Part III Symmetry and Bonding

Chapter 6 Hückel Molecular Orbitals

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6. Hückel molecular orbitals (HMO)
休克尔分子轨道

- So far we have just been drawing up ***qualitative MO diagrams*** aided by symmetry considerations *without computing* ***the energies and forms of any molecular orbitals***.
- Of course, it is now possible to compute the detailed form and energy of the MOs using a computer program such as ***Hyperchem, G16 , Dmol3, ADF, Molpro*** *etc*.
- Anyway, it is both useful and instructive to ***do some MO calculations 'by hand'***. This topic will be talked about in this chapter.

6.1 The LCAO method

- The simplest and most intuitive way to construct molecular orbitals is to use ***the linear combination of atomic orbitals*** (LCAO) method, which we have been doing up to now.

  Each MO ψ is expressed as a linear combination of atomic orbitals, $\Phi_1, \Phi_2, \ldots,$

$$\psi = c_1\Phi_1 + c_2\Phi_2 + c_3\Phi_3 + \cdots$$

Φ_i ~ *i*th AO (also known as one of the ***basis functions***) used to construct the MO.

c_i ~ the coefficient which indicates the relative contribution of an AO Φ_i to the MO.

- The problem we have to solve is finding the values of the ***coefficients*** and the corresponding ***energy for each MO***.

The key principle to solve such a problem is ***the variation theorem.***

6.1.1 Derivation of the secular equations – Variation Theorem

- For a MO expressed as an ***LCAO*** sum: $$\psi = \sum_{i=1}^{N} c_i \Phi_i$$

the expectation value ***E*** of the ***Hamiltonian*** is calculated in the usual way:

$$E = \langle \hat{H} \rangle = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi \psi d\tau} = \frac{\int (\sum_i c_i \Phi_i) \hat{H} (\sum_j c_j \Phi_j) d\tau}{\int (\sum_i c_i \Phi_i)(\sum_j c_j \Phi_j) d\tau} = \frac{\sum_{i,j} c_i c_j \int \Phi_i \hat{H} \Phi_j \, d\tau}{\sum_{i,j} c_i c_j \int \Phi_i \Phi_j \, d\tau}$$

end up here with a certain value of *E* if we knew every terms within this expression.

which involves computation of the following two types of integrals :

$$H_{ij} = \int \Phi_i \hat{H} \Phi_j d\tau \qquad S_{ij} = \int \Phi_i \Phi_j d\tau$$

S_{ij} ~ the ***overlap integral*** between the two basis functions Φ_i and Φ_j.

H_{ij} ~ a ***matrix element*** of the operator $\hat{H}$ (the ***Hamiltonian*** for the system).

- According to the ***variation principle***, we need to minimize ***E*** with respect to the coefficients c_i, i.e. $\partial E / \partial c_i = 0$.
- Now we rewrite the equation as, $E \sum_{i,j} c_i c_j S_{ij} = \sum_{i,j} c_i c_j H_{ij}$

6.1.1 Derivation of the secular equations

- We then take the (partial) derivative of both sides with respect to the coefficient ***c**$_i$*.

$$\frac{\partial}{\partial c_i}\left[E\sum_{ij} c_i c_j S_{ij}\right] = \frac{\partial}{\partial c_i}\left[\sum_{ij} c_i c_j H_{ij}\right]$$

($i = 1,2,\ldots,N$; i.e., a total of ***N*** equations!)

$$\frac{\partial E}{\partial c_i}\sum_{ij} c_i c_j S_{ij} + E\sum_{j} c_j S_{ij} = \sum_{j} c_j H_{ij}$$

- Demanding $\partial E/\partial c_i=0$, then we have

$$E\sum_{j} c_j S_{ij} = \sum_{j} c_j H_{ij} \longrightarrow \sum_{j}(H_{ij}-ES_{ij})c_j = 0$$

($i = 1,2,\ldots,N$; i.e., a total of ***N*** equations!)

Derivation of the secular equations

- The ***N*** equations can be conveniently expressed in ***matrix form*** (***N*** is the number of basis functions):

$$\left[\begin{pmatrix} H_{11} & H_{12} & H_{13} & \dots & H_{1N} \\ H_{21} & H_{22} & H_{23} & \dots & H_{2N} \\ H_{31} & H_{32} & H_{33} & \dots & H_{3N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ H_{N1} & H_{N2} & H_{N3} & \dots & H_{NN} \end{pmatrix} - E \begin{pmatrix} S_{11} & S_{12} & S_{13} & \dots & S_{1N} \\ S_{21} & S_{22} & S_{23} & \dots & S_{2N} \\ S_{31} & S_{32} & S_{33} & \dots & S_{3N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ S_{N1} & S_{N2} & S_{N3} & \dots & S_{NN} \end{pmatrix}\right] \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} = \mathbf{0}$$

N^2 H_{ij}-type integrals and N^2 S_{ij}-type integrals to be computed!!! !

- These are called the ***secular equations*** (久期方程) and in general their solution will lead to ***N*** different values of ***E*** , each corresponding to ***a*** MO.
- By ***substituting the corresponding value*** of the energy ***E*** back into the ***secular equations***, the coefficients $\{c_i\}$ corresponding to ***a*** particular MO can be found.

6.1.2 The Hückel approximations

- The ***Hückel approximations***:   1) set ***$S_{ij} = \int \phi_i \phi_j d\tau = 0\ (i \neq j)$ or $1\ (i = j)$***

Then the ***secular equations*** look simpler,

$$\left[\begin{pmatrix} H_{11} & H_{12} & H_{13} & \dots & H_{1N} \\ H_{21} & H_{22} & H_{23} & \dots & H_{2N} \\ H_{31} & H_{32} & H_{33} & \dots & H_{3N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ H_{N1} & H_{N2} & H_{N3} & \dots & H_{NN} \end{pmatrix} - E \begin{pmatrix} 1 & 0 & 0 & \dots & 0 \\ 0 & 1 & 0 & \dots & 0 \\ 0 & 0 & 1 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & 1 \end{pmatrix}\right] \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = 0$$

and can be rewritten as

Secular matrix
(久期矩阵)

$$\begin{pmatrix} H_{11} - E & H_{12} & H_{13} & \dots & H_{1N} \\ H_{21} & H_{22} - E & H_{23} & \dots & H_{2N} \\ H_{31} & H_{32} & H_{33} - E & \dots & H_{3N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ H_{N1} & H_{N2} & H_{N3} & \dots & H_{NN} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = 0.$$

These equations can be solved by firstly setting *the determinant of the secular matrix*, namely *the secular determinant (久期行列式)*, to be *zero*.

6.1.2 The Hückel approximations

2) Calculating the actual values of the matrix elements H_{ij} is itself a *formidable* task, so we sidestep this by simply leaving them as parameters,

$$H_{ii} = \int \phi_i \hat{H} \phi_i d\tau = \alpha_i$$ (approx. as the energy of the AO ϕ_i)

$$H_{ij} = \int \phi_i \hat{H} \phi_j d\tau = \beta_{ij}$$ (resonance integral)

Hückel approximations

β_{ij} is zero unless the two orbitals are on adjacent atoms, i.e., directly overlapping!

- Accordingly, the secular equations become

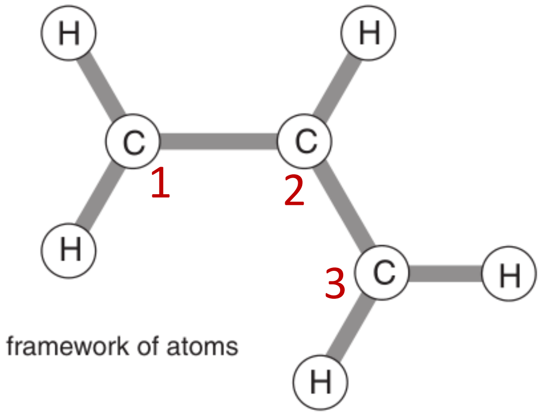
$$\begin{pmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} & \cdots & \beta_{1N} \\ \beta_{21} & \alpha_2 - E & \beta_{23} & \cdots & \beta_{2N} \\ \beta_{31} & \beta_{32} & \alpha_3 - E & \cdots & \beta_{3N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \beta_{N1} & \beta_{N2} & \beta_{N3} & \cdots & \alpha_N - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = 0.$$

Q2: For an allylic π_3^x system, write out the secular equation!

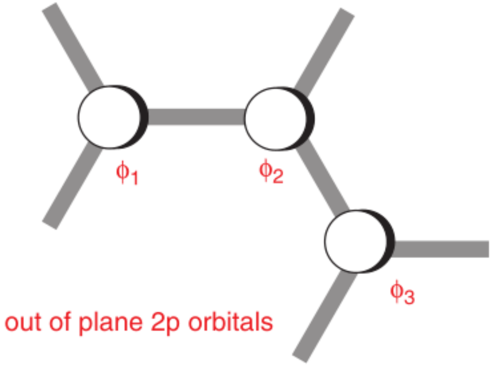
- Some of the β_{ij} terms can be zero case by case!
- The values of α_i, β_{ij} can be determined semi-empirically!
- Quite easy for dealing with π-conjugation systems!
- Q1: how to determine α_c & β_{cc}?

6.1.3 The allyl system

- ***The allyl fragment***: the π-type MOs formed from these p_π orbitals, $\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$



framework of atoms



out of plane 2p orbitals

The ***secular eq***s. are

$$\begin{pmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} \\ \beta_{21} & \alpha_2 - E & \beta_{23} \\ \beta_{31} & \beta_{32} & \alpha_3 - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$

Can the eqs. be further simplified?!

- These are C $2p_\pi$ orbitals. Set $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$, $\beta_{12} = \beta_{21} = \beta_{23} = \beta_{32} = \beta$ (***Hückel approx***.).

The ***secular eq***s. thus become

$$\begin{pmatrix} (\alpha - E)/\beta & 1 & 0 \\ 1 & (\alpha - E)/\beta & 1 \\ 0 & 1 & (\alpha - E)/\beta \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \mathbf{0}$$

Now set $x = (\alpha - E)/\beta$!

6.1.3 The allyl system

- Now we have the simplified *secular equations* as (with *x = (α-E)/β*)

$$\begin{pmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$

- As usual, set the corresponding *secular determinant* to *zero*:

$$det\begin{pmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{pmatrix} = 0 \longrightarrow$$

$$x(x^2-1) - 1 \times (x-0) + 0 \times (1-0) = 0$$

$$x(x^2-1) - x = 0$$

$$x(x^2-2) = 0 \longrightarrow \boldsymbol{x = 0, \pm\sqrt{2}}$$

$$\Rightarrow \quad E_1 = \alpha + \sqrt{2}\beta, \qquad E_2 = \alpha, \qquad E_3 = \alpha - \sqrt{2}\beta$$

- Let us start with $x = -\sqrt{2}$ that gives $E_1 = \alpha + \sqrt{2}\beta$ and the *secular equations* as

$$\begin{pmatrix} -\sqrt{2} & 1 & 0 \\ 1 & -\sqrt{2} & 1 \\ 0 & 1 & -\sqrt{2} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0 \Rightarrow$$

$$\boldsymbol{-\sqrt{2}c_1 + c_2 = 0} \qquad [\boldsymbol{A}]$$

$$\boldsymbol{c_1 - \sqrt{2}c_2 + c_3 = 0} \qquad [\boldsymbol{B}]$$

$$\boldsymbol{c_2 - \sqrt{2}c_3 = 0} \qquad [\boldsymbol{C}]$$

Three eqs. are not independent!

6.1.3 The allyl system

- The normalization relationship can be introduced to make the **eq**s. solvable,

$$c_1^2 + c_2^2 + c_3^2 = 1$$

- There are two practical approaches to find the coefficients.

- ***First method***: use the equations to write all of the coefficients in terms of one of them.

From eq. **[A]** we have: $-\sqrt{2}c_1 + c_2 = 0$ hence $c_2 = \sqrt{2}c_1$.

Now use eq. **[C]**: $c_2 - \sqrt{2}c_3 = 0 \quad [C]$

Substitute $c_2 = \sqrt{2}c_1$ → $\sqrt{2}c_1 - \sqrt{2}c_3 = 0 \rightarrow c_3 = c_1$

now insert these values into the normalization condition, and hence find c_1:

$$c_1^2 + c_2^2 + c_3^2 = 1 \quad \rightarrow c_1^2 + (\sqrt{2}c_1)^2 + c_1^2 = 1 \quad \rightarrow 4c_1^2 = 1 \quad \rightarrow c_1 = 1/2$$

$$\rightarrow c_2 = \sqrt{2}/2\ , \quad c_3 = 1/2; \quad \rightarrow \psi_1 = (\Phi_1 + \sqrt{2}\Phi_2 + \Phi_3)/2$$ with $E_1 = \alpha + \sqrt{2}\beta$

6.1.3 The allyl system

- ***The second method***: as we know ***the relationship between the coefficients,*** we might just set one of them to have the value ***1*** and ***work out the rest,*** then ***normalize at the end***.
- Let us set $c_1 = 1$; from **[A]** we have:

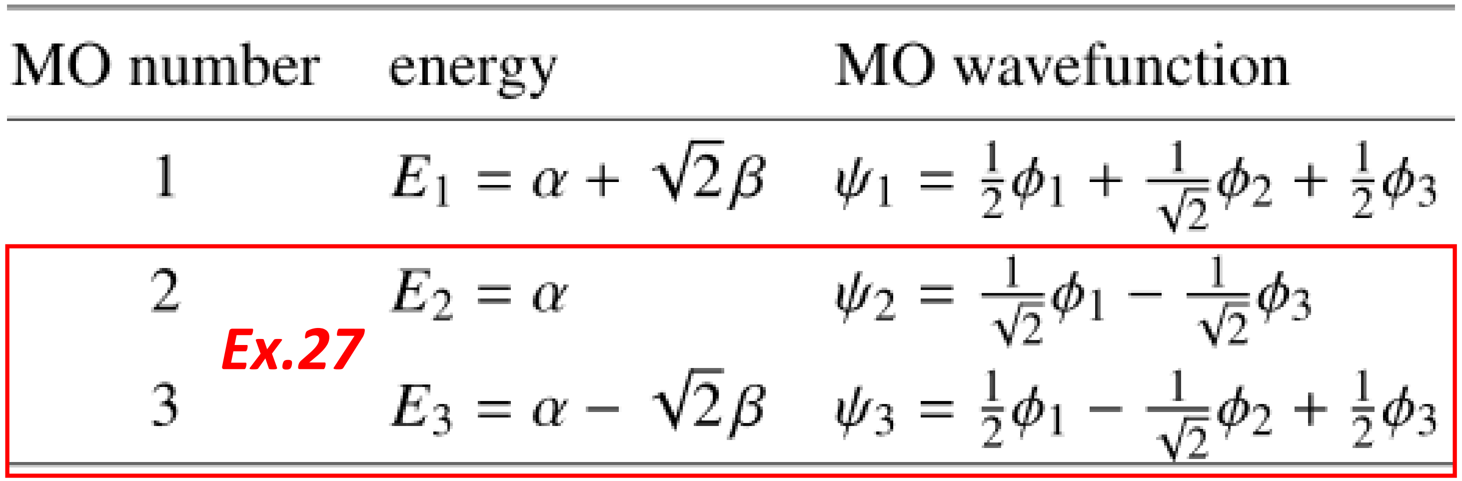
$$-\sqrt{2}c_1 + c_2 = 0, \text{ put } c_1 = 1, \text{ giving } c_2 = \sqrt{2}$$

- Now we use this value for c_2 in **[C]**: $c_2 - \sqrt{2}c_3 = 0$, giving $c_3 = 1$
- The coefficients are therefore: $c_1 = 1$ $c_2 = \sqrt{2}$ $c_3 = 1$
- Now normalize the coefficients: $\sqrt{c_1^2 + c_2^2 + c_3^2} = \sqrt{1 + 2 + 1} = 2$
- The normalized coefficients are: $c_1 = 1/2$ $c_2 = \sqrt{2}/2$ $c_3 = 1/2$

Which method do you recommend?

6.1.3 The allyl system

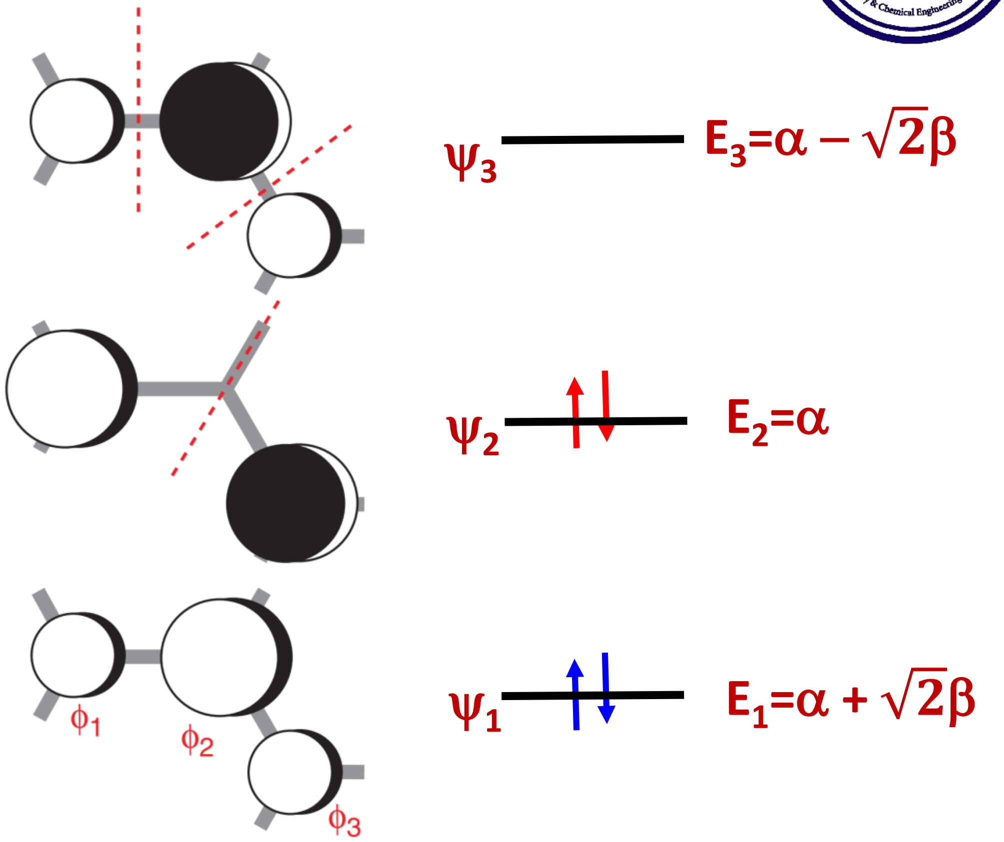
- The final results are summarized in the table.

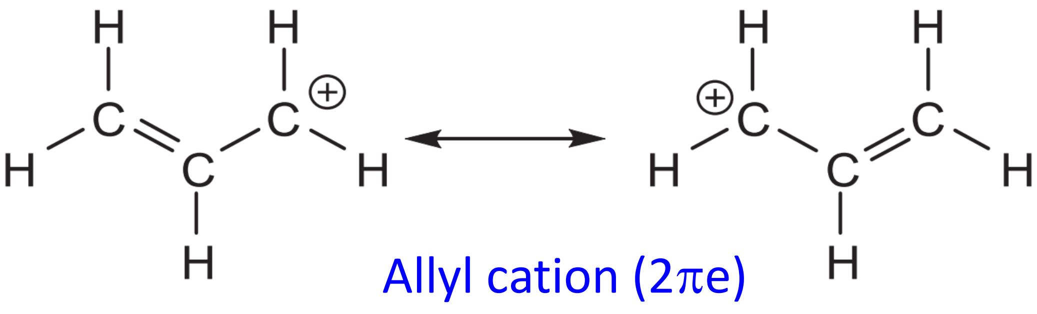


MO number	energy	MO wavefunction
1	$E_1 = \alpha + \sqrt{2}\beta$	$\psi_1 = \frac{1}{2}\phi_1 + \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3$
2	$E_2 = \alpha$	$\psi_2 = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3$
3	$E_3 = \alpha - \sqrt{2}\beta$	$\psi_3 = \frac{1}{2}\phi_1 - \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3$

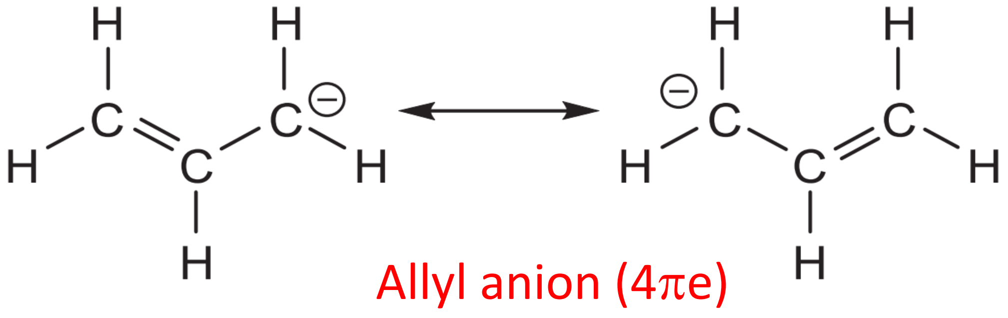
Ex.27

(please recall that we once employed a graphical method to deal with the π-MOs of this molecule in the first semester!)





Allyl cation (2πe)



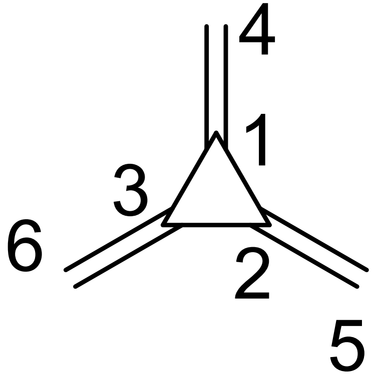
Allyl anion (4πe)

小测验

I. H_3^+可能具有直线形和正三角形两种结构, 休克尔近似 下,可令$\alpha_H = \alpha$, $\beta_{H\text{-}H}=\beta$, 分别写出两种结构的久期行列式;

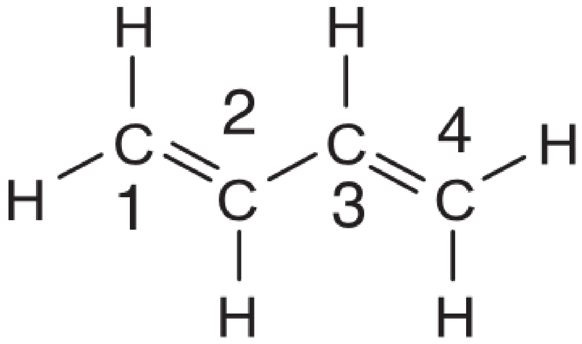
II. 折叠苯C_6H_6的结构图右图所示, 其π_6^6由C原子p_z轨道组成, 休克尔近似下有$\alpha_C = \alpha$, $\beta_{C\text{-}C}=\beta$.

1. 快速写出其π分子轨道的久期方程(矩阵形式);
2. 运用对称性, 推导其π分子轨道的能量及组成形式.



6.1.4 1,3-Butadiene

- The π system of ***butadiene*** comprises four ***p*** orbitals in a row:



- The ***secular equations*** are:

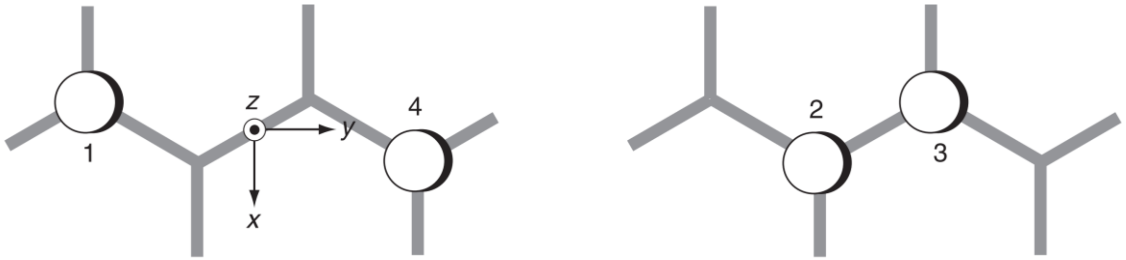
$$\begin{pmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

- To solve this problem, we would first need to find the determinant of the 4 × 4 matrix, ***set it to zero*** and then ***solve the resulting quartic in E***.
- This already sounds like very hard work and although in this case it might just be possible to do this by hand.
- Luckily, ***symmetry*** comes to our aid and reduces this problem to something very much easier.

6.2 Using symmetry to simplify the calculations

6.2.1 Butadiene

- The point group is C_{2h}.



C_{2h}	E	C_2^z	i	σ^{xy}		
A_g	1	1	1	1	R_z	$x^2; y^2; z^2; xy$
B_g	1	-1	1	-1	$R_x; R_y$	$xz; yz$
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	$x; y$	

$\Gamma \quad 2 \quad 0 \quad 0 \quad -2 \quad = A_u \oplus B_g$

- The four p_π (p_z) AOs can be divided into two sets of basis, (ϕ_1, ϕ_4) and (ϕ_2, ϕ_3), and can be dealt with separately.
- Both sets transform as $A_u \oplus B_g$.
- For the basis (ϕ_1, ϕ_4),

  z transforms like A_u; $\theta_{A_u} = (\phi_1 + \phi_4)$ is z-like.

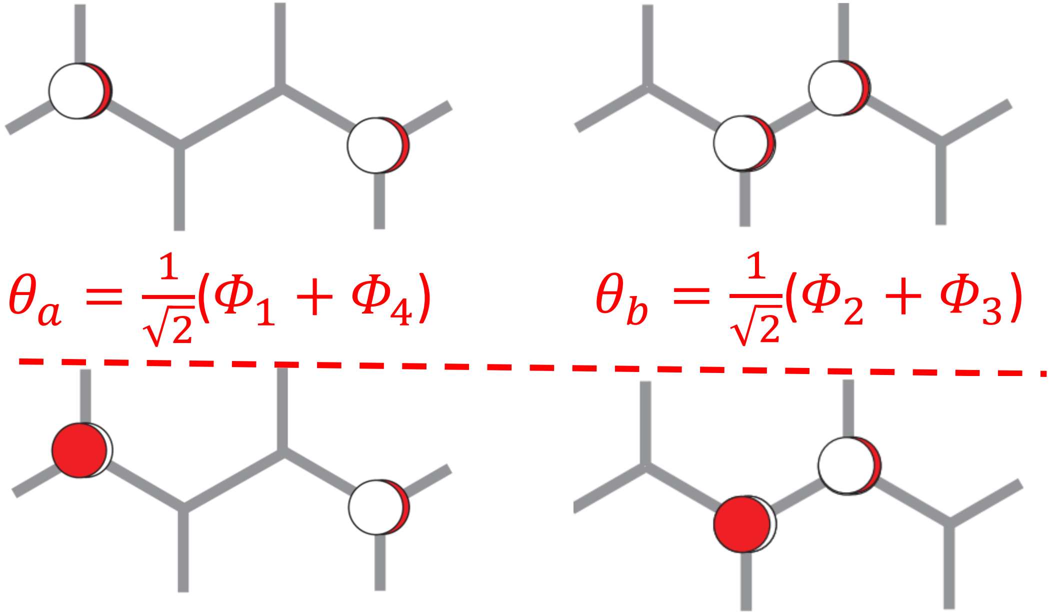
  yz transforms like B_g; $\theta_{B_g} = (-\phi_1 + \phi_4)$ is yz-like!

- Similarly the basis (ϕ_2, ϕ_3) gives rise to two SOs, $\theta_{A_u} = (\phi_2 + \phi_3)$ & $\theta_{B_g} = (-\phi_2 + \phi_3)$

Note: The normalization coefficients for these **SO**s have the same value, $1/\sqrt{2}$.

6.2.1 Butadiene

- Now we have four normalized SOs:
- Only SOs of the same symmetry interact. The symmetry analysis has reduced the problem to the two-way overlap of $\boldsymbol{\theta_a}$ and $\boldsymbol{\theta_b}$, and the two-way overlap of $\boldsymbol{\theta_c}$ and $\boldsymbol{\theta_d}$.



$\boldsymbol{A_u}$ $\theta_a = \frac{1}{\sqrt{2}}(\Phi_1 + \Phi_4)$ $\quad$ $\theta_b = \frac{1}{\sqrt{2}}(\Phi_2 + \Phi_3)$

$\boldsymbol{B_g}$ $\theta_c = \frac{1}{\sqrt{2}}(-\Phi_1 + \Phi_4)$ $\quad$ $\theta_d = \frac{1}{\sqrt{2}}(-\Phi_2 + \Phi_3)$

- At this stage, the secular equations can be developed by thinking about forming MOs by ***the linear combination of any other kind of orbitals***, such as ***symmetry orbitals***.

6.2.1 Butadiene

- Generally we may write an MO as a linear combination of symmetry orbitals θ_a, θ_b, . . .

$$\psi = c_a\theta_a + c_b\theta_b + c_c\theta_c + \cdots$$

We will consistently use *1,2,3, . . .* as the label for **AOs** and *a,b,c, . . .* as the label for **SOs**.

Written in terms of SOs, the secular equations upon ***Hückel approx.*** are:

$$\begin{pmatrix} H_{aa}-E & H_{ab} & H_{ac} & \dots & H_{aN} \\ H_{ba} & H_{bb}-E & H_{bc} & \dots & H_{bN} \\ H_{ca} & H_{cb} & H_{cc}-E & \dots & H_{cN} \\ \dots & \dots & \dots & \dots & \dots \\ H_{Na} & H_{Nb} & H_{Nc} & H_{Nd} & H_{NN}-E \end{pmatrix} \begin{pmatrix} c_a \\ c_b \\ c_c \\ \dots \\ c_N \end{pmatrix} = 0 \text{ with } \boldsymbol{H_{ab} = \int \theta_a \hat{H} \theta_b d\tau}$$

- For butadiene, we therefore have two sets of secular equations to solve: a 2×2 problem for the A_u SOs θ_a and θ_b, and another 2×2 problem for the B_g SOs θ_c and θ_d.

6.2.1 Butadiene

A_u SOs: $\theta_a = \frac{1}{\sqrt{2}}(\Phi_1 + \Phi_4)$, $\theta_b = \frac{1}{\sqrt{2}}(\Phi_2 + \Phi_3)$

- For the A_u SOs, the MOs are written as: $\boldsymbol{\psi_{A_u} = c_a\theta_a + c_b\theta_b}$

and the corresponding secular equations are: $\begin{pmatrix} H_{aa} - E & H_{ab} \\ H_{ba} & H_{bb} - E \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$

- Now compute the matrix elements by applying the ***Hückel Approx***.:

$$H_{aa} = \int \theta_a \hat{H} \theta_a \, \mathrm{d}\tau$$

$$= \int \frac{1}{\sqrt{2}}(\phi_1 + \phi_4)\, \hat{H} \frac{1}{\sqrt{2}}(\phi_1 + \phi_4)\, \mathrm{d}\tau$$

$$= \frac{1}{2}(H_{11} + H_{14} + H_{41} + H_{44})$$

$$= \frac{1}{2}(\alpha_1 + \beta_{14} + \beta_{41} + \alpha_4)$$

$$= \alpha.$$

$$H_{bb} = \int \theta_b \hat{H}\, \theta_b d\tau = \frac{1}{2}(H_{22} + H_{23} + H_{32} + H_{33})$$

$$= \frac{1}{2}(\alpha_2 + \beta_{23} + \beta_{32} + \alpha_3) = \alpha + \beta$$

$$H_{ab} = \int \theta_a \hat{H} \theta_b \, \mathrm{d}\tau$$

$$= \int \frac{1}{\sqrt{2}}(\phi_1 + \phi_4)\, \hat{H} \frac{1}{\sqrt{2}}(\phi_2 + \phi_3)\, \mathrm{d}\tau$$

$$= \frac{1}{2}(H_{12} + H_{13} + H_{42} + H_{43})$$

$$= \frac{1}{2}(\beta_{12} + \beta_{13} + \beta_{42} + \beta_{43}) = \beta$$

6.2.1 Butadiene

- Now the ***secular equations*** become: $$\begin{pmatrix} \alpha - E & \beta \\ \beta & \alpha + \beta - E \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$
- Divide both sides by $\boldsymbol{\beta}$ and then set $\boldsymbol{\frac{\alpha - E}{\beta} = x}$: $$\begin{pmatrix} x & 1 \\ 1 & x+1 \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$
- Demand the ***determinant*** to be ***zero***: $$\det \begin{pmatrix} x & 1 \\ 1 & x+1 \end{pmatrix} = x(x+1) - 1 = 0$$

$\rightarrow x^2 + x - 1 = 0$ ➡ $x = (-1 \mp \sqrt{5})/2 = -1.618 \text{ or } 0.618$

➡ $E_{A_u,1} = \alpha + 1.618\beta$ $\quad E_{A_u,2} = \alpha - 0.618\beta$

- Now we have *two equations* to solve with $\boldsymbol{x}$ being known:

$$x c_a + c_b = 0 \quad [\text{A}] \qquad c_a + (1 + x) c_b = 0 \quad [\text{B}]$$

6.2.1 Butadiene

- The first value of x is 0.618; putting this into **[A]** enables us to find c_b in terms of c_a:

$$\mathbf{0.618}c_a + c_b = 0 \qquad \rightarrow\ c_b = -\mathbf{0.618}c_a$$

- Now make use of the normalization condition: $c_a^2 + c_b^2 = 1$
- Hence $c_a = 0.851 \rightarrow c_b = -0.526$.

$$\begin{aligned}\psi_{A_u,2} &= 0.851\,\theta_a - 0.526\,\theta_b \\ &= 0.851\frac{1}{\sqrt{2}}(\phi_1 + \phi_4) - 0.526\frac{1}{\sqrt{2}}(\phi_2 + \phi_3) \\ &= 0.602\,\phi_1 - 0.372\,\phi_2 - 0.372\,\phi_3 + 0.602\,\phi_4\end{aligned}$$

- To find another A_u MO, we repeat the process with $x = -1.618$.

$$\begin{aligned}\psi_{A_u,1} &= 0.526\,\theta_a + 0.851\,\theta_b \\ &= 0.526\frac{1}{\sqrt{2}}(\phi_1 + \phi_4) + 0.851\frac{1}{\sqrt{2}}(\phi_2 + \phi_3) \\ &= 0.372\,\phi_1 + 0.602\,\phi_2 + 0.602\,\phi_3 + 0.372\,\phi_4\end{aligned}$$

6.2.1 Butadiene

Ex. 28

- We now need to repeat the process for the B_g SOs. The MOs are written as

$$\psi_{B_g} = c_c\theta_c + c_d\theta_d$$

B_g SOs: $\theta_c = \frac{1}{\sqrt{2}}(-\Phi_1 + \Phi_4)$, $\theta_d = \frac{1}{\sqrt{2}}(-\Phi_2 + \Phi_3)$

and the ***secular equations*** are $\begin{pmatrix} H_{cc} - E & H_{cd} \\ H_{dc} & H_{dd} - E \end{pmatrix}\begin{pmatrix} c_c \\ c_d \end{pmatrix} = 0$

- Compute the matrix elements; then $\begin{pmatrix} \alpha - E & \beta \\ \beta & \alpha-\beta-E \end{pmatrix}\begin{pmatrix} c_c \\ c_d \end{pmatrix}=0 \rightarrow \begin{pmatrix} x & 1 \\ 1 & x-1 \end{pmatrix}\begin{pmatrix} c_c \\ c_d \end{pmatrix}=0$

  ($H_{cc} = \alpha$, $H_{dd}=\alpha-\beta$, $H_{cd}= H_{dc}= \beta$)

  ($x = (\alpha-E)/\beta$)

$$det\begin{pmatrix} x & 1 \\ 1 & x-1 \end{pmatrix}=0 \qquad x = (1\mp\sqrt{5})/2$$

- The solutions are $x = -0.618$ and 1.618. The corresponding MOs are

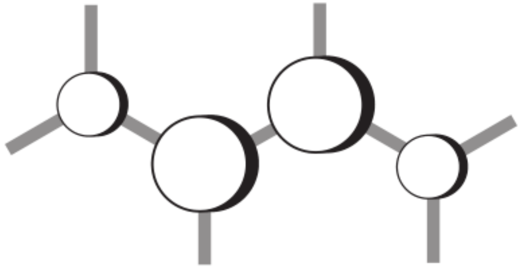
$$\psi_{B_g,1} = -0.602\,\phi_1 - 0.372\,\phi_2 + 0.372\,\phi_3 + 0.602\,\phi_4 \qquad E_{B_g,1} = \alpha + 0.618\,\beta$$

$$\psi_{B_g,2} = -0.372\,\phi_1 + 0.602\,\phi_2 - 0.602\,\phi_3 + 0.372\,\phi_4 \qquad E_{B_g,2} = \alpha - 1.618\,\beta.$$

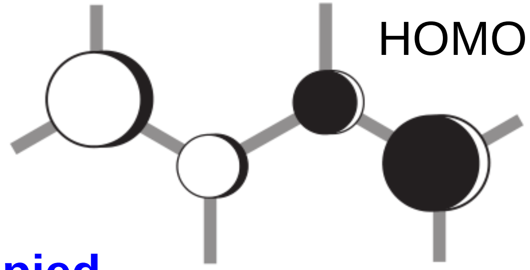
6.2.1 Butadiene

Ex.29 (allyl)

- The complete set of four MOs are shown below.

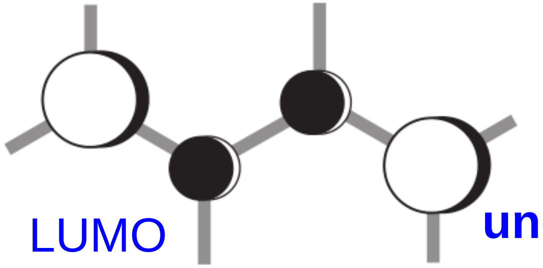


$\psi(A_{u,1})\;\; E_1 = \alpha + 1.618\beta$



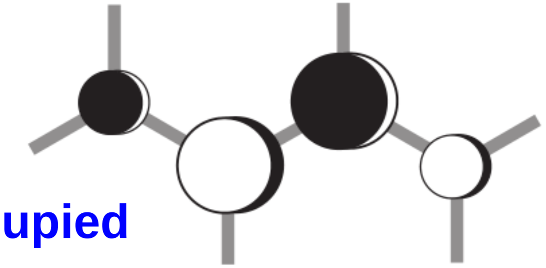
$\psi(B_{g,1})\;\; E_2 = \alpha + 0.618\beta$

Occupied

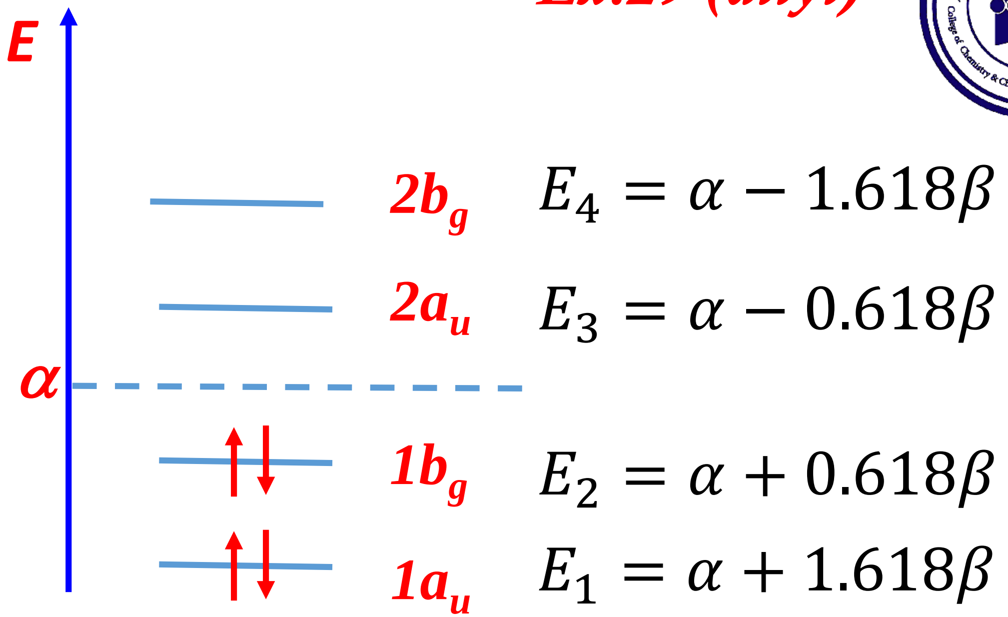


$\psi(A_{u,2})\;\; E_3 = \alpha - 0.618\beta$

unoccupied



$\psi(B_{g,2})\;\; E_4 = \alpha - 1.618\beta$



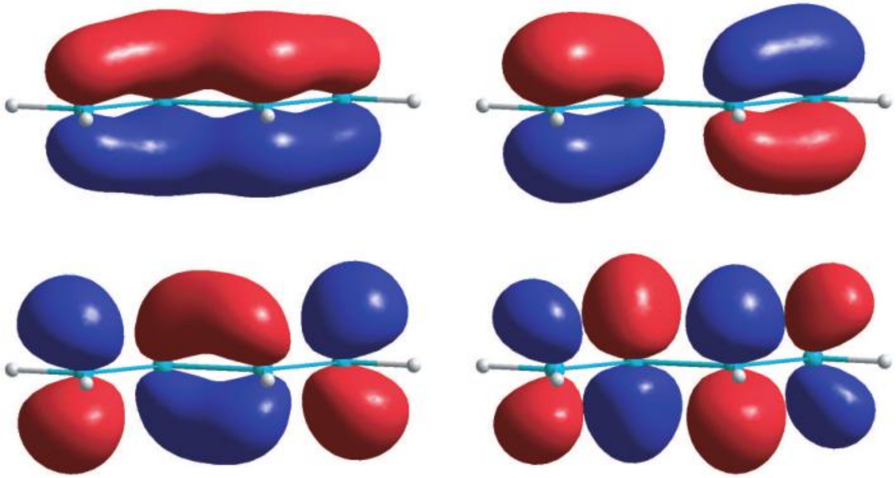
$2b_g$ $\quad E_4 = \alpha - 1.618\beta$

$2a_u$ $\quad E_3 = \alpha - 0.618\beta$

$1b_g$ $\quad E_2 = \alpha + 0.618\beta$

$1a_u$ $\quad E_1 = \alpha + 1.618\beta$

Results from Computer-based calculations



- π-electron population on *i*th atom:

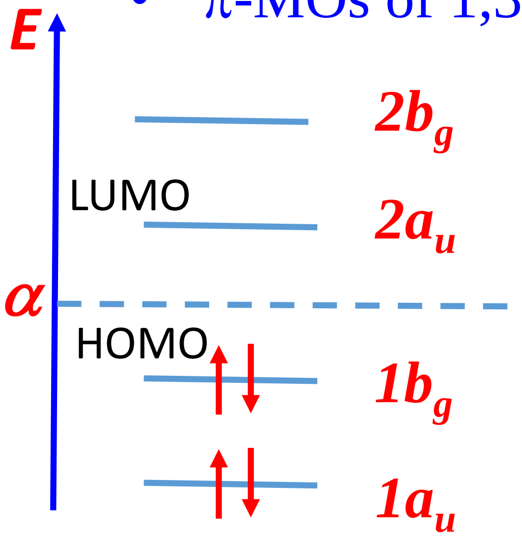
$$P_i = \sum_j n_j c_{ij}^2$$

(sum over all occupied MOs)

regioreactivity of butadiene?

6.2.1 Butadiene

- π-MOs of 1,3-butadiene



$$E_4 = \alpha - 1.618\beta$$

$$E_3 = \alpha - 0.618\beta$$

$$E_2 = \alpha + 0.618\beta$$

$$E_1 = \alpha + 1.618\beta$$

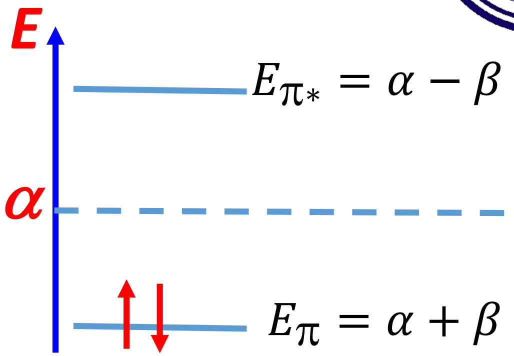
- Total π electron energy of butadiene:

$$E^{4\pi e}_{delocalized} = 2E_1 + 2E_2$$

$$= 4\alpha + 4.472\beta$$

$$\psi_\pm = \frac{p_1 \pm p_2}{\sqrt{2}} \rightarrow E_\pm = \int \psi_\pm \hat{H} \psi_\pm d\tau = \alpha \pm \beta$$

- π-MOs of a localized C-C π-bond (e.g., in CH_2=CH_2):



$$E_{\pi*} = \alpha - \beta$$

$$E_\pi = \alpha + \beta$$

$$\psi_{\pi_2^2} = c_1\phi_1 + c_2\phi_2$$

Secular eqs. (set $x=\frac{\alpha-E}{\beta}$) :

$$\begin{pmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \rightarrow \begin{pmatrix} x & 1 \\ 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

0

→ $x = \pm 1$, $E = \alpha \pm \beta$

- Total π electron energy of two localized C-C π-bonds:

$$E^{4\pi e}_{localized} = 2 \times 2E_\pi = 4(\alpha + \beta)$$

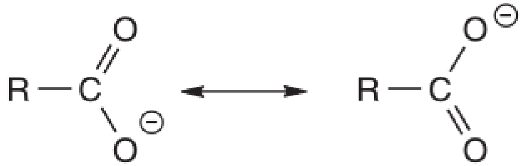
- ***Delocalization energy***: the difference between the energy of electrons in the ***delocalized π system*** (e.g., butadiene) and ***the energy of the electrons in hypothetical localized π-orbitals*** (e.g., of ethene).

Delocalization energy $= E^{4\pi e}_{delocalized} - E^{4\pi e}_{localized} = 0.472\beta < 0$

Delocalization of the electrons lowers the energy!

Q: plz derive the delocalization energy for allyl anion!

6.2.2 Carboxylate anion



carboxylate anion

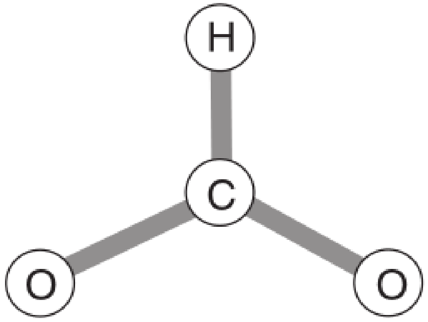
- This species has a *delocalised π system* (π_3^4) involving the two oxygen atoms and the carbonyl carbon.
- The carboxylate fragment has C_{2v} symmetry.
- **$2p_y$** AOs: C ~ ϕ_2 (**B_2**);

  O_1, O_3 ~ (ϕ_1, ϕ_3)

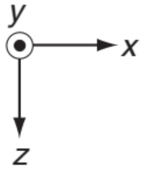
- The basis (ϕ_1, ϕ_3) transforms as $A_2 \oplus B_2$.

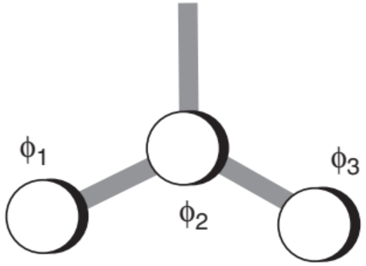
  B_2 SO (*y*-like): $\theta_a = (\phi_1 + \phi_3)/\sqrt{2}$

  A_2 SO (*xy*-like): $\theta_c = (-\phi_1 + \phi_3)/\sqrt{2}$



framework of atoms

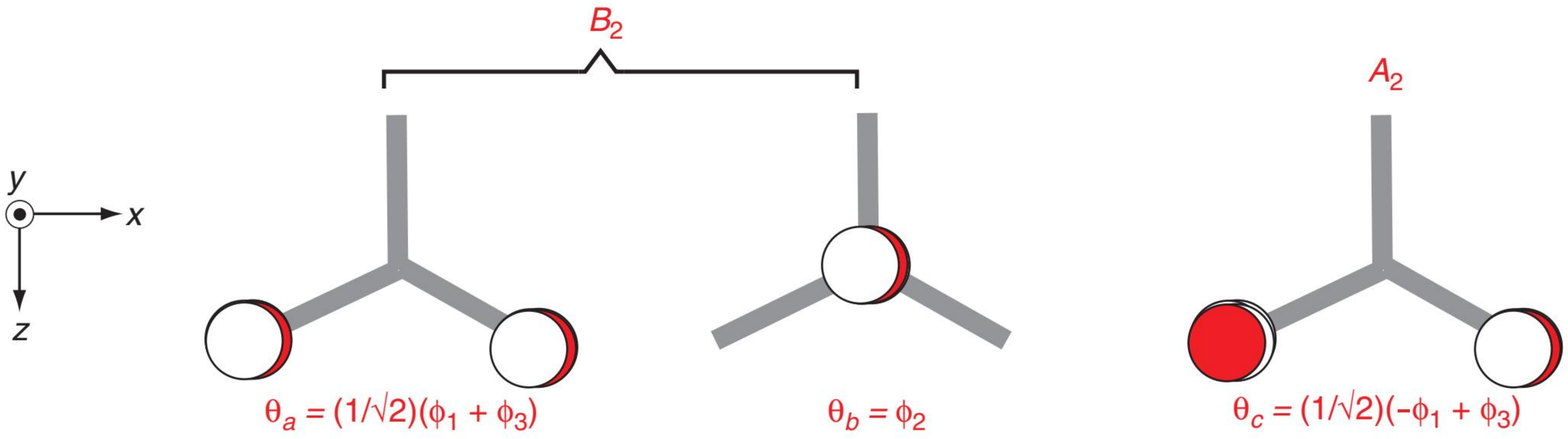




out of plane 2p orbitals

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz
Γ	**2**	**0**	**-2**	**0**	$= A_2 \oplus B_2$		

SOs of carboxylate anion



→ The A_2 SO (θ_c) itself gives a non-bonding MO, $\psi(A_2) = \theta_c = (-\phi_1 + \phi_3)/\sqrt{2}$

MOs of IR B_2: $\psi(B_2) = c_a\theta_a + c_b\theta_b$

6.2.2 Carboxylate anion

- Now consider the overlap of the two B_2 SOs and define $\theta_b = \phi_2$. Then

$$\begin{pmatrix} H_{aa}-E & H_{ab} \\ H_{ba} & H_{bb}-E \end{pmatrix}\begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

- Now compute H_{aa}, H_{bb}, H_{ab} etc.

$$H_{aa} = \int \theta_a \hat{H} \theta_a \, d\tau$$

$$= \int \tfrac{1}{\sqrt{2}}(\phi_1+\phi_3)\,\hat{H}\,\tfrac{1}{\sqrt{2}}(\phi_1+\phi_3)\, d\tau$$

$$= \tfrac{1}{2}(H_{11}+H_{13}+H_{31}+H_{33})$$

$$= (\alpha_1+\beta_{13}+\beta_{31}+\alpha_3)/2$$

$$= (\alpha_O+0+0+\alpha_O)/2$$

$$= \alpha_O$$

$$H_{ab} = \int \theta_a \hat{H} \theta_b \, d\tau$$

$$= \int \tfrac{1}{\sqrt{2}}(\phi_1+\phi_3)\,\hat{H}\phi_2\, d\tau$$

$$= \tfrac{1}{\sqrt{2}}(H_{12}+H_{32}) = \frac{1}{\sqrt{2}}(\beta_{12}+\beta_{32}) = \sqrt{2}\beta$$

$$(\beta_{12}=\beta_{32}=\beta_{OC}=\beta)$$

$$H_{bb} = \int \theta_b \hat{H} \theta_b \, d\tau$$

$$= \int \phi_2 \hat{H} \phi_2 \, d\tau = H_{22} = \alpha_C$$

$$\Rightarrow \begin{pmatrix} \alpha_O-E & \sqrt{2}\beta \\ \sqrt{2}\beta & \alpha_C-E \end{pmatrix}\begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

- Now suppose $\alpha_O = \alpha_C + \beta = \alpha + \beta$.

$$\begin{pmatrix} \alpha+\beta-E & \sqrt{2}\beta \\ \sqrt{2}\beta & \alpha-E \end{pmatrix}\begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

6.2.2 Carboxylate anion

- Define $x = (\alpha - E)/\beta$ and solve the ***secular equations***,

$$\begin{pmatrix} x+1 & \sqrt{2} \\ \sqrt{2} & x \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0 \longrightarrow \det \begin{pmatrix} x+1 & \sqrt{2} \\ \sqrt{2} & x \end{pmatrix} = 0 \longrightarrow \begin{matrix} x^2 + x - 2 = 0 \\ x_1 = -2, x_2 = 1 \end{matrix}$$

- The resulting normalized MOs of B_2 symmetry are

$$E_{B_{2,1}} = \alpha + 2\beta \quad (x = -2) \qquad \psi_{B_{2,1}} = 0.577\phi_1 + 0.577\phi_2 + 0.577\phi_3 \qquad \text{Bonding}$$

$$E_{B_{2,2}} = \alpha - \beta \quad (x = 1) \qquad \psi_{B_{2,2}} = 0.408\phi_1 - 0.816\phi_2 + 0.408\phi_3 \qquad \text{Anti-bonding}$$

- The energy of the MO of A_2 symmetry is simply given as

$$H_{cc} = \int \theta_c \hat{H} \theta_c \, d\tau$$

$$= \int \frac{1}{\sqrt{2}}(-\phi_1 + \phi_3)\hat{H}\frac{1}{\sqrt{2}}(-\phi_1 + \phi_3)\, d\tau = \frac{1}{2}(\overset{\alpha_O}{H_{11}} - \overset{0}{H_{13}} - \overset{0}{H_{31}} + \overset{\alpha_O}{H_{33}}) = \alpha_O = \alpha + \beta$$

$$\psi_{A_2,1} = -0.707\,\phi_1 + 0.707\,\phi_3 \qquad E_{A_2,1} = \alpha + \beta. \qquad \text{non-bonding}$$

6.2.2 Carboxylate anion

- The diagram below shows the energy levels and MOs with the contributions from each ***p*** orbital drawn roughly to scale.

$\psi_{1b_2} = 0.408\phi_1 - 0.816\phi_2 + 0.408\phi_3$

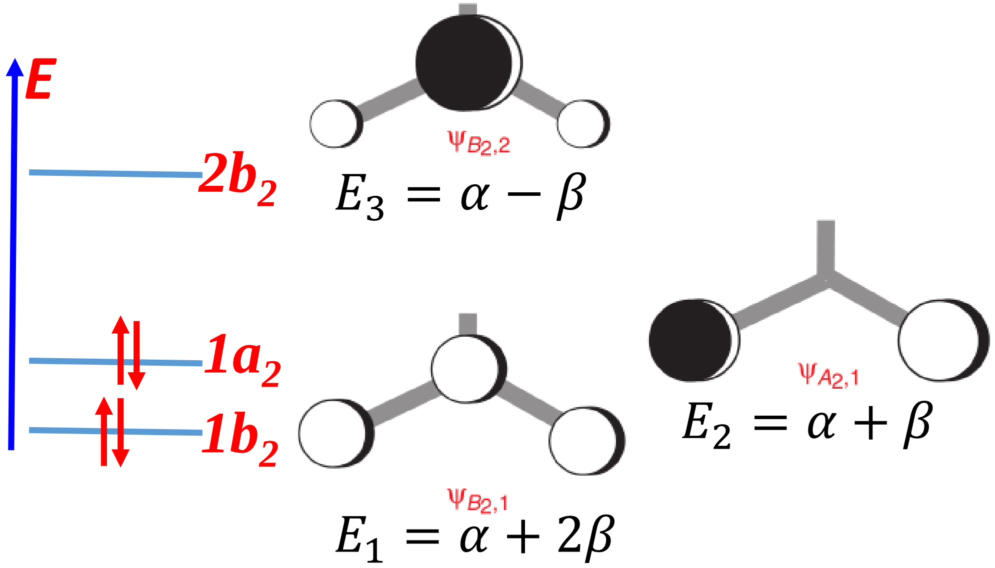
$E_3 = E_{B_2,2} = \alpha - \beta$

$\psi_{1a_2} = -0.707\phi_1 + 0.707\phi_3$ *(nonbonding)*

$E_2 = E_{A_2,1} = \alpha + \beta$

$\psi_{1b_2} = 0.577\phi_1 + 0.577\phi_2 + 0.577\phi_3$

$E_1 = E_{B_2,1} = \alpha + 2\beta$



- The total π electron energy is

$$E_\pi = 2E_1 + 2E_2$$

$$= 2(\alpha + 2\beta) + 2(\alpha + \beta)$$

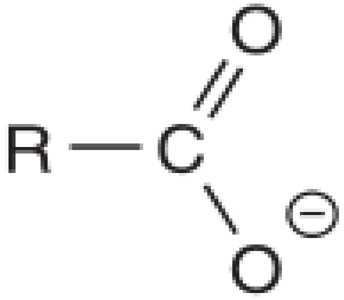
$$= 4\alpha + 6\beta$$

Ex.30-31

Delocalization energy

- Of great interest is the energy difference between the electrons in the ***delocalized π system*** and ***the energy of the electrons in hypothetical localized orbitals***.

- A localized picture of the carboxylate anion:



two π-electrons in the *C-O π bond*, and the remaining two π-electrons in a $\boldsymbol{p_y}$ orbital on the other oxygen.

- For the localized C–O π bond, the ***secular equations*** become

$$\begin{pmatrix} \alpha_O - E & \beta \\ \beta & \alpha_C - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \xrightarrow[\alpha_C = \alpha]{\alpha_O = \alpha + \beta} \begin{pmatrix} x+1 & 1 \\ 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$x = (\alpha - E)/\beta$$

$$\rightarrow E_1 = \alpha + 1.618\beta, \ \ E_2 = \alpha - 0.618\beta.$$

- The total localized electron energy is $E_{loc.} = \underset{\text{2e of a C-O }\pi\text{-MO}}{2(\alpha + 1.618\beta)} + \underset{\text{O }p_\pi\text{ lone pair}}{2(\alpha+\beta)} = 4\alpha + 5.236\beta$

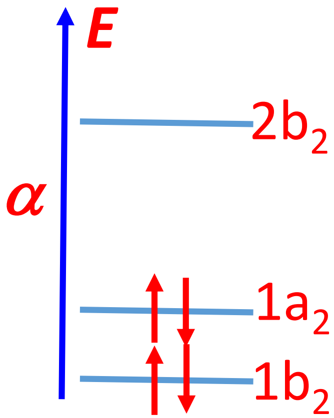
- *Delocalization energy* $= E_{deloc.} - E_{loc.} = (4\alpha + 6\beta) - (4\alpha + 5.236\beta) = 0.764\beta$

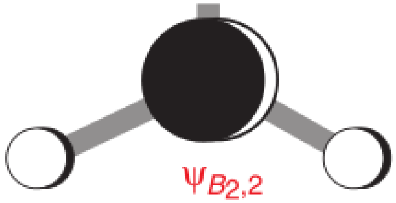
6.2.3 Relationship between the energies of the AOs and MOs

- A consequence of the *Hückel approximations* is that ***the sum of the energies of the AOs*** (i.e. the H_{ii}) must be equal to ***the sum of the energies of the MOs***.
- Example: carboxylate anion.

$$
\begin{aligned}
E(\pi\text{-AOs}) &= 2E_{(O\text{-}2p)} + E_{(c\text{-}2p)} \\
&= 2(\alpha+\beta) + \alpha \\
&= 3\alpha+2\beta
\end{aligned}
$$

$$
\begin{aligned}
E(\pi\text{-MOs}) &= E_1 + E_2 + E_3 \\
&= (\alpha+2\beta)+(\alpha+\beta)+(\alpha-\beta) \\
&= 3\alpha+2\beta
\end{aligned}
$$



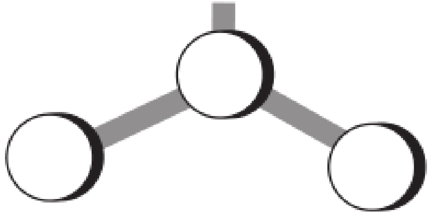


$\psi_{B2,2}$

$E_3 = \alpha - \beta$

$\psi_{A2,1}$

$E_2 = \alpha + \beta$



$\psi_{B2,1}$

$E_1 = \alpha + 2\beta$

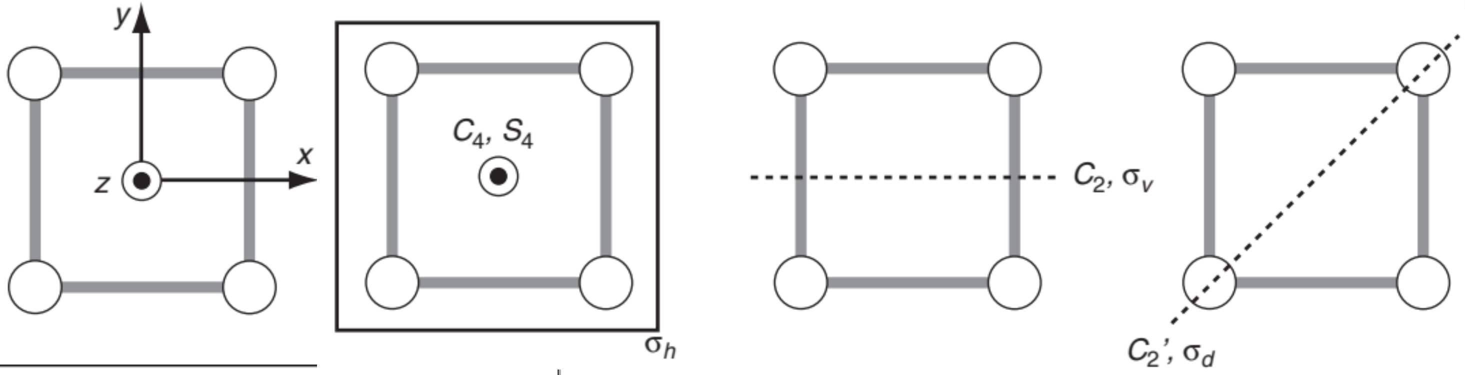
Q1: please check if this statement holds true for 1,3-butadiene?

Q2: How to make use of this relationship?

6.3 Cyclobutadiene
(π_4^4)

C_4H_4 (D_{4h})

Basis set: 4 $2p_\pi^z$(C) AOs!



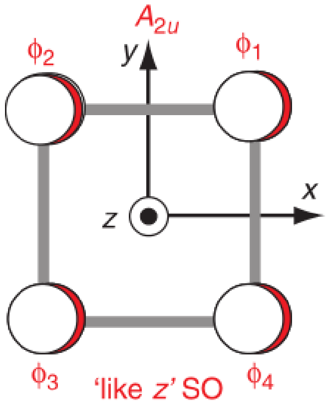
D_{4h}	E	$2C_4$	C_4^2	$2C_2$	$2C_2'$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2; z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		xyz
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	
$\chi(R)$	4	0	0	0	−2	0	0	−4	0	2	$= E_g \oplus A_{2u} \oplus B_{1u}$	

- A_{2u} SO ~ z-like
- E_g SOs ~ xz- & yz-like
- B_{1u} SO xyz-like ?

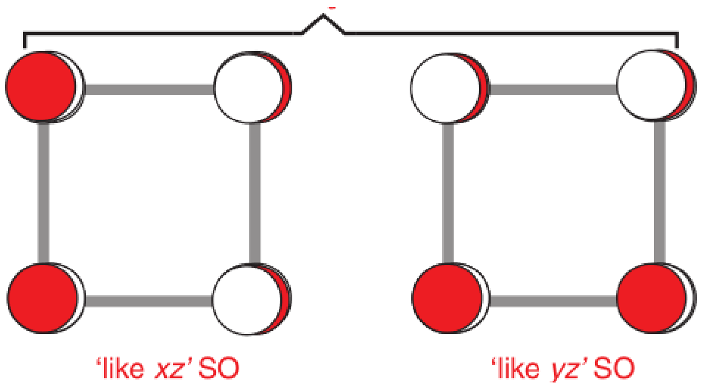
Indeed $B_{1u} = B_{2g} \otimes A_{2u}$

6.3 Cyclobutadiene

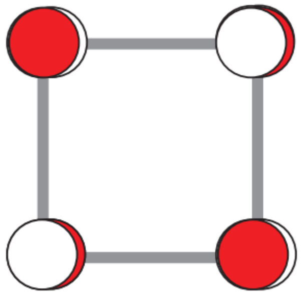
A_{2u}~*z*-like



E_g~*xz* & *yz*-like



B_{1u}~*xyz*-like



- The normalized SOs are

$$A_{2u}\ \textit{like } z \quad \theta_a = (\phi_1 + \phi_2 + \phi_3 + \phi_4)/2$$

$$E_g\ \textit{like } xz \quad \theta_b = (\phi_1 - \phi_2 - \phi_3 + \phi_4)/2$$

$$E_g\ \textit{like } yz \quad \theta_c = (\phi_1 + \phi_2 - \phi_3 - \phi_4)/2$$

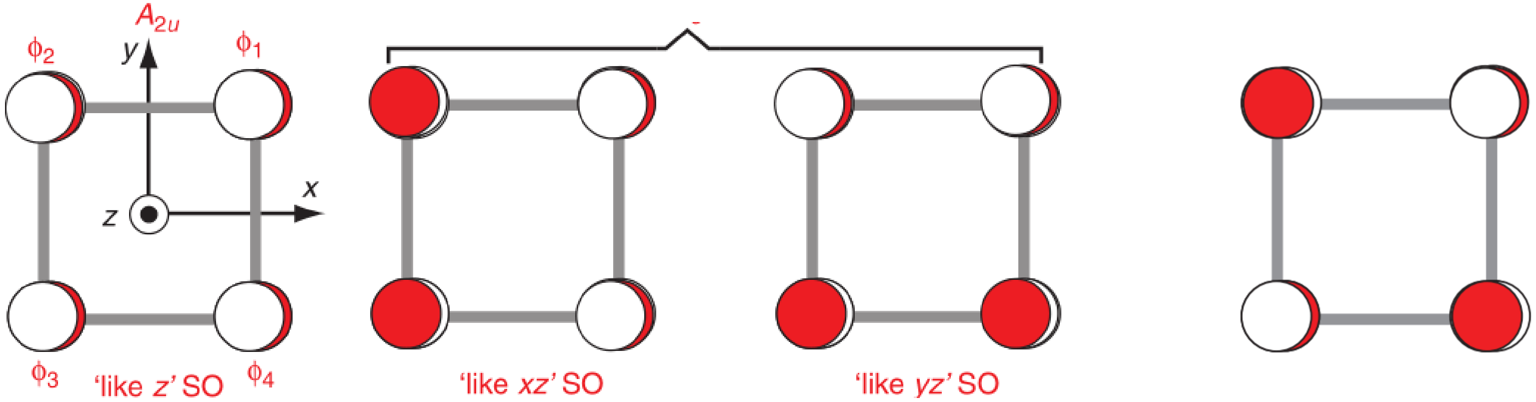
$$B_{1u}\ \textit{like } xyz \quad \theta_d = (\phi_1 - \phi_2 + \phi_3 - \phi_4)/2$$

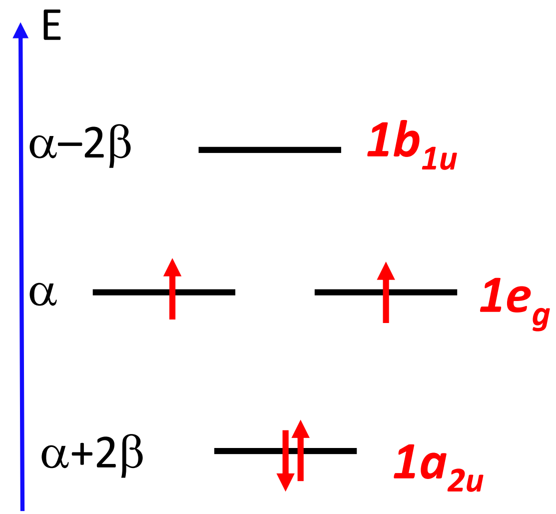
- These SOs are themselves π-MOs.

$$\begin{aligned} E_1 = H_{aa} &= \int \theta_a \hat{H} \theta_a \, \mathrm{d}\tau \\ &= \int \tfrac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)\, \hat{H}\, \tfrac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)\, \mathrm{d}\tau \\ &= \tfrac{1}{4}(H_{11} + H_{12} + H_{13} + H_{14} + H_{21} + H_{22} + H_{23} + H_{24} \\ &\qquad + H_{31} + H_{32} + H_{33} + H_{34} + H_{41} + H_{42} + H_{43} + H_{44}) \\ &= \tfrac{1}{4}(\alpha + \beta + 0 + \beta + \beta + \alpha + \beta + 0 \\ &\quad + 0 + \beta + \alpha + \beta + \beta + 0 + \beta + \alpha) = \alpha + 2\beta \end{aligned}$$

6.3 Cyclobutadiene

A_{2u}~z-like $\quad$ E_g~xz & yz-like $\quad$ B_{1u}~xyz-like





Diradical! Anti-aromatic!

- The normalized SOs are

$$\boldsymbol{A_{2u}} \quad \theta_a = (\phi_1 + \phi_2 + \phi_3 + \phi_4)/2 \qquad E_1 = H_{aa} = \alpha + 2\beta$$

$$\boldsymbol{E_g}\ \textit{like}\ \boldsymbol{xz} \quad \theta_b = (\phi_1 - \phi_2 - \phi_3 + \phi_4)/2 \qquad E_2 = H_{bb} = \int \theta_b \hat{H} \theta_b d\tau = \alpha$$

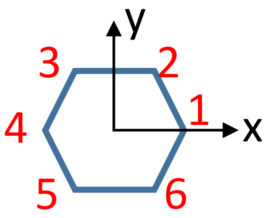
$$\boldsymbol{E_g}\ \textit{like}\ \boldsymbol{yz} \quad \theta_c = (\phi_1 + \phi_2 - \phi_3 - \phi_4)/2 \qquad E_3 = H_{cc} = \int \theta_c \hat{H} \theta_c d\tau = \alpha$$

Indeed degenerate!

$$\boldsymbol{B_{1u}} \quad \theta_d = (\phi_1 - \phi_2 + \phi_3 - \phi_4)/2 \qquad E_4 = H_{dd} = \int \theta_d \hat{H} \theta_d d\tau = \alpha - 2\beta$$

- The total π energy is ***4α+4β***. (Is it stable than two localized C=C π-bonds?)

6.4 benzene (C_6H_6) -- π_6^6 π-MOs (by p_z AOs)

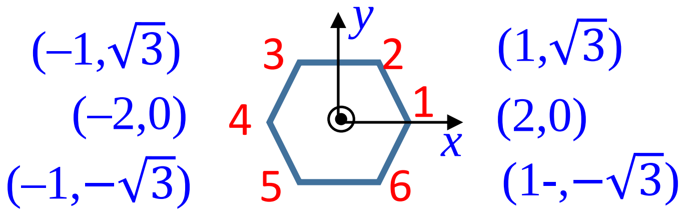


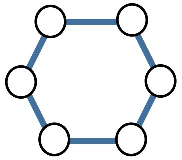
$\mathcal{D}_{6h}$	E	$2C_6$	$2C_6^2$	C_6^3	$3C_2$	$3C_2'$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	linear	quadratic	cubic
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		$x^2+y^2;z^2$	
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	R_z		
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	$\boxed{-1}$	1	−1			
B_{2g}	1	−1	1	−1	$\boxed{-1}$	1	1	−1	1	$\boxed{-1}$	−1	$\boxed{1}$	$B_{2g}=B_{1u}\otimes A_{2u}$		$x(x^2-3y^2)z$
E_{1g}	2	1	−1	−2	0	0	2	1	−1	$\boxed{-2}$	0	0	(R_x,R_y)	(xz,yz)	
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0		$(x^2-y^2,2xy)$	
A_{1u}	1	1	1	1	1	1	−1	−1	−1	$\boxed{-1}$	−1	−1			
A_{2u}	1	1	1	1	$\boxed{-1}$	−1	−1	−1	−1	$\boxed{-1}$	1	$\boxed{1}$	z		
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1			$x(x^2-3y^2)$
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1			$y(3x^2-y^2)$
E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	(x,y)		
E_{2u}	2	−1	−1	2	0	0	−2	1	1	$\boxed{-2}$	0	0	$E_{2u}=E_{2g}\otimes A_{2u}$		$[(x^2-y^2)z, 2xyz]$
$\Gamma(6\ p_z)$	6	0	0	0	-2	0	0	0	0	-6	0	2	$A_{2u}\oplus B_{2g}\oplus E_{1g}\oplus E_{2u}$		

Please complete the character tables (given in the databook) with additional cubic functions!

C_6H_6 -- π_6^6 $A_{2u} \oplus B_{2g} \oplus E_{1g} \oplus E_{2u}$

(Note that p_z ifself is z-like!)



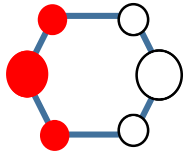


A_{2u}, z-like,

$$\theta_{A_{2u}} = (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)/\sqrt{6}$$

(节面数 =0)

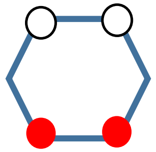
$$E(a_{2u}) = \int \theta_{A_{2u}} \hat{H} \theta_{A_{2u}} d\tau = \alpha + 2\beta$$



E_{1g}, xz-like,

$$\theta_{E_{1g},xz} = (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)/\sqrt{12}$$

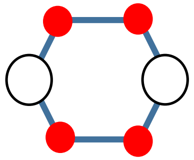
(节面数 =1)



E_{1g}, yz-like,

$$\theta_{E_{1g},yz} = (\phi_2 + \phi_3 - \phi_5 - \phi_6)/2$$

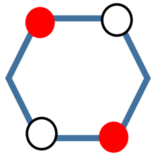
$$E(e_{1g}) = \int \theta_{E_{1g}} \hat{H} \theta_{E_{1g}} d\tau = \alpha + \beta$$



E_{2u}, $(x^2$-$y^2)z$-like,

$$\theta_{E_{2u},(x^2-y^2)z} = (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)/\sqrt{12}$$

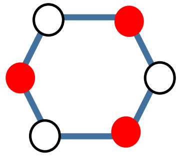
(节面数 =2)



E_{2u}, xyz-like,

$$\theta_{E_{2u},xyz} = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/2$$

$$E(e_{2u}) = \int \theta_{E_{2u}} \hat{H} \theta_{E_{2u}} d\tau = \alpha - \beta$$



B_{2g}, $x(x^2$-$3y^2)z$-like,

$$\theta_{B_{2g}} = (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)/\sqrt{6}$$

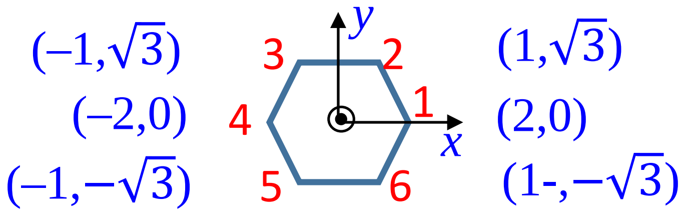
(节面数 =3)

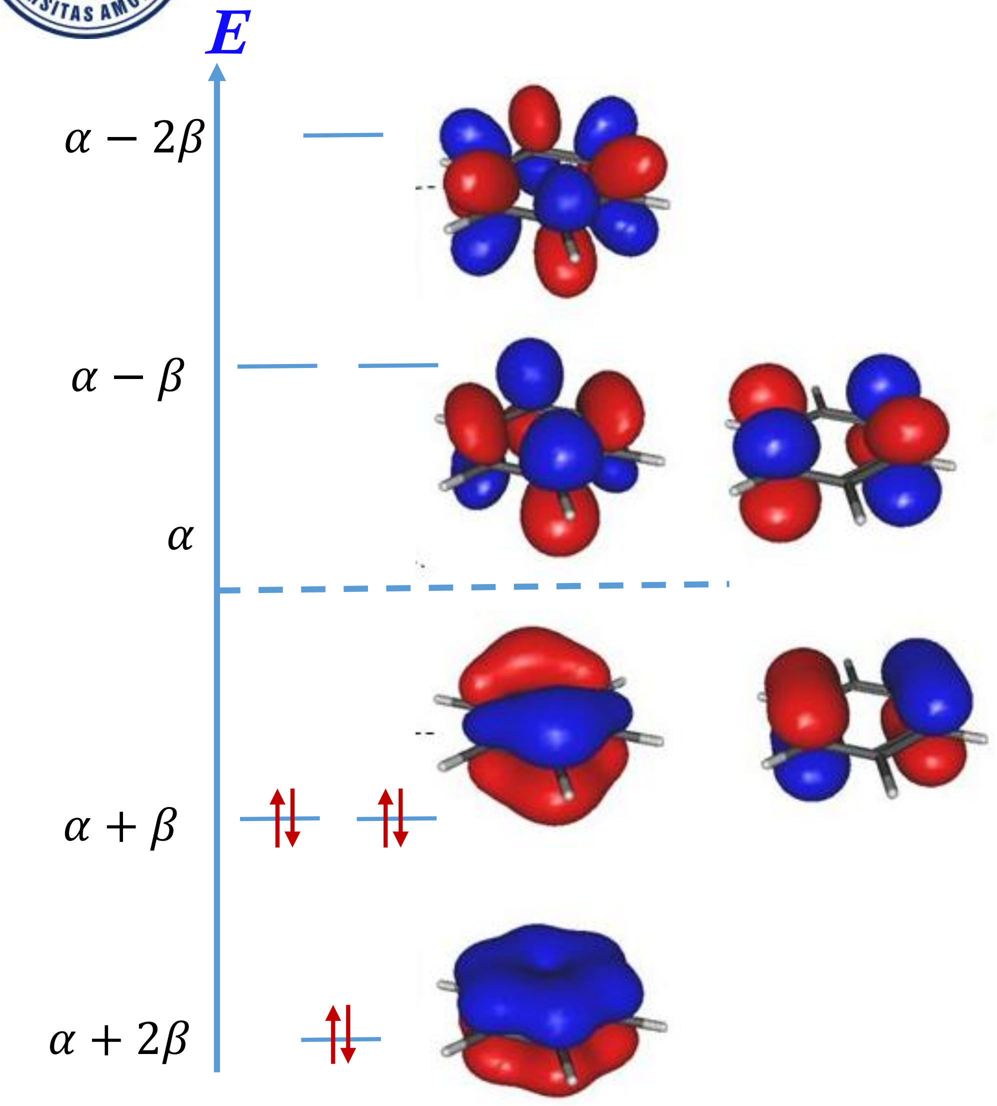
$$E(b_{2g}) = \int \theta_{B_{2g}} \hat{H} \theta_{B_{2g}} d\tau = \alpha - 2\beta$$

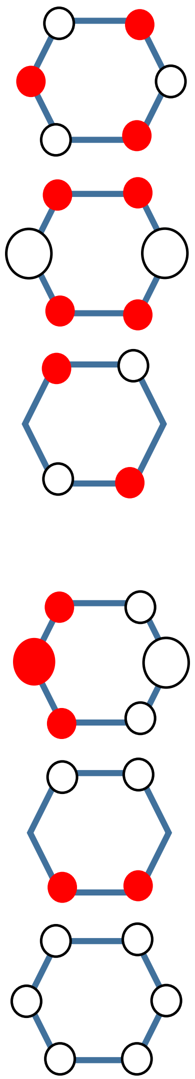
MO节面数增加, 能量上升!

C_6H_6 -- π_6^6

$A_{2u} \oplus B_{2g} \oplus E_{1g} \oplus E_{2u}$







$$\psi_{b_{2g}} = (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)/\sqrt{6}$$

$$\psi_{e_{2u},1} = (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)/\sqrt{12}$$

$$\psi_{e_{2u},2} = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/2$$

$$\psi_{e_{1g},1} = (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)/\sqrt{12}$$

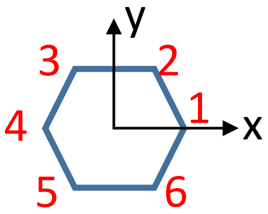
$$\psi_{e_{1g},2} = (\phi_2 + \phi_3 - \phi_5 - \phi_6)/2$$

$$\psi_{a_{2u}} = (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)/\sqrt{6}$$

Delocalization energy = $E_{delocalized}^{6\pi e} - E_{localized}^{6\pi e}$ = $[2(\alpha+2\beta)+4(\alpha+\beta)] - [3\times2(\alpha+\beta)] = 2\beta$

6.4 benzene -- π_6^6 π-MOs (by p_z AOs)

using the projection operator



- Reduce the symmetry of the molecule from D_{6h} to purely rotational symmetry C_6. $(\omega = \exp(2\pi i/6))$

$\mathcal{G}_6$	$\mathcal{C}_6$	E	C_6	C_3	C_2	C_3^2	C_6^5
R_0	A	1	1	1	1	1	1
R_3	B	1	-1	1	-1	1	-1
R_1	E_1^a	1	ω	ω^2	ω^3	ω^4	ω^5
R_5	E_1^b	1	ω^5	ω^4	ω^3	ω^2	ω
R_2	E_2^a	1	ω^2	ω^4	1	ω^2	ω^4
R_4	E_2^b	1	ω^4	ω^2	1	ω^4	ω^2
	ϕ_1	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6

$$\hat{P}^{(k)}\phi_1 = \frac{1}{h}\left\{\sum_R [\chi^{(k)}(R)]^* \hat{R}\right\}\phi_1$$

$$\Psi_a = \theta_A = (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)/\sqrt{6}$$

$$\Psi_b = \theta_B = (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)/\sqrt{6}$$

- For cyclic group, the six equivalent AOs span as

$$\Gamma = A \oplus B \oplus E_1 \oplus E_2$$

$$\left.\begin{aligned}\theta(E_1{}^a) &= (\phi_1 + \omega^5\phi_2 + \omega^4\phi_3 + \omega^3\phi_4 + \omega^2\phi_5 + \omega\phi_6)/6\\ \theta(E_1{}^b) &= (\phi_1 + \omega\phi_2 + \omega^2\phi_3 + \omega^3\phi_4 + \omega^4\phi_5 + \omega^5\phi_6)/6\end{aligned}\right\}$$

$$\Psi(e_1{}^a) = N[\theta(E_1{}^a) + \theta(E_1{}^b)] = (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)/\sqrt{12}$$

$$\Psi(e_1{}^b) = N[\theta(E_1{}^a) - \theta(E_1{}^b)] = (\phi_2 + \phi_3 - \phi_5 - \phi_6)/2$$

$$\left.\begin{aligned}\theta(E_2{}^a) &= (\phi_1 + \omega^4\phi_2 + \omega^2\phi_3 + \phi_4 + \omega^4\phi_5 + \omega^2\phi_6)/6\\ \theta(E_2{}^b) &= (\phi_1 + \omega^2\phi_2 + \omega^4\phi_3 + \phi_4 + \omega^2\phi_5 + \omega^4\phi_6)/6\end{aligned}\right\}$$

$$\Psi(e_2{}^a) = N[\theta(E_2{}^a) + \theta(E_2{}^b)] = (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)/\sqrt{12}$$

$$\Psi(e_2{}^b) = N[\theta(E_2{}^a) - \theta(E_2{}^b)] = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/2$$

思考题

1. 运用休克尔分子轨道理论推导线式[n]共轭烯烃π分子轨道的正弦波规律：

k 为分子轨道能级 (k =1,2,3,…n)

第k个能级的能量为：$E_k = \alpha + 2\beta\cos(k\theta)$　　其中 $\theta = \pi/(n+1)$

第k个能级的π分子轨道为：$\psi_k^{\pi} = \sum_{m=1}^{n} \phi_m \sin(mk\theta)$

2. 运用休克尔分子轨道理论推导环[n]共轭体系π分子轨道的能量和组成为：

$\theta = 2\pi/n$　　k与能级有关，k =0, 1,2, …, (n-1)/2 (for n=odd) or n/2 (n=even)

$$E_k = \alpha + 2\beta\cos(k\theta) \qquad \psi_k^{cos} = \sum_{m=1}^{n} \phi_m \cos[(m-1)k\theta] \qquad \psi_k^{sin} = \sum_{m=1}^{n} \phi_m \sin[(m-1)k\theta]$$

(when $k\theta = 0$ or π, no ψ_k^{sin})

6.4 Summary

- The energies of MOs and the particular combinations of AOs from which they are formed can be found by *solving the secular equations*.

- The solution to these equations is simplified by adopting *the Hückel approximations*:

  (1) the overlap between orbitals is neglected, i.e. $S_{ij} = 0$;

  (2) AOs are assumed to be normalized i.e. $S_{ii} = 1$;

  (3) only adjacent orbitals have an interaction i.e. $H_{ij} = 0$ if i and j are not adjacent.

- In the secular equations H_{ii} is written α_i; this is approximately the energy of orbital i, and is *negative*.

- In the secular equations H_{ij} is written β_{ij}; this is the energy of interaction of adjacent orbitals i and j; it is *negative*.

6.5 Summary

- The ***secular equations*** are of the form:

$$\begin{pmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} & \dots & \beta_{1N} \\ \beta_{21} & \alpha_2 - E & \beta_{23} & \dots & \beta_{2N} \\ \beta_{31} & \beta_{32} & \alpha_3 - E & \dots & \beta_{3N} \\ \dots & \dots & \dots & \dots & \dots \\ \beta_{N1} & \beta_{N2} & \beta_{N3} & \dots & \alpha_N - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \dots \\ c_N \end{pmatrix} = 0$$

Hückel approximations

$$\boldsymbol{S_{ij} = \int \phi_i \phi_j d\tau = \delta_{ij} = 1\ (i = j)}$$
$$\boldsymbol{= 0\ (i \neq j)}$$

$$\boldsymbol{H_{ii} = \int \phi_i \hat{H} \phi_i d\tau = \alpha_i}$$

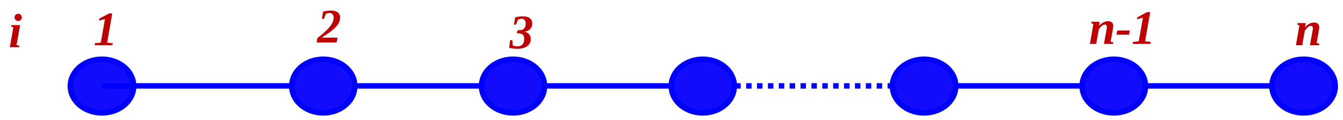
$$\boldsymbol{H_{ij} = \int \phi_i \hat{H} \phi_j d\tau = \beta_{ij}}$$

= 0 *(i-j non-bonding)*

- ***The solution to the secular equations can be simplified by first constructing symmetry orbitals (SOs); only SOs of the same symmetry overlap, thereby reducing the dimensionality of the secular matrix. (That is why we use symmetry and group theory!!!!!!!!!!)***
- However, the forms and energies of HMOs solely depend on the atomic connectivity!
- The delocalization energy of a π system is the difference between the energy of electrons in delocalized orbitals and the energy of the electrons in localized orbitals.

6.5 More considerations –graphical method for for linear [n]polyenes

Graphical method to predefine the coefficients of HMOs for conjugated systems (developed by ***Qianer Zhang*** et al.)



$$\psi^{\pi} = \sum_{i=1}^{n} c_i \phi_i$$

- For a linear [***n***]polyene, we have ***n*** secular equations ($x = (\alpha\text{-}E)/\beta$) :

$$\begin{pmatrix} x & 1 & \dots & 0 & 0 \\ 1 & x & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & x & 1 \\ 0 & 0 & \dots & 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \dots \\ c_{n-1} \\ c_n \end{pmatrix} = 0 \Rightarrow \left\{ \begin{array}{l} xc_1 + c_2 = 0 \\ c_1 + xc_2 + c_3 = 0 \\ \dots\dots \\ c_{i-1} + xc_i + c_{i+1} = 0 \\ \text{(cyclic formula)} \\ \dots\dots \\ c_{n-2} + xc_{n-1} + c_n = 0 \\ c_{n-1} + xc_n = 0 \end{array} \right.$$

$$c_{i+1} + c_{i-1} = -xc_i$$

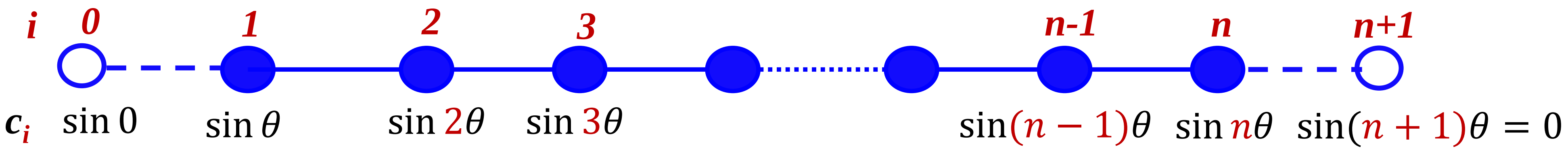
$$\sin A + \sin B = 2\sin\frac{A+B}{2}\cos\frac{A-B}{2}$$

$$\text{if } A = (i+1)\theta, \quad B = (i-1)\theta$$

$$\text{then } x = -2\cos\theta$$

$$\& \quad c_i = \sin i\theta$$

6.6 General process for [n]polyenes



$$\psi^{\pi} = \sum_{i=1}^{n} c_i\phi_i$$

For a linear **[n]**polyene, we have ***n*** secular equations (***x = (α-E)/β***) :

$xc_1 + c_2 = 0;$

$c_1 + xc_2 + c_3 = 0;$ ……

$c_{i-1} + xc_i + c_{i+1} = 0;$

(cyclic formula)

……; $c_{n-1} + xc_n = 0$

$$\xrightarrow[c_1 = \sin\theta]{\text{set} \quad x = -2\cos\theta} \begin{cases} c_2 = -xc_1 = \sin 2\theta \\ c_3 = \sin 3\theta \\ \cdots \\ c_i = \sin i\theta \\ \cdots \\ c_n = \sin n\theta \end{cases}$$

Boundary condition:

$c_{n+1} = \sin(n+1)\theta = 0$

$\theta_k = k\pi/(n+1) \quad (k=1,\ldots,n)$

$E_k = \alpha + 2\beta\cos\theta_k$

$$\psi_k^{\pi} = \sum_{i=1}^{n} \phi_i \sin(i\theta_k)$$

(***k*** defines the energy level!)

Now recall the sine wave rule we learnt in the 1st semester!

cyclic [n]polyenes

$\theta = 2\pi/n$

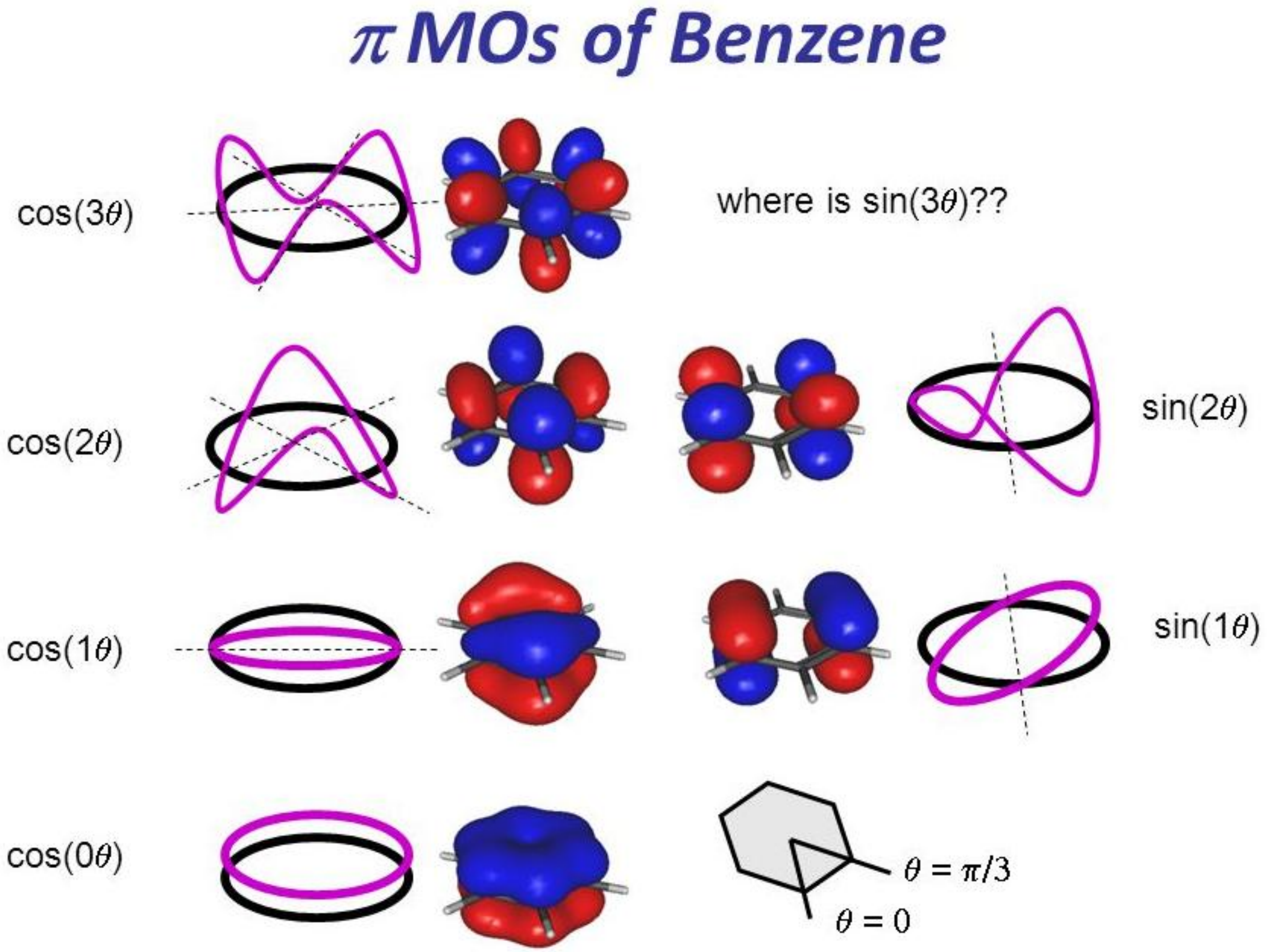
k= 0, 1, …, (n-1)/2 (for n =odd) or n/2 (for n= even)

$$E_k = \alpha + 2\beta\cos(k\theta)$$

$$\psi_k^{cos} = \sum_{m=1}^{n} \phi_m \cos[(m-1)k\theta]$$

$$\psi_k^{sin} = \sum_{m=1}^{n} \phi_m \sin[(m-1)k\theta]$$

(*when* $k\theta = 0$ or π, no ψ_k^{sin})



π MOs of Benzene

- The method can be used for dealing with more complicated systems.
- Recent work developed by Prof. Zhenhua Chen can be found as “*Graphical representation of Hückel Molecular Orbitals*” in *J. Chem. Educ.* 2020, 97(2), 448-456.

(https://pubs.acs.org/doi/10.1021/acs.jchemed.9b00687)

- FYI： “Introduction to Computational Chemistry: Teaching Hückel Molecular Orbital Theory Using an Excel Workbook for Matrix Diagonalization”

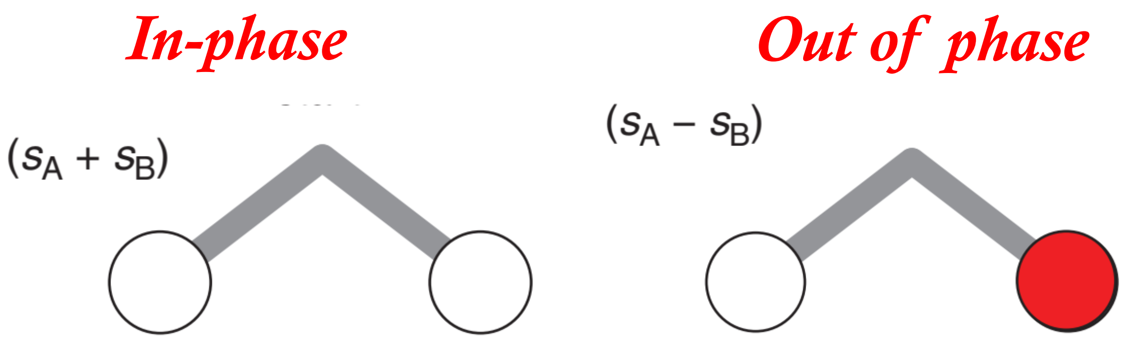
in *J. Chem. Educ.* 2015, 92(2), 291-295.
(https://pubs.acs.org/doi/full/10.1021/ed500376q)

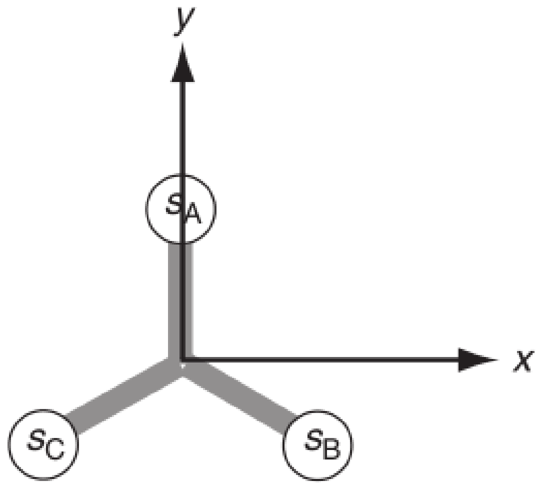
Work out SOs quickly by using trend & sinspection!

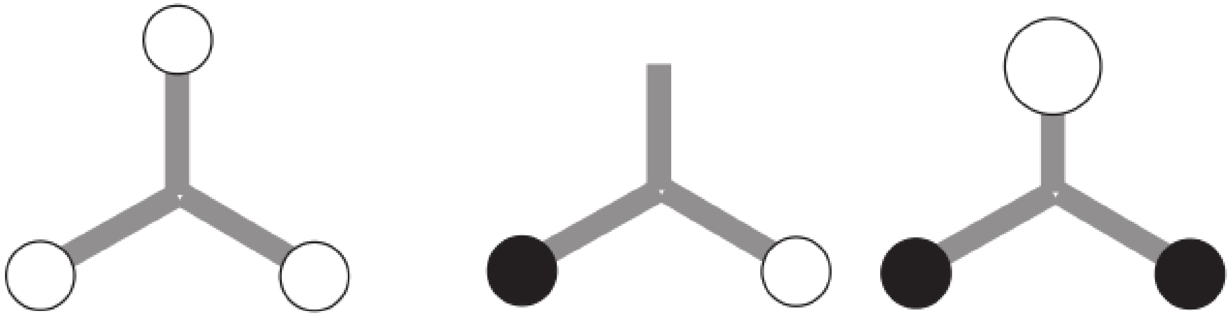
Trend in SOs arising from

i) 2 equivalent AOs ($C_2/\sigma/i$)

ii) 3 equivalent AOs (C_3)





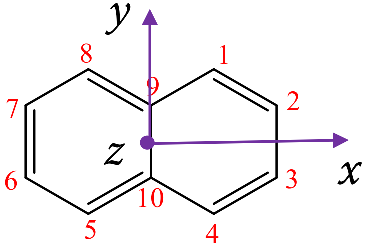


$\theta_{A_1'} = s_A + s_B + s_C$ $\theta_{E,x} = s_B - s_C$ $\theta_{E,y} = s_A - 1/2 s_B - 1/2 s_C$

- The aforementioned trend of SOs consisting of 2,3,4-equivalent-basis-functions can be used to quickly work out the SOs as well as the corresponding ***IR***s by inspection.

Work out SOs quickly by using trends and inspection!

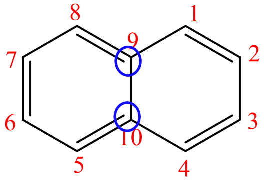
- Example: Naphthalene (D$_{2h}$)



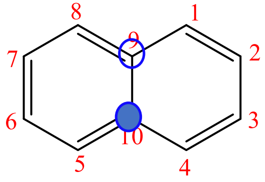
π_{10}^{10} formed by 10 p$_z$ AOs:

(1,4,5,8)(2,3,6,7)(9,10)

(9,10):



z-like, ***B$_{1u}$***



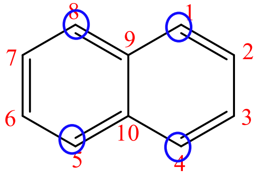
yz-like, ***B$_{3g}$***

$\theta_a=(\phi_9+\phi_{10})/\sqrt{2}$ $\theta_b=(\phi_9-\phi_{10})/\sqrt{2}$

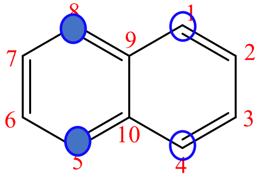
D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2; y^2; z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		xyz
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

$B_{1g}\otimes B_{1u}=A_u$

(1,4,5,8):

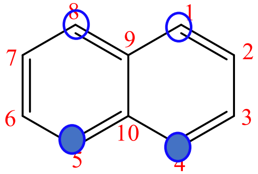


z-like, ***B$_{1u}$***

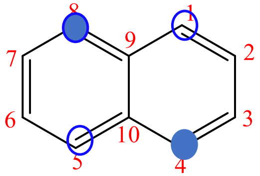


xz-like, ***B$_{2g}$***

$\theta_c=(\phi_1+\phi_4+\phi_5+\phi_8)/2$ $\theta_d=(\phi_1+\phi_4-\phi_5-\phi_8)/2$



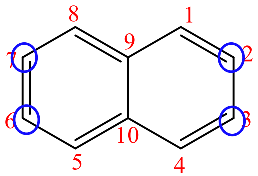
yz-like, ***B$_{3g}$***



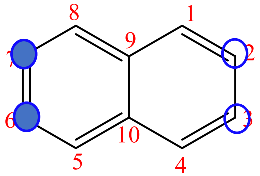
xyz-like, ***A$_u$***

$\theta_e=(\phi_1-\phi_4-\phi_5+\phi_8)/2$ $\theta_f=(\phi_1-\phi_4+\phi_5-\phi_8)/2$

(2,3,6,7):

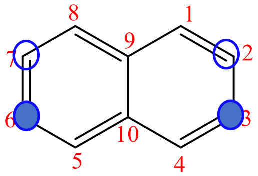


z-like, ***B$_{1u}$***

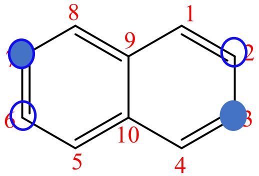


xz-like, ***B$_{2g}$***

$\theta_g=(\phi_2+\phi_3+\phi_6+\phi_7)/2$ $\theta_h=(\phi_2+\phi_3-\phi_6-\phi_7)/2$



yz-like, ***B$_{3g}$***



xyz-like, ***A$_u$***

$\theta_i=(\phi_2-\phi_3-\phi_6+\phi_7)/2$ $\theta_j=(\phi_2-\phi_3+\phi_6-\phi_7)/2$

- MOs of B_{1u} symmetry: $\psi(B_{1u}) = c_a\theta_a + c_c\theta_c + c_g\theta_g$

$$\begin{pmatrix} H_{aa}-E & H_{ac} & H_{ag} \\ H_{ca} & H_{cc}-E & H_{cg} \\ H_{ga} & H_{gc} & H_{gg}-E \end{pmatrix}\begin{pmatrix} c_a \\ c_c \\ c_g \end{pmatrix}=0$$

$H_{aa}=(H_{99} + H_{1010}+H_{910} +H_{109})/2= \alpha+\beta$

$H_{cc}=(H_{11} + H_{44}+H_{55} +H_{88})/4 = \alpha$

$H_{gg}= \alpha +\beta$

$H_{ac}=(H_{91} + H_{98}+H_{104} +H_{105})/2\sqrt{2}= \sqrt{2}\,\beta$ $H_{ag}= 0$ $H_{cg}= \beta$

$$\begin{pmatrix} x+1 & \sqrt{2} & 0 \\ \sqrt{2} & x & 1 \\ 0 & 1 & x+1 \end{pmatrix}\begin{pmatrix} c_a \\ c_c \\ c_g \end{pmatrix}=0 \qquad \det\begin{pmatrix} x+1 & \sqrt{2} & 0 \\ \sqrt{2} & x & 1 \\ 0 & 1 & x+1 \end{pmatrix}=0$$

………