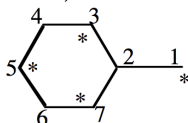OR   Either is OK.

For odd AHs, the number of *'s must be greater than the number of non-* atoms.

$$\left[\text{For non-AH, one cannot do this:} \quad \text{} \right]$$

■ **Example 2.5.4 | Hückel computation on butadiene.**
The following shows the energy and coefficient matrix for butadiene.

```
 Energies
        1          2(HOMO)   3(LUMO)   4
        1.618034   .618034  -.618034 -1.618034    MO energies

MO coefficients
    0    .371748  -.601501   .601501  -.371748    <- AO1
    1    .601501  -.371748  -.371748   .601501    <- AO2
    2    .601501   .371748  -.371748  -.601501    <- AO3
    3    .371748   .601501   .601501   .371748    <- AO4
         MO1       MO2       MO3       MO4
```

Note that the energies and coefficients of MOs 1 and 4 and MOs 2 and 3 are paired. Do not forget that the sign of MO as a whole is arbitrary. i.e. ψ_i or $-\psi_i$ are both OK.   ■

■ **Example 2.5.5 | Hückel computation on allyl radical.**
The following shows the energy and coefficient matrix for the allyl radical.

```
 Energies
        1          2(SOMO)   3(LUMO)
        1.414214 .000000 -1.414214     MO energies

MO coefficients
    0   -.500000 -.707107   .500000    <- AO1
    1   -.707107  .000000  -.707107    <- AO2
    2   -.500000  .707107   .500000    <- AO3
         MO1       MO2       MO3

DENSITY AND BOND ORDER MATRIX
          1        2        3
    1   1.000000
    2    .707107 1.000000
    3    .000000  .707107  1.000000

DEGENERACIES: HOMO=0 LUMO = 0 TOTAL ENERGY = 3 ALPHA + 2.828427 BETA
```

Note that the energies and coefficients of MOs 1 and 3 are paired.   ■

When MOs are degenerate (i.e., two MOs have same energy), their MO coefficients can not be uniquely determined. Any linear combination of degenerate MOs is also acceptable MO of the same energy. Appropriate transformation among degenerate MOs is needed to show pairing.

2.6 Symmetry of MOs

Each MO is symmetric or antisymmetric with respect to symmetry operations of the system.

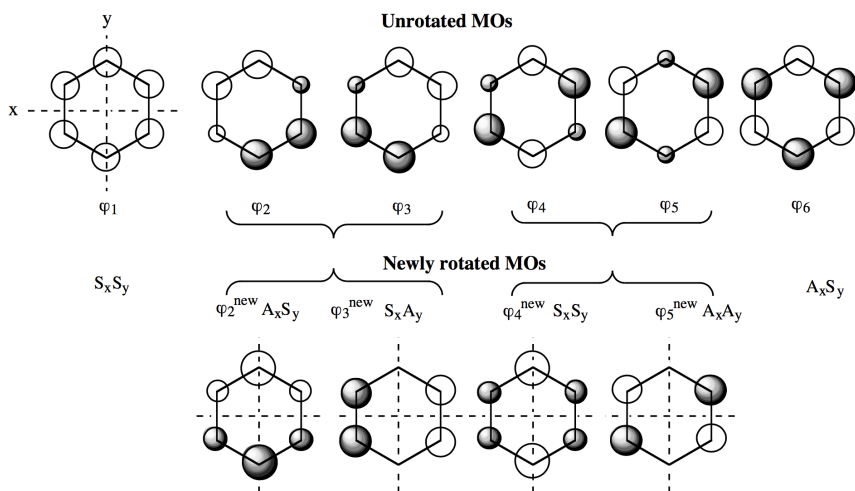■ **Example 2.6.1** | **Symmetry of the orbitals in butadiene.**

LUMO of butadiene   S (symetric wrt reflection)

HOMO of butadiene   A (antisymmetric)

■
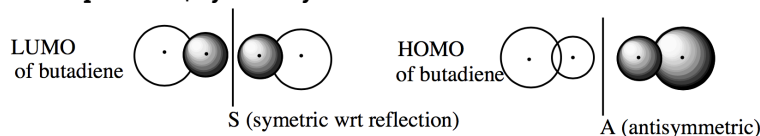
■ **Example 2.6.2** | **Symmetry of the orbitals in the allyl radical.**

Allyl radical

S (symmetric)

A (anti-symmetric)

S (symmetric)

symmetry axis

■
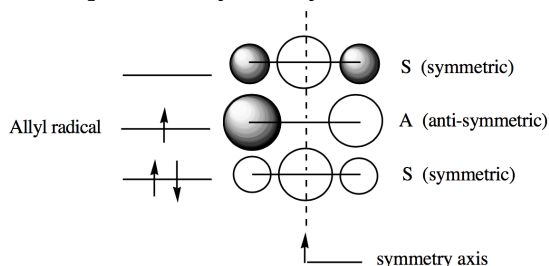
■ **Example 2.6.3** | **Symmetry of the orbitals in benzene.**
This example shows that when MOs are degenerate, appropriate linear combinations of degenerate MOs can be made to satisfy symmetry.

Unrotated MOs

φ_1 φ_2 φ_3 φ_4 φ_5 φ_6

$S_x S_y$

Newly rotated MOs

φ_2^{new} $A_x S_y$ φ_3^{new} $S_x A_y$ φ_4^{new} $S_x S_y$ φ_5^{new} $A_x A_y$

$A_x S_y$

In this example, the MOs of the benzene molecule were transformed according to

$$\psi_2^{\text{new}} = +\cos\theta\,\psi_2 + \sin\theta\,\psi_3$$
$$\psi_3^{\text{new}} = -\sin\theta\,\psi_2 + \cos\theta\,\psi_3$$

and chosen either to be such that $|C_{12}|$ is maximized, which in this case is also equivalent to $C_{13} = 0$.

    Energies

```
            1          2          3          4          5          6
         2.000000   1.000000   1.000000  -1.000000  -1.000000  -2.000000

MO coefficients

    1    .408248    .455142    .355218    .567622   -.105541   -.408248
    2    .408248    .535198   -.216555   -.192409    .544345    .408248
    3    .408248    .080057   -.571773   -.375212   -.438804   -.408248
    4    .408248   -.455142   -.355218    .567622   -.105541    .408248
    5    .408248   -.535198    .216555   -.192409    .544345   -.408248
    6    .408248   -.080057    .571773   -.375212   -.438804    .408248
            1          2          3          4          5          6

New Energies
            1          2          3          4          5          6
         2.000000   1.000000   1.000000  -1.000000  -1.000000  -2.000000

New MO coefficients
    1    .408248    .577350    .000000    .577350    .000000   -.408248
    2    .408248    .288675   -.500000   -.288675    .500000    .408248
    3    .408248   -.288675   -.500000   -.288675   -.500000   -.408248
    4    .408248   -.577350    .000000    .577350    .000000    .408248
    5    .408248   -.288675    .500000   -.288675    .500000   -.408248
    6    .408248    .288675    .500000   -.288675   -.500000    .408248
            1          2          3          4          5          6

 DEGENERACIES:  HOMO=  2    LUMO=  2
```

Shown above are two sets of orbitals for benzene. Note that orbitals 2 and 3 and 4 and 5 are degenerate. Therefore, we are allowed to separately mix them without changing the orbital energies.
∎

2.7   MO electron density and bond order, total electron density and total bond order

Recall that i-th MO can be expanded in terms of the AOs (χ_μ = AO) and the coefficient matrix ($C_{\mu i}$) as:

$$\psi_i = \sum_\mu^N \chi_\mu C_{\mu i}. \tag{2.33}$$

[2]Recall that in quantum mechanics $|\Psi|^2 = \Psi^* \Psi$ is a probability density.

Since each MO is normalized we can write:[2]

$$1 = \langle \psi_i | \psi_i \rangle = \sum_{\mu\nu}^N C_{\mu i}^* \underbrace{\langle \chi_\mu | \chi_\nu \rangle}_{S_{\mu\nu}} C_{\nu i} = \sum_\mu^N C_{\mu i}^* C_{\mu i} S_{\mu\mu} + \sum_\mu^N \sum_{\substack{\nu \\ \nu \neq \mu}}^N C_{\mu i}^* C_{\nu i} S_{\mu\nu}$$
$$= \sum_\mu |C_{\mu i}|^2 + \sum_{\mu \neq \nu} C_{\mu i}^* C_{\nu i} S_{\mu\nu}. \tag{2.34}$$

[3]To simplify the notation we will write $\sum_\mu \sum_{\nu \neq \mu}$ as $\sum_{\mu \neq \nu}$ and omit the superscript N.

[3] We can interpret the last two terms in the following way

- $q_\mu^i = |C_{\mu i}|^2$ is the probability of finding an electron in MO ψ_i on the atomic orbital χ_μ. Therefore, we call this the **electron density** on AO χ_μ due to the MO ψ_i.

- $p_{\mu\nu}^i = C_{\mu i}^* C_{\nu i}$ may be interpreted as the **bond order** for bond μ-ν in MO ψ_i (recall that the Hückel method assumes $S_{\mu\nu} = 0$ when $\mu \neq \nu$).

■ **Example 2.7.1 | Electron density for the first and second MOs of the allyl radical.**
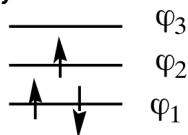
For ψ_1

AO	MO Coefficient ($C_{\mu i}$)	Electron density ($q_\mu^i = |C_{\mu i}|^2$)
1	$C_{11} = -0.5$	$q_1^1 = 0.25$
2	$C_{21} = -0.7071$	$q_2^1 = 0.5$
3	$C_{31} = -0.5$	$q_3^1 = 0.25$
Sum		$\sum_{\mu=1}^{N} q_\mu^1 = 1.0$

For ψ_2

AO	MO Coefficient ($C_{\mu i}$)	Electron density ($q_\mu^i = |C_{\mu i}|^2$)
1	$C_{12} = 0.7071$	$q_1^2 = 0.5$
2	$C_{22} = 0$	$q_2^2 = 0$
3	$C_{32} = -0.7071$	$q_3^2 = 0.5$
Sum		$\sum_{\mu=1}^{N} q_\mu^2 = 1.0$

■

Using these quantities we define:

- **Total density on atom μ (q_μ):**

$$q_\mu = \sum_i^{MO} n_i |C_{\mu i}|^2 = \sum_i^{MO} n_i q_\mu^i \quad n_i = \text{occupation (2, 1, or 0)} \quad (2.35)$$

- **Total charge on atom μ (N_μ):**

$$N_\mu = (\text{number of } \pi \text{ electrons donated by atom } \mu) - q_\mu \quad (2.36)$$

- **Total bond order between atoms μ and ν ($p_{\mu\nu}$):**

$$p_{\mu\nu} = \sum_i^{MO} n_i C_{\mu i}^* C_{\nu i} = \sum_i^{MO} n_i p_{\mu\nu}^i \quad (2.37)$$

Note that the orbital energy may be rewritten using the orbital density ($q_\mu^i = |C_{\mu i}|^2$) and bond order ($p_{\mu\nu}^i = C_{\mu i}^* C_{\nu i}$)

$$\epsilon_i = \langle \psi_i | \hat{h} | \psi_i \rangle = \sum_\mu q_\mu^i \alpha_\mu + 2 \sum_{\mu < \nu} p_{\mu\nu}^i \beta_{\mu\nu}. \quad (2.38)$$

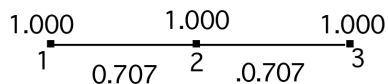and the total energy can be also expressed using the total density and bond order as

$$E = \sum_i^{occ} n_i \epsilon_i = \sum_\mu q_\mu \alpha_\mu + 2 \sum_{\mu < \nu} p_{\mu\nu} \beta_{\mu\nu}. \quad (2.39)$$

■ Example 2.7.2 | Hückel computation on allyl radical.
The following shows the density and bond order matrix for the allyl radical.

```
Density and bond order matrix
          1         2         3
    1   1.000000  0.707107  0.000000
    2   0.707107  1.000000  0.707107
    3   0.000000  0.707107  1.000000
```


$$p_{12} = 2C_{11}C_{21} + C_{12}C_{22} = 2 \times 0.5 \times (-0.7071) + 0.7071 \times 0 = 0.7071. \qquad (2.40)$$

Note that for alternant hydrocarbons the pairing theorem always gives $q_\mu = 1$.   ■

■ Example 2.7.3 | Hückel computation on butadiene.
The following shows the density and bond order matrix for butadiene.

```
Density and bond order matrix
          1         2         3         4
    1   1.000000  0.894427  0.000000 -0.447214
    2   0.894427  1.000000  0.447214  0.000000
    3   0.000000  0.447214  1.000000  0.894427
    4  -0.447214  0.000000  0.894427  1.000000
```

Note that the 1-2 and 3-4 bonds ($p_{12} = p_{34} = 0.894427$) are stronger than the 2-3 bond ($p_{23} = 0.447214$). Also, ignore the negative values for non-nearneighbor atoms.   ■

■ Example 2.7.4 | Hückel computation on pyridine.
The following shows a full Hückel computation for pyridine.

```
NATOMS  NELECS  NINDEX   NLAB   NHOMO   NLUMO
   6       6       0       1       3       4

 Input Matrix
       1       2       3       4       5       6
   1   .5000
   2  1.1000    .0000
   3   .0000  1.0000    .0000
   4   .0000    .0000  1.0000    .0000
   5   .0000    .0000    .0000  1.0000    .0000
   6  1.1000    .0000    .0000    .0000  1.0000    .0000

 Energies
    1         2         3         4         5         6
  2.199322  1.206641  1.000000  -.916933 -1.000000 -1.989029

MO coefficients
   1    .558416   .525891   .000000   .528265   .000000  -.364069
   2    .431331   .168916   .500000  -.340234   .500000   .411900
   3    .334378  -.374659   .500000  -.269119  -.500000  -.418804
   4    .304074  -.620995   .000000   .586999   .000000   .421114
   5    .334378  -.374659  -.500000  -.269119   .500000  -.418804
```

```
   6    .431331    .168916   -.500000   -.340234   -.500000    .411900


Total energy = 6 ALPHA +  8.811924 BETA


Density and bond-order matrix
        1           2          3          4          5          6
   1  1.176780
   2  0.659388    0.929159
   3 -0.020615    0.661883   1.004356
   4 -0.313552    0.052521   0.668674   0.956191
   5 -0.020615   -0.338117   0.004356   0.668674   1.004356
   6  0.659388   -0.070841  -.338117   0.052521   0.661883   0.929159


 Total charges:
N1: 1 - 1.177= -0.177
C2: 1 - 0.929= +0.071
C3: 1 - 1.004= -0.104
C4: 1 - 0.956= +0.044
```

∎

∎ Example 2.7.5 | Hückel computation on pyrrole.
The following shows a full Hückel computation for pyrrole.

```
NATOMS  NELECS  NINDEX   NLAB   NHOMO   NLUMO
   5       6       0       1       3       4


 Input Matrix
      1       2       3       4       5
   1   .8000
   2   .9000    .0000
   3   .0000  1.0000    .0000
   4   .0000    .0000  1.0000    .0000
   5   .9000    .0000    .0000  1.0000    .0000


 Energies
        1          2          3          4          5
     2.120048    .920296    .618034 -1.240344 -1.618034


MO coefficients
   1  -.583903  -.643479    .000000    .494968    .000000
   2  -.428211  -.043004  -.601501   -.561058   -.371748
   3  -.382315   .539554  -.371748    .250434    .601501
   4  -.382315   .539554   .371748    .250434   -.601501
   5  -.428211  -.043004   .601501   -.561058    .371748


Total energy = 6 ALPHA +  7.316756 BETA


Density and bond-order matrix
        1          2          3          4          5
   1  1.510014
   2   .555412   1.094034
   3  -.247914    .728230   1.150959
   4  -.247914   -.166198    .598172   1.150959
   5   .555412   -.353179   -.166198    .728230   1.094034


 Total charges:
   N1: 2 - 1.510= +0.490
```

```
C2: 1 - 1.094= -0.094
C3: 1 - 1.151= -0.151
```

∎

2.8 Orbital Interactions and Symmetry

Hückel theory can be used to qualitatively understand how the interaction of orbitals leads to the stabilization or destabilization intermediate species formed during a chemical reaction. To estimate the interaction of a molecule with a reagent (R) use second order perturbation theory. Consider the case of an electrophile reagent (R) that interacts with atom μ of a given molecule. In Hückel theory the matrix element corresponding to this interaction can be represented with a scaled version of the resonance integral β

$$\langle \chi_\mu | \hat{h}' | \chi_R \rangle = \gamma\beta, \tag{2.41}$$

where $0 \leq \gamma < 1$ is a parameter that describes the strength of this interaction.

molecule	reagent	transition state
MO ϕ_i	χ_R	interaction
ϵ_i	$\alpha_R = \alpha$	$\langle \chi_\mu | \hat{h}' | \chi_R \rangle = \gamma\beta$
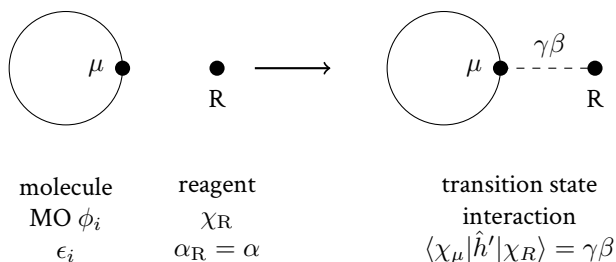
Each molecular orbital ψ_i from Hückel theory gets stabilized by an energy amount given by

$$\Delta E_i^{(2)} = \frac{|\langle \psi_i | \hat{h}' | \chi_R \rangle|^2}{\epsilon_i - \epsilon_R}. \tag{2.42}$$

Note that there is no summation here because there is only one perturbing state (the empty orbital of the reagent). Here is a molecular orbital scheme that shows how the interaction of the reagent empty orbital stabilizes the orbitals in the transition state
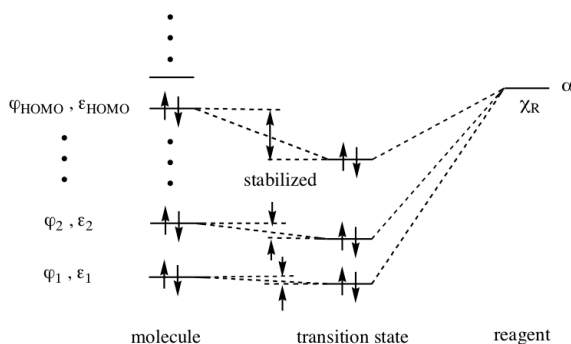
The numerator of the expression for $\Delta E_i^{(2)}$ may be easily computed as

$$\langle \psi_i | \hat{h}' | \chi_R \rangle = \sum_\nu C_{\mu i} \langle \chi_\nu | \hat{h}' | \chi_R \rangle = C_{\mu i} \langle \chi_\mu | \hat{h}' | \chi_R \rangle = \gamma\beta C_{\mu i}. \tag{2.43}$$

because $\psi_i = \sum_\mu^N \chi_\mu C_{\mu i}$ and only the matrix element $\langle \chi_\mu | \hat{h}' | \chi_R \rangle$ is nonzero. The denominator is instead given by

$$\epsilon_i - \epsilon_R = \alpha + \lambda_i \beta - \alpha = \lambda_i \beta, \tag{2.44}$$

where we assumed that the electrophile is a carbon atom ($\epsilon_R = \alpha$). Putting everything together we get

$$\Delta E_i^{(2)} = \frac{(\gamma \beta C_{\mu i})^2}{\lambda_i \beta} = \frac{C_{\mu i}^2}{\lambda_i} \gamma^2 \beta. \tag{2.45}$$

If we sum this contribution over all the doubly occupied orbitals we get a total energy stabilization equal to

$$2 \sum_i^{\text{occ}} \Delta E_i^{(2)} = 2 \sum_i^{\text{occ}} \frac{C_{\mu i}^2}{\lambda_i} \gamma^2 \beta = S_R^{\text{E}} \gamma^2 \beta. \tag{2.46}$$

This equation partitions the interaction energy into a molecule specific part S_R^{E}, called the *superdelocalizability* and $\gamma^2 \beta$, a term that depends on the strength of the interaction.

The largest contribution to S_R^{E} comes form the MO with the smallest $|\lambda_i|$, which is called highest occupied molecular orbital (HOMO) and is given by the single term

$$2 \frac{C_{\mu,\text{HOMO}}^2}{\lambda_{\text{HOMO}}} \tag{2.47}$$

If we ignore the denominator we can consider a simplified reactivity index, the *frontier electron density*, given by

$$f_\mu^{\text{El}} = 2 C_{\mu,\text{HOMO}}^2. \tag{2.48}$$

The most reactive atom towards an electrophile is the one with the largest value of f_μ^{El}, among all possible values of μ. This means that the atom with the largest absolute coefficient in the HOMO is the most reactive. One can repeat the same analysis for nucleophilic reactions, in which case the reactivity can be connected to a corresponding frontier electron density

$$f_\mu^{\text{Nuc}} = 2 C_{\mu,\text{LUMO}}^2, \tag{2.49}$$

where LUMO indicates the lowest unoccupied MO. These two indices allow to identify the atoms (labeled with μ) with the highest reactivity towards electrophiles and nucleophiles by just looking at the HOMO and LUMO of a molecule. For radical reactions, on considers instead the average of f_μ^{El} and f_R^{Nuc}

$$f_\mu^{\text{Rad}} = \frac{1}{2}(f_\mu^{\text{El}} + f_\mu^{\text{Nuc}}). \tag{2.50}$$

2.9 Two-center interactions

Another important application of Hückel theory is in reactions that involve two centers, like cyclization of unsaturated hydrocarbons. If we now consider two molecules, A and B, with centers μ and ν on A interacting with centers μ' and ν' on B, we can ask how much is the energy of the complex A + B stabilized by the interaction of the frontier orbitals (HOMO/LUMO) on each fragment.
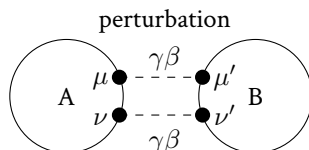
Assuming again that each pair of orbitals interacts with a term equal to $\gamma \beta$, we can write

$$\langle \chi_\mu | \hat{h}' | \chi_{\mu'} \rangle = \gamma \beta,$$
$$\langle \chi_\nu | \hat{h}' | \chi_{\nu'} \rangle = \gamma \beta. \tag{2.51}$$

Each orbital ψ_i^A on A will be stabilized by the interaction with the unoccupied orbitals on B

$$\Delta E_i^{A,(2)} = \sum_{k \neq i}^{\text{virtual B}} \frac{|\langle \psi_i^A | \hat{h}' | \psi_k^B \rangle|^2}{\epsilon_i^A - \epsilon_k^B}. \tag{2.52}$$

Similarly, an orbital ψ_i^B on B will be stabilized by the interaction with the unoccupied orbitals on A by an amount

$$\Delta E_i^{B,(2)} = \sum_{k \neq i}^{\text{virtual B}} \frac{|\langle \psi_i^B | \hat{h}' | \psi_k^A \rangle|^2}{\epsilon_i^B - \epsilon_k^A}. \tag{2.53}$$

Now let us suppose that the most important contribution comes from the interaction of the HOMO on A with the LUMO on B. The numerator for this contribution is given by

$$\Delta E_{\text{HOMO}}^{A,(2)} = \frac{|\langle \psi_{\text{HOMO}}^A | \hat{h}' | \psi_{\text{LUMO}}^B \rangle|^2}{\epsilon_{\text{HOMO}}^A - \epsilon_{\text{LUMO}}^B}. \tag{2.54}$$

If we plug in the definition of these two orbitals we get for the numerator

$$\langle \psi_{\text{HOMO}}^A | \hat{h}' | \psi^{B_{\text{LUMO}}} \rangle = \sum_{\rho\sigma} \langle \chi_\rho | \hat{h}' | \chi_\sigma \rangle C_{\rho,\text{HOMO}}^A C_{\sigma,\text{LUMO}}^B$$

$$= \langle \chi_\mu | \hat{h}' | \chi_{\mu'} \rangle C_{\mu,\text{HOMO}}^A C_{\mu',\text{LUMO}}^B + \langle \chi_\nu | \hat{h}' | \chi_{\nu'} \rangle C_{\nu,\text{HOMO}}^A C_{\nu',\text{LUMO}}^B$$

$$= \gamma\beta \underbrace{(C_{\mu,\text{HOMO}}^A C_{\mu',\text{LUMO}}^B + C_{\nu,\text{HOMO}}^A C_{\nu',\text{LUMO}}^B)}_{\delta} = \gamma\beta\delta$$

$$\tag{2.55}$$

We can now use this result to analyze the cyclization reaction between two molecules.

2.10   Cyclization Reaction Between Two Molecules

Consider the case of the HOMO of butadiene interacting with the LUMO of ethylene. In this case we can use simple symmetry considerations to learn something about the interaction of these two molecules in a cyclization reaction. The following plot show the HOMO and LUMO of butadiene and ethylene
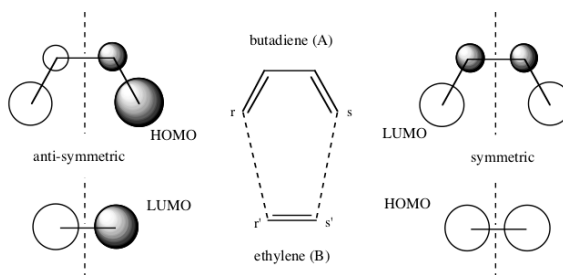
For butadiene (A) the HOMO is antisymmetric, that is, it takes values with opposite signs on the two interacting atoms

$$C_{\mu,\text{HOMO}}^A = -C_{\nu,\text{HOMO}}^A \tag{2.56}$$

and this is also true for the LUMO of ethylene (B)

$$C_{\mu',\text{LUMO}}^B = -C_{\nu',\text{LUMO}}^B. \tag{2.57}$$

Taking these results into considerations we obtain

$$\delta = C_{\mu,\text{HOMO}}^A C_{\mu',\text{LUMO}}^B + C_{\nu,\text{HOMO}}^A C_{\nu',\text{LUMO}}^B = 2C_{\mu,\text{HOMO}}^A C_{\mu',\text{LUMO}}^B \tag{2.58}$$

This interaction leads to a lowering in energy since $\epsilon^{\mathrm{A}}_{\mathrm{HOMO}} - \epsilon^{\mathrm{B}}_{\mathrm{LUMO}} < 0$, therefore, we say that this interaction is **allowed**. In general, the interaction of orbitals with the same symmetry is allowed. For example, the interaction of the butadiene LUMO with the ethylene HOMO (the opposite of what we considered above) is a case where both orbitals are symmetric since

$$C^{\mathrm{A}}_{\mu,\mathrm{LUMO}} = C^{\mathrm{A}}_{\nu,\mathrm{LUMO}}, \tag{2.59}$$

and

$$C^{\mathrm{B}}_{\mu',\mathrm{HOMO}} = C^{\mathrm{B}}_{\nu',\mathrm{HOMO}}. \tag{2.60}$$

For this case the quantity δ is also nonzero

$$\delta = 2C^{\mathrm{A}}_{\mu,\mathrm{LUMO}}C^{\mathrm{B}}_{\mu',\mathrm{HOMO}} \tag{2.61}$$

The interaction of two ethylene molecules is an example where the HOMO and LUMO have different symmetry

HOMO of ethylene (A)

symmetric

LUMO of ethylene (B)

anti-symmetric
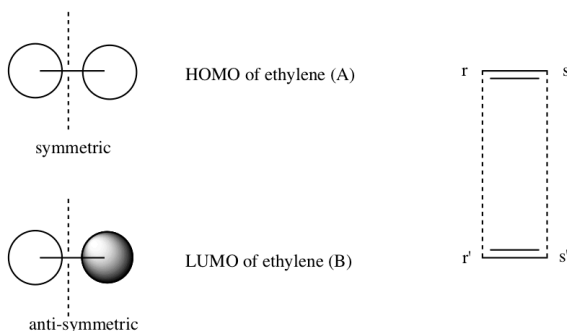
In this case since

$$C^{\mathrm{A}}_{\mu,\mathrm{HOMO}} = C^{\mathrm{A}}_{\nu,\mathrm{HOMO}}, \tag{2.62}$$

and

$$C^{\mathrm{B}}_{\mu',\mathrm{LUMO}} = -C^{\mathrm{B}}_{\nu',\mathrm{LUMO}}. \tag{2.63}$$

we find that $\delta = 0$. This means that the interaction between orbitals of different symmetry is **forbidden**. For general polyenes one has the following result:

$$(4n + 2) + (4n') \rightarrow 4n'' + 2 \quad \text{symmetry allowed}, \tag{2.64}$$

while

$$\begin{aligned} (4n + 2) + (4n' + 2) &\rightarrow 4n'' + 4 \quad \text{forbidden}, \\ (4n) + (4n') &\rightarrow 4n'' \quad \text{forbidden}. \end{aligned} \tag{2.65}$$

2.11 Orbital mixing rules

Let's consider two atomic orbitals ψ_i and ψ_j and let them interact by, for example, bringing them together. The interacting orbitals may be described by a two by two matrix of the form

$$\mathbf{h} = \begin{pmatrix} \langle \psi_i | \hat{h} | \psi_i \rangle & \langle \psi_i | \hat{h} | \psi_j \rangle \\ \langle \psi_j | \hat{h} | \psi_i \rangle & \langle \psi_j | \hat{h} | \psi_j \rangle \end{pmatrix} = \begin{pmatrix} \epsilon_i & v \\ v & \epsilon_j \end{pmatrix}. \tag{2.66}$$

By examining the properties of the eigenvalues/eigenvectors of this matrix we can deduce some useful rules that can help us predict how orbitals mix.

- **Rule 1**. A pair of orbitals with zero overlap (orthogonal) do not mix. This is the case $v = 0$, which basically means that the two orbitals do not interact due to symmetry.
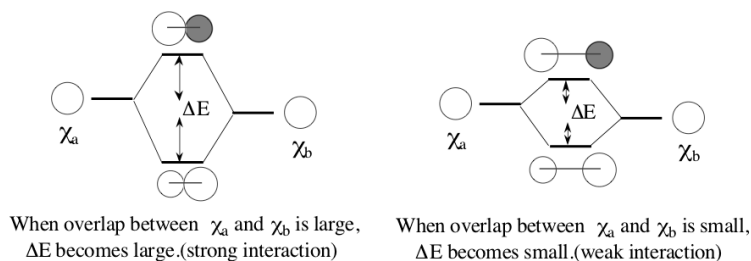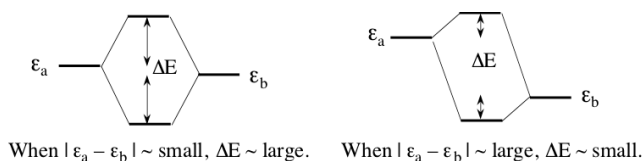

no mix

mix

- **Rule 2**. When a pair of orbitals interact, they form a bonding (in-phase) orbital and an anti-bonding (out-of-phase) orbital. The bonding orbital is lower in energy than the antibonding orbital.

orbital energy diagram of hydrogen molecule
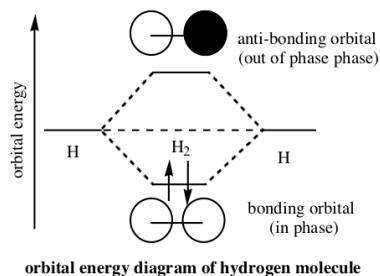
This rule follows from the equation for the eigenvalues of $\mathbf{h}$

$$\lambda_\pm = \frac{1}{2}(\epsilon_i + \epsilon_j) \pm \frac{1}{2}\sqrt{(\epsilon_i - \epsilon_j)^2 + 4v^2}. \tag{2.67}$$

- **Rule 3**. When the energy difference between a pair of orbitals before mixing is small and/or the overlap between a pair of orbitals is large, the energy separation becomes large after mixing.

When $|\varepsilon_a - \varepsilon_b| \sim$ small, $\Delta E \sim$ large.   When $|\varepsilon_a - \varepsilon_b| \sim$ large, $\Delta E \sim$ small.

When overlap between χ_a and χ_b is large, ΔE becomes large.(strong interaction)   When overlap between χ_a and χ_b is small, ΔE becomes small.(weak interaction)

- **Rule 4**. When a pair of orbitals with different energies interact, the newly formed MO has large contribution of the original orbital whose energy is closest to the newly formed MO.
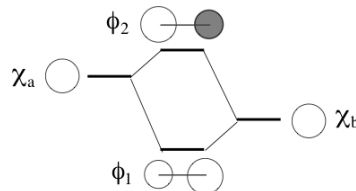
In the case of $\varepsilon_a > \varepsilon_b$,

    bonding orbital is

$$\phi_1 = C_{1a}\,\chi_a + C_{1b}\,\chi_b \,, \quad C_{1a} < C_{1b}$$

    anti-bonding orbital is

$$\phi_2 = C_{2a}\,\chi_a + C_{2b}\,\chi_b \,, \quad C_{2a} > -C_{2b}$$

- **Rule 5**. The same number of new MOs are created from the original orbitals before mixing (N MOs from N AOs).

- **Rule 6**. Suppose another orbital χ_c affects the two orbitals ϕ_1 and ϕ_2, which were formed mainly by interacting two orbitals χ_a and χ_b. The perturbation caused by the third orbital χ_c causes a small change of the orbital shape of ϕ_1 and ϕ_2. When the energy of χ_c is higher than the energies of ϕ_1 and ϕ_2, the mixing of χ_c with ϕ_1 and ϕ_2 is in-phase. When the energy of χ_c is lower than the energies of ϕ_1 and ϕ_2, the mixing

of χ_c into ϕ_1 and ϕ_2 is out-of-phase. When three orbitals are interacting, the newly formed three MO's can be expressed with a linear combination of the original three orbitals. The mixing coefficients depend on the energies of the original three orbitals.
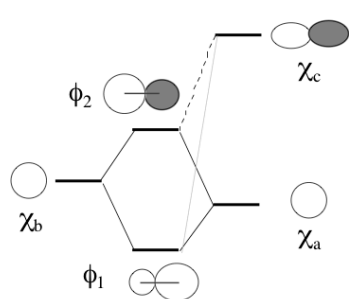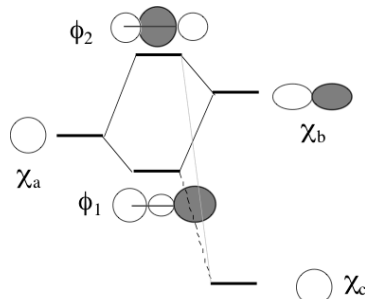
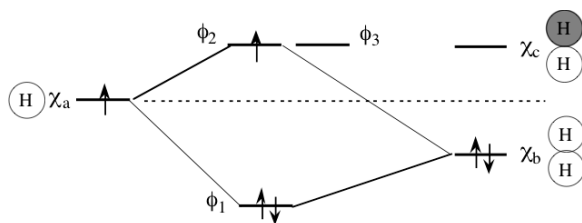In the case of $\varepsilon_c \gg \varepsilon_a, \varepsilon_b$.   In the case of $\varepsilon_c \ll \varepsilon_a, \varepsilon_b$.

2.12 Examples and Problems
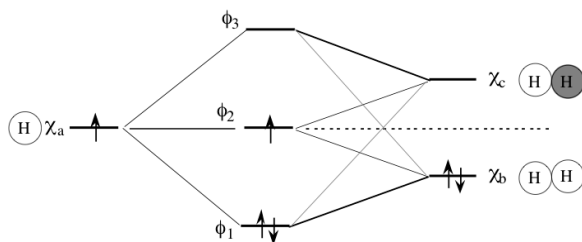
2.12.1 Molecular orbitals of H_3

Let us construct the molecular orbitals for the triangular and linear H_3 species from the hydrogen atom and the molecular orbital of the H_2 molecule.

Triangular H_3

In the case of triangular H_3, let us assume that atomic hydrogen approaches on the bisecting axis of the hydrogen molecule. Note that χ_a interacts only with χ_b since the symmetry of χ_c is such that no mixing happens. The newly formed molecular orbital ψ_1 is the bonding combination between χ_a and χ_b, and the molecular orbital ψ_2 is the corresponding anti-bonding combination. ψ_3 is the original χ_c.

Linear H_3 (H $\cdots$ H–H)

In the linear form of H_3, an hydrogen atom approaches the molecular axis of the hydrogen molecule. The situation becomes different from the triangular H_3 case, because all orbitals χ_a, χ_b, and χ_c interact with each other. Comparing these two cases, we predict that the hydrogen exchange reaction H_2+H prefers the linear transition-state structure since orbital interactions lead to an overall stabilization of the energy.

Problem 2.12.1 — Molecular orbitals of H₄. Construct the molecular orbitals for square H_4 and linear H_4 species from the two sets of molecular orbitals of the H_2 molecule. Draw the orbital energy diagrams and discuss which structure is more stable.

Orbital energy diagram of hydrogen molecule
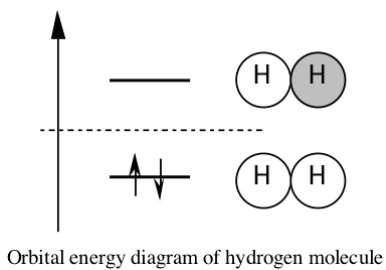
Problem 2.12.2 — π MOs of benzene. Create the six π-molecular orbitals of benzene by combining the two sets of π-orbitals of the allyl radical. The picture shows only one side of π-plane (top view).