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 $\boldsymbol{\psi}$ is expressed as a linear combination of atomic orbitals, $\boldsymbol{\Phi_1, \Phi_2, . . .,}$

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

$\boldsymbol{\Phi_i}$ ~ *i*th AO (also known as one of the ***basis functions***) used to construct the MO.

$\boldsymbol{c_i}$ ~ the coefficient which indicates the relative contribution of an AO $\boldsymbol{\Phi_i}$ 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 :

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

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.

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

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

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

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

(i = 1,2,…,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):

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

N^2 $\boldsymbol{H_{ij}}$-type integrals and N^2 $\boldsymbol{S_{ij}}$-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.

- The coefficients c_i corresponding to ***a*** particular MO can be found by ***substituting the corresponding value*** of the energy ***E*** back into the ***secular equations***.

6.1.2 The Hückel approximations

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

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 setting *the determinant of the secular matrix*, namely *the secular determinant*, to be *zero*.

6.1.2 The Hückel approximations

- 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,

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

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

$$\left.\begin{matrix} \alpha_i \\ \beta_{ij} \end{matrix}\right\} \text{Negative values}$$

β_{ij} is non-zero unless the two orbitals are on adjacent atoms!

- Accordingly, the secular equations become

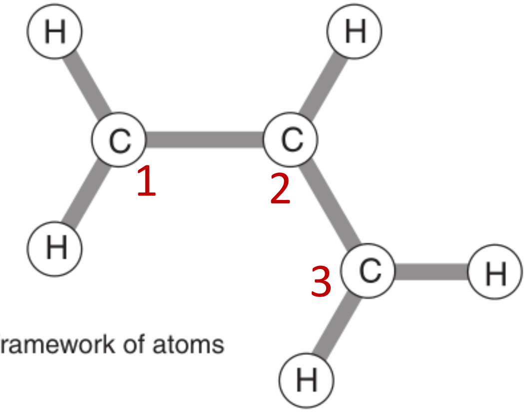
$$\begin{pmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} & \dots & \beta_{1N} \\ \beta_{21} & \alpha_2 - E & \beta_{23} & \dots & \beta_{2N} \\ \beta_{31} & \beta_{32} & \alpha_3 - E & \dots & \beta_{3N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \beta_{N1} & \beta_{N2} & \beta_{N3} & \dots & \alpha_N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

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

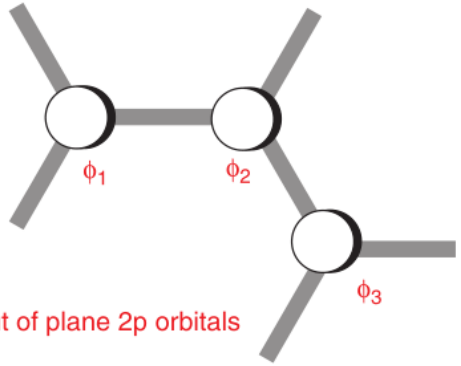
- Some of the β_{ij} terms can be zero case by case!
- The values of α_i, β_{ij} can be determined semi-empirically!
- Quite easy for dealing with π-conjugation systems!
- Q1: how to determine α_c & β_{cc}?

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?!

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

the ***secular eq***s. thus become

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

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

6.1.3 The allyl system

- Now ***divide both sides by β*** and then ***set*** $\boldsymbol{\frac{\alpha-E}{\beta}=x}$, we have: $\begin{pmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}=0$

- As usual, set the 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 $E_1=\alpha+\sqrt{2}\beta$

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

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

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

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

Three eqs. are
not independent!

6.1.3 The allyl system

- The normalization relationship can be introduced to make the eqs. 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:

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

$\rightarrow c_2 = \sqrt{2}/2$, $c_3 = 1/2$; $\rightarrow \psi_1 = (\Phi_1 + \sqrt{2}\Phi_2 + \Phi_3)/2$ 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: $c_1 = 1 \qquad c_2 = \sqrt{2} \qquad c_3 = 1$
- Now normalize the coefficients: $\sqrt{c_1^2 + c_2^2 + c_3^2} = \sqrt{1+2+1} = 2$
- The normalized coefficients are: $c_1 = 1/2 \qquad c_2 = \sqrt{2}/2 \qquad c_3 = 1/2$

Which method do you recommend?

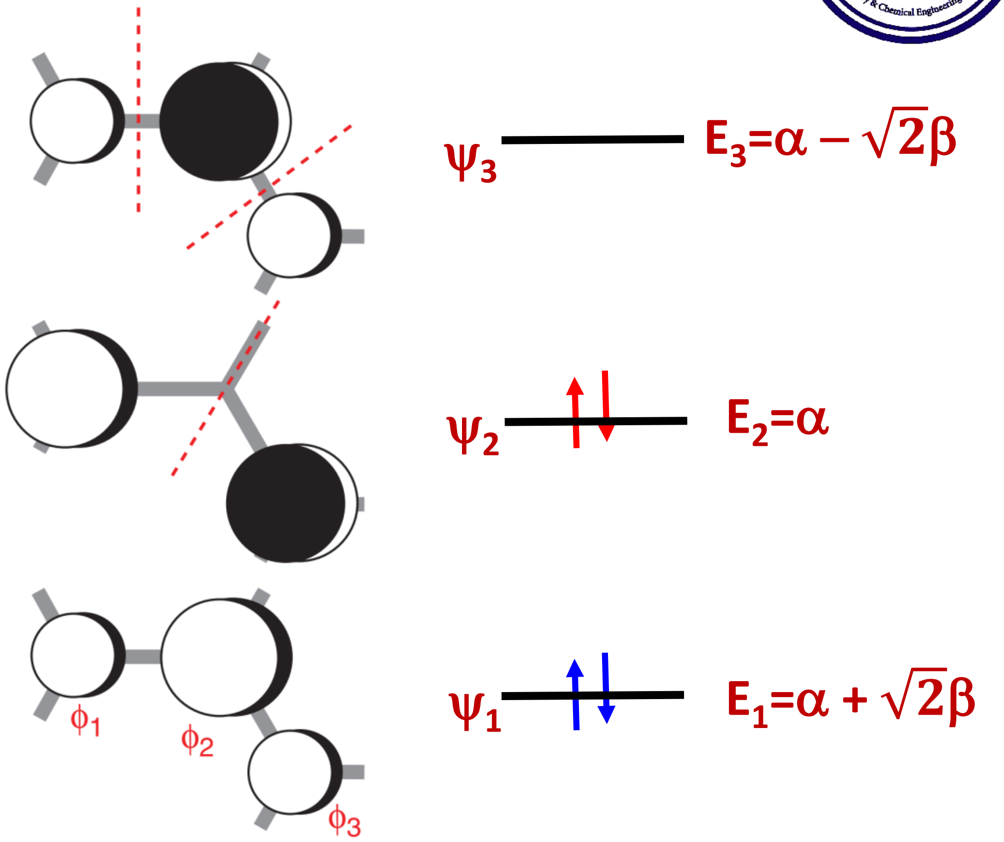
6.1.3 The allyl system

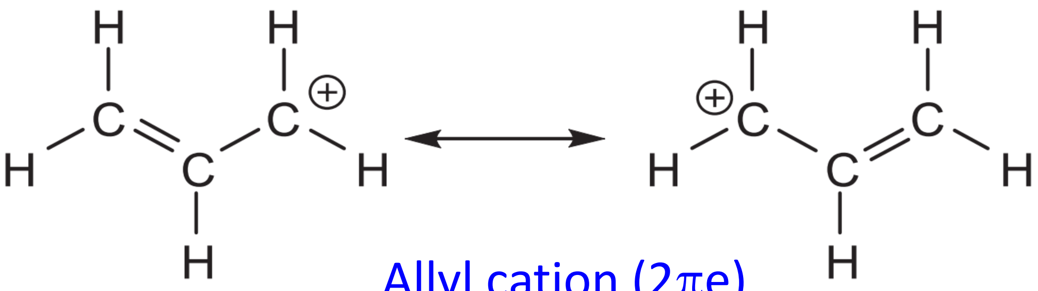
- The final results are summarized in the table.

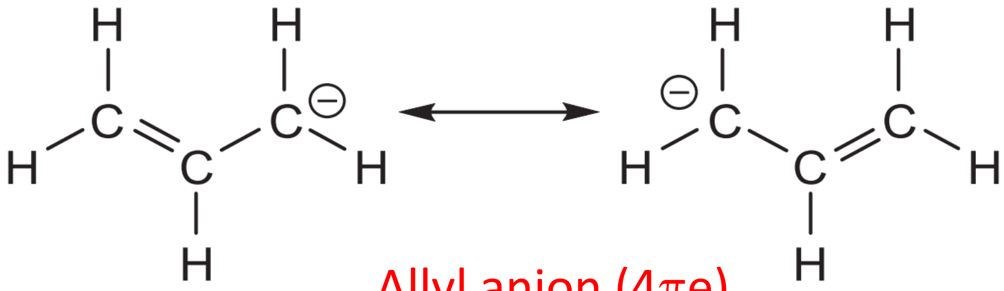
MO number	energy	MO wavefunction
1	$E_1 = \alpha + \sqrt{2}\beta$	$\psi_1 = \frac{1}{2}\phi_1 + \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3$
2	$E_2 = \alpha$	$\psi_2 = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3$
3	$E_3 = \alpha - \sqrt{2}\beta$	$\psi_3 = \frac{1}{2}\phi_1 - \frac{1}{\sqrt{2}}\phi_2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

Ex.27

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

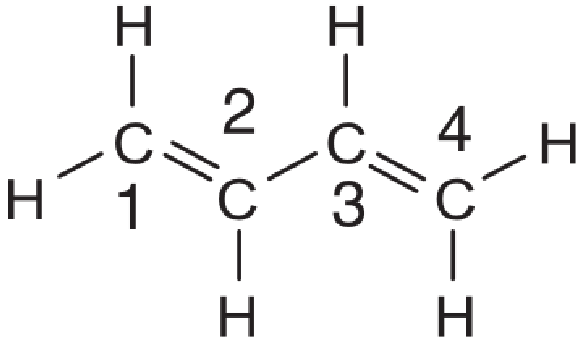



Allyl cation (2πe)


Allyl anion (4πe)

6.1.4 1,3-Butadiene

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



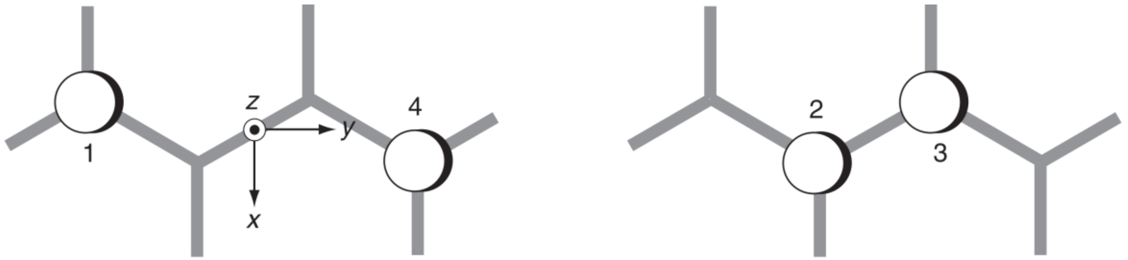
- The secular equations are:

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

- 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 symmetry elements: C_2, i, σ_h.
- 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	$x; y$	

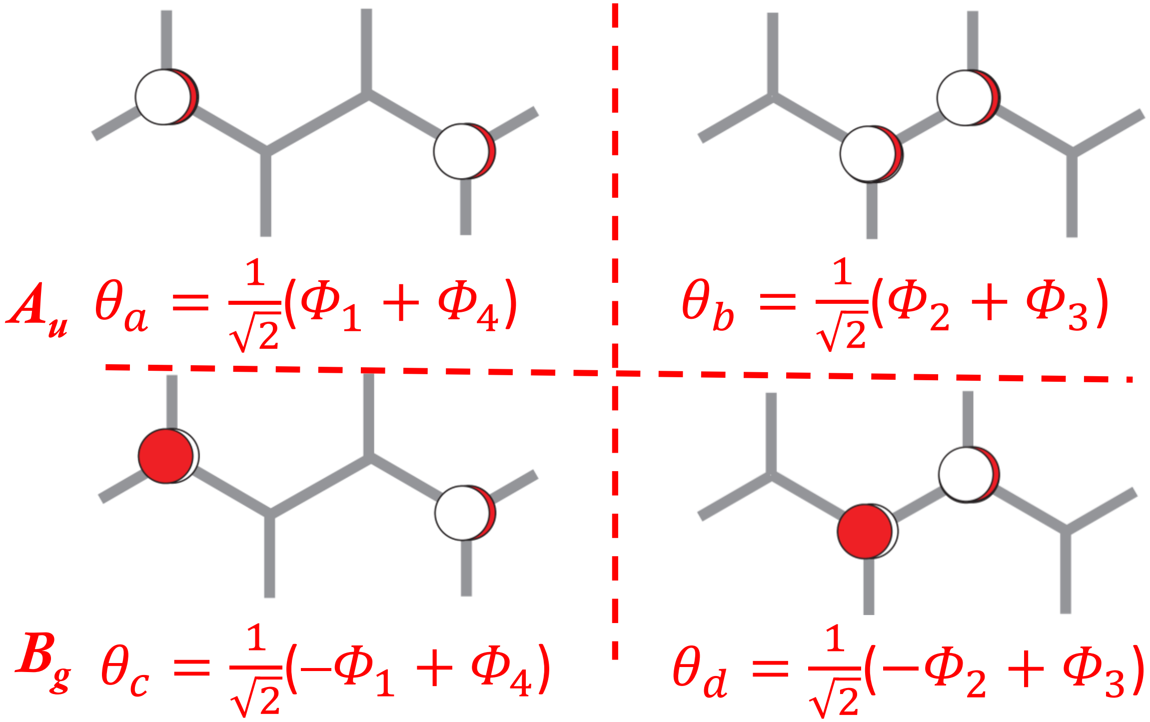
Γ 2 0 0 -2 $= A_u \oplus B_g$

- 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 $A_u \oplus B_g$.
- 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, $\theta_{A_u} = (\phi_2 + \phi_3)$ & $\theta_{B_g} = (-\phi_2 + \phi_3)$

6.2.1 Butadiene

- Now we have four normalized SOs:



A_u $\theta_a = \frac{1}{\sqrt{2}}(\Phi_1 + \Phi_4)$

$\theta_b = \frac{1}{\sqrt{2}}(\Phi_2 + \Phi_3)$

B_g $\theta_c = \frac{1}{\sqrt{2}}(-\Phi_1 + \Phi_4)$

$\theta_d = \frac{1}{\sqrt{2}}(-\Phi_2 + \Phi_3)$

- 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 $\boldsymbol{\theta}_d$.

- 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 $\boldsymbol{\theta_a}$, $\boldsymbol{\theta_b}$, . . .

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

We will consistently use *1,2,3, . . .* as the label for AOs and *a,b,c, . . .* for 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 $\boldsymbol{A_u}$ SOs $\boldsymbol{\theta_a}$ and $\boldsymbol{\theta_b}$, and another 2×2 problem for the $\boldsymbol{B_g}$ SOs $\boldsymbol{\theta_c}$ and $\boldsymbol{\theta_d}$.

6.2.1 Butadiene

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

- For the A_u SOs, the MOs are written as: $\boldsymbol{\psi_{A_u} = c_a\theta_a + c_b\theta_b}$
- And the 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 (how many?) by applying the ***Hückel Approx***.:

$$
\begin{aligned}
H_{aa} &= \int \theta_a \hat{H} \theta_a \, \mathrm{d}\tau \\
&= \int \frac{1}{\sqrt{2}} (\phi_1 + \phi_4) \, \hat{H} \frac{1}{\sqrt{2}} (\phi_1 + \phi_4) \, \mathrm{d}\tau \\
&= \frac{1}{2} (H_{11} + H_{14} + H_{41} + H_{44}) \\
&= \frac{1}{2} (\alpha_1 + \beta_{14} + \beta_{41} + \alpha_4) \\
&= \alpha.
\end{aligned}
$$

$$
\begin{aligned}
H_{ab} &= \int \theta_a \hat{H} \theta_b \, \mathrm{d}\tau \\
&= \int \frac{1}{\sqrt{2}} (\phi_1 + \phi_4) \, \hat{H} \frac{1}{\sqrt{2}} (\phi_2 + \phi_3) \, \mathrm{d}\tau \\
&= \frac{1}{2} (H_{12} + H_{13} + H_{42} + H_{43}) \\
&= \frac{1}{2} (\beta_{12} + \beta_{13} + \beta_{42} + \beta_{43}) = \beta
\end{aligned}
$$

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

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 ***β*** and then set $\frac{\alpha - E}{\beta} = x$: $\begin{pmatrix} x & 1 \\ 1 & x+1 \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$

- Demand the determinant to be zero: $\det \begin{pmatrix} x & 1 \\ 1 & x+1 \end{pmatrix} = x(x+1) - 1 = 0$

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

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

- Now we have two equations to solve with ***x*** being known:

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

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:

$$0.618c_a + c_b = 0 \qquad \rightarrow \; c_b = -0.618c_a$$

- 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*

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

Ex. 28

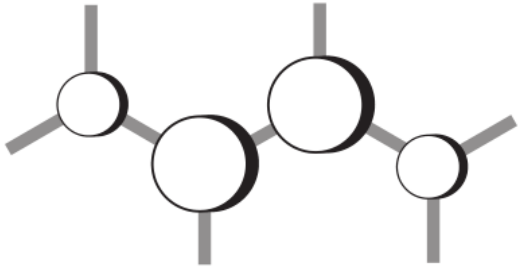
$(x = (\alpha\text{-}E)/\beta)$

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

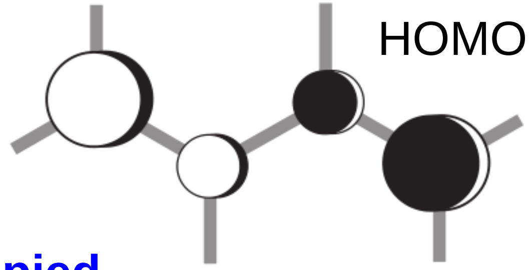
$$\psi_{B_g,1} = -0.602\,\phi_1 - 0.372\,\phi_2 + 0.372\,\phi_3 + 0.602\,\phi_4 \qquad E_{B_g,1} = \alpha + 0.618\,\beta$$
$$\psi_{B_g,2} = -0.372\,\phi_1 + 0.602\,\phi_2 - 0.602\,\phi_3 + 0.372\,\phi_4 \qquad E_{B_g,2} = \alpha - 1.618\,\beta.$$

6.2.1 Butadiene

- The complete set of four MOs are shown below.



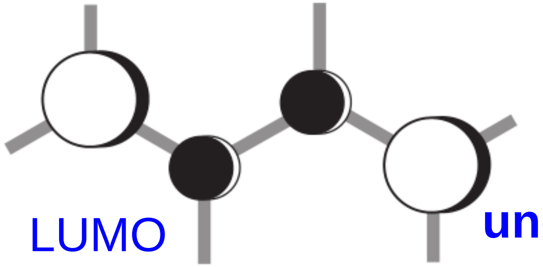
$\psi(A_{u,1})$ $E_1 = \alpha + 1.618\beta$



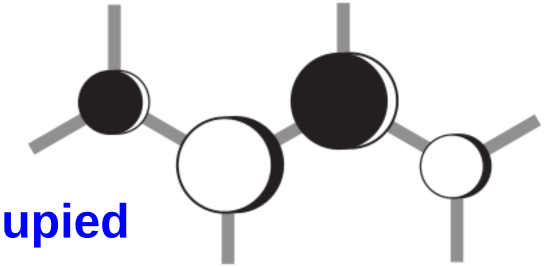
$\psi(B_{g,1})$ $E_2 = \alpha + 0.618\beta$

Occupied

unoccupied



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



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

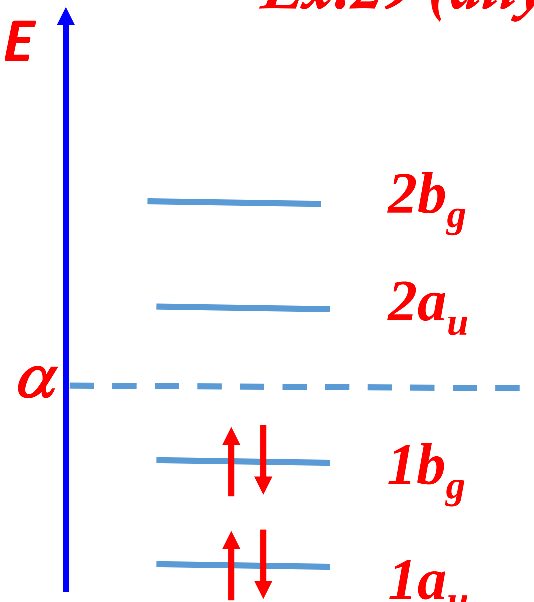
- Electron population on *i*th atom:

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

(sum over all occupied MOs)

regioreactivity of butadiene?

Ex.29 (allyl)



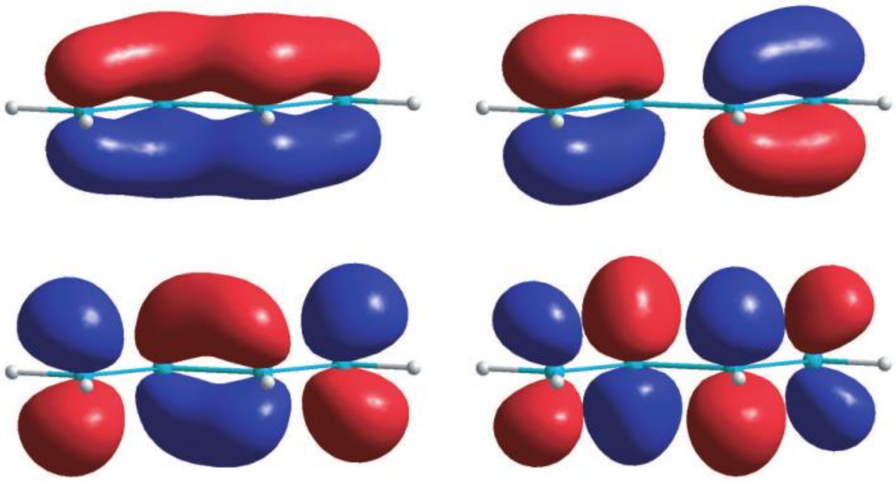
2b_g $E_4 = \alpha - 1.618\beta$

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

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

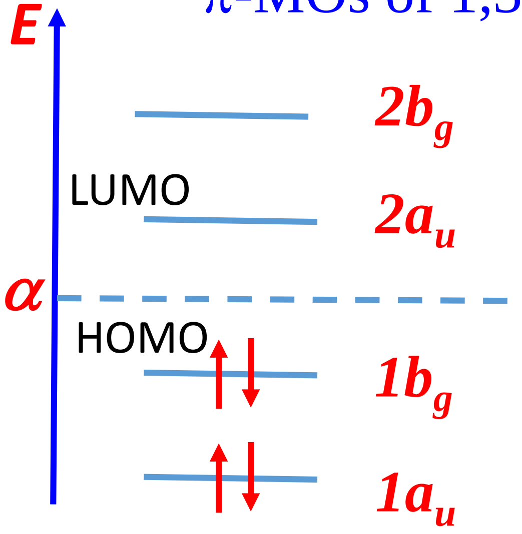
1a_u $E_1 = \alpha + 1.618\beta$

Results from Computer-based calculations



6.2.1 Butadiene

- π-MOs of 1,3-butadiene



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

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

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

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

- Total π electron energy of butadiene:

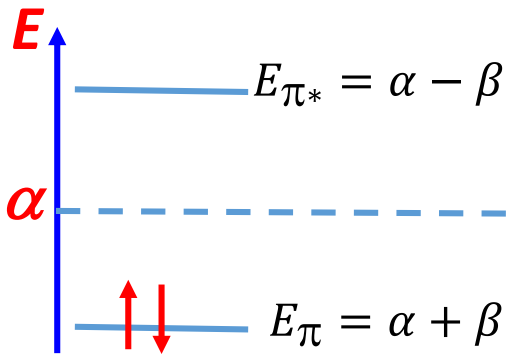
$$E^{4\pi e}_{delocalized} = 2E_1 + 2E_2$$
$$= 4\alpha + 4.472\beta$$

- π-MOs of a localized C-C π bond:

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

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

$$\begin{pmatrix} x & 1 \\ 1 & x \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}=0 \rightarrow x=\pm1,\ E=\alpha\pm\beta$$



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

$E_\pi = \alpha + \beta$

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

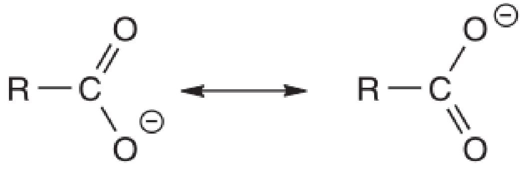
$$E^{4\pi e}_{localized} = 2 \times 2E_\pi = 4(\alpha + \beta)$$

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

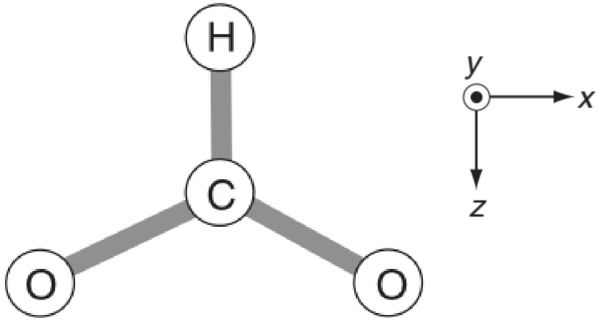
Delocalization of the electrons lowers the energy!

6.2.2 Carboxylate anion

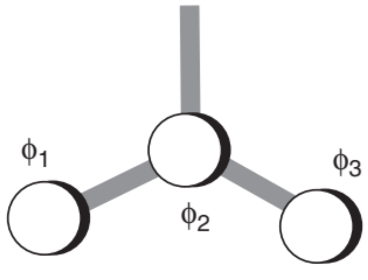


carboxylate anion

- This species has a *delocalised π system* 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)



framework of atoms



out of plane 2p orbitals

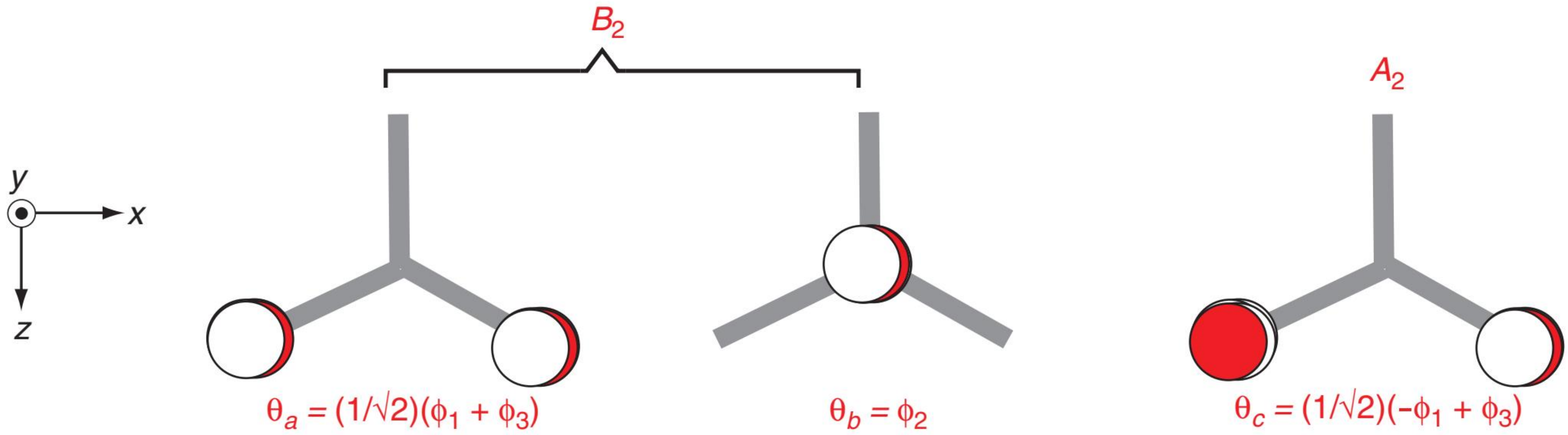
- The basis (ϕ_1, ϕ_3) transforms as $A_2 \oplus B_2$.

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

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

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} etc.

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

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

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

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

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

$$= \alpha_O$$

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

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

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

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

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

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

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

- 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,

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

- The resulting normalized MOs of $\boldsymbol{B_2}$ symmetry are

$$\boldsymbol{E_{B_{2,1}} = \alpha + 2\beta} \qquad \psi_{B_{2,1}} = 0.577\phi_1 + 0.577\phi_2 + 0.577\phi_3$$

Bonding

$$\boldsymbol{E_{B_{2,2}} = \alpha - \beta} \qquad \psi_{B_{2,2}} = 0.408\phi_1 - 0.816\phi_2 + 0.408\phi_3$$

Anti-bonding

- The energy of the MO of $\boldsymbol{A_2}$ symmetry is simply given as

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

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

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

non-bonding

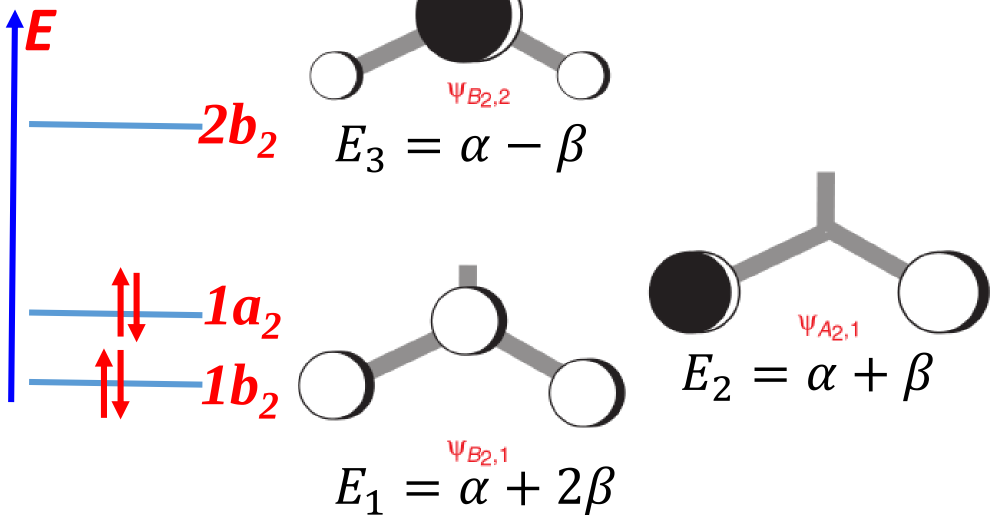
6.2.2 Carboxylate anion

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

$$\psi_{B_{2,2}} = 0.408\phi_1 - 0.816\phi_2 + 0.408\phi_3 \qquad E_3 = \alpha - \beta$$

$$\psi_{A_2} = -0.707\phi_1 + 0.707\phi_3 \qquad E_2 = \alpha + \beta$$

$$\psi_{B_{2,1}} = 0.577\phi_1 + 0.577\phi_2 + 0.577\phi_3 \qquad E_1 = \alpha + 2\beta$$



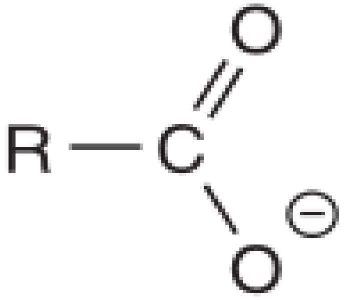
- The total π electron energy is

$$\begin{aligned} E_\pi &= 2 \times E_{B_2,1} + 2 \times E_{A_2,1} \\ &= 2 \times (\alpha + 2\beta) + 2 \times (\alpha + \beta) \\ &= 4\alpha + 6\beta \end{aligned}$$

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

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

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

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

- The total localized electron energy is $E_{loc.} = \overset{\text{2e of a C-O }\pi\text{-MO}}{2(\alpha + 1.618\beta)} + \overset{\text{O }p_\pi\text{ lone pair}}{2(\alpha+\beta)} = 4\alpha + 5.236\beta$
- *Delocalization energy* $= E_{deloc.} - E_{loc.} = (4\alpha + 6\beta) - (4\alpha + 5.236\beta) = 0.764\beta$

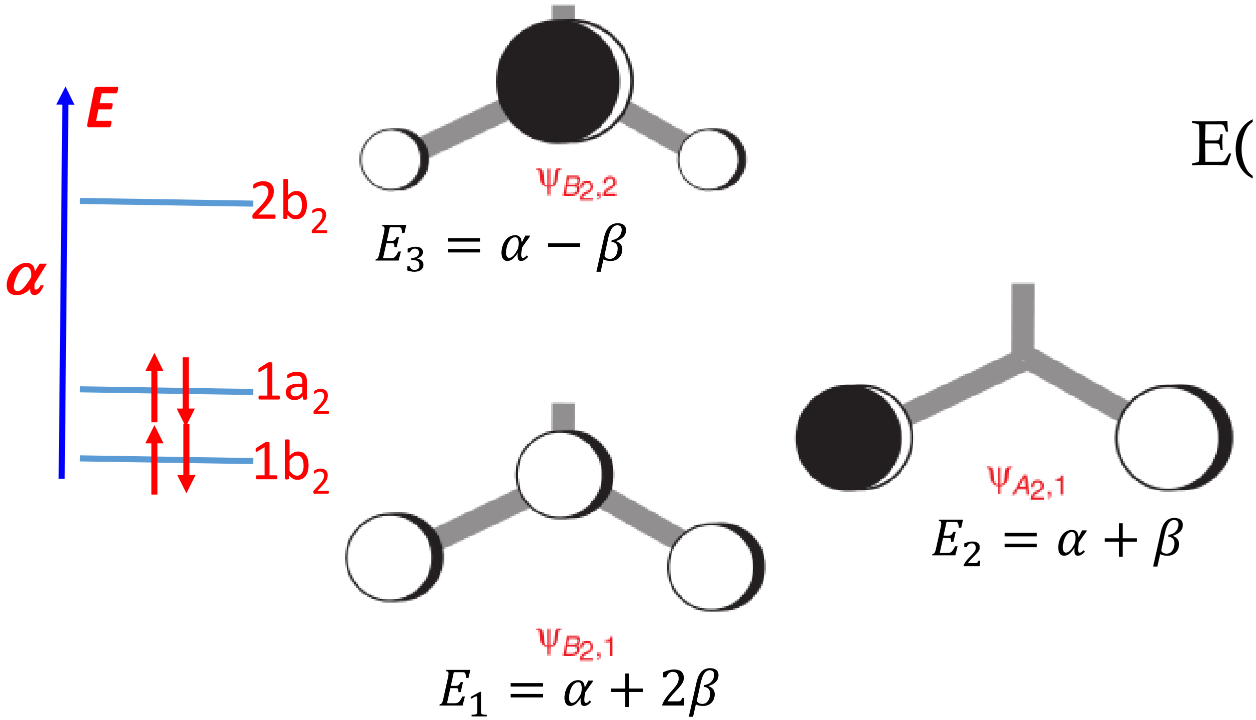
6.2.3 Relationship between the energies of the AOs and MOs

- 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.

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

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



$E_3 = \alpha - \beta$

$E_2 = \alpha + \beta$

$E_1 = \alpha + 2\beta$

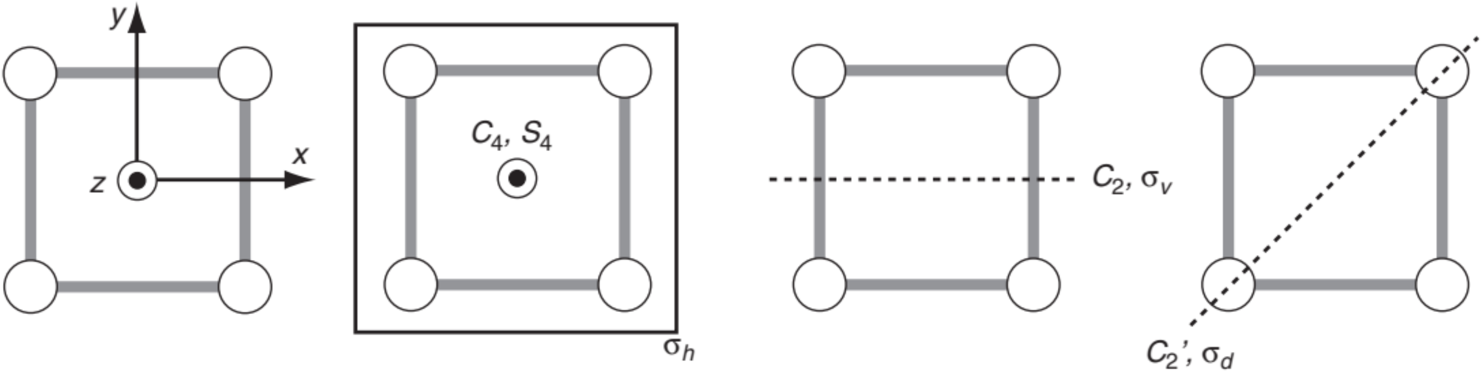
Q1: please check if this statement holds true for 1,3-butadiene?

Q2: How to make use of this relationship?

6.3 Cyclobutadiene

C_4H_4, (D_{4h})

Basis set: 4C $2p_z$ AOs!



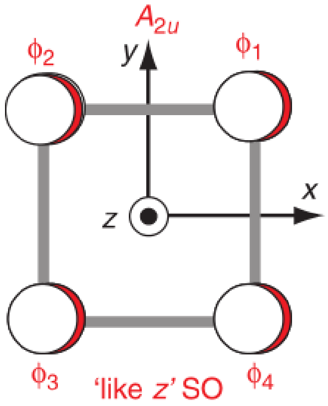
D_{4h}	E	$2C_4$	C_4^2	$2C_2$	$2C_2'$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2; z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1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

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

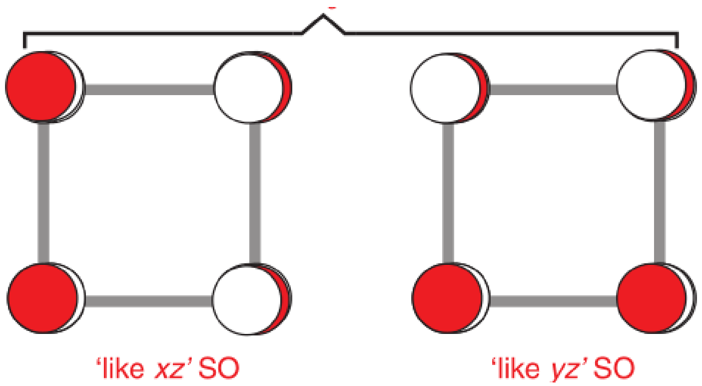
($B_{2g} \otimes A_{2u} = B_{1u}$)

6.3 Cyclobutadiene

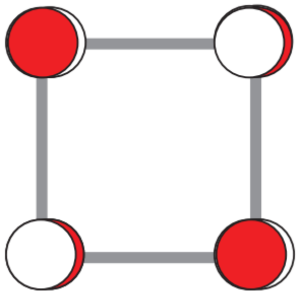
A_{2u}~*z*-like



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.

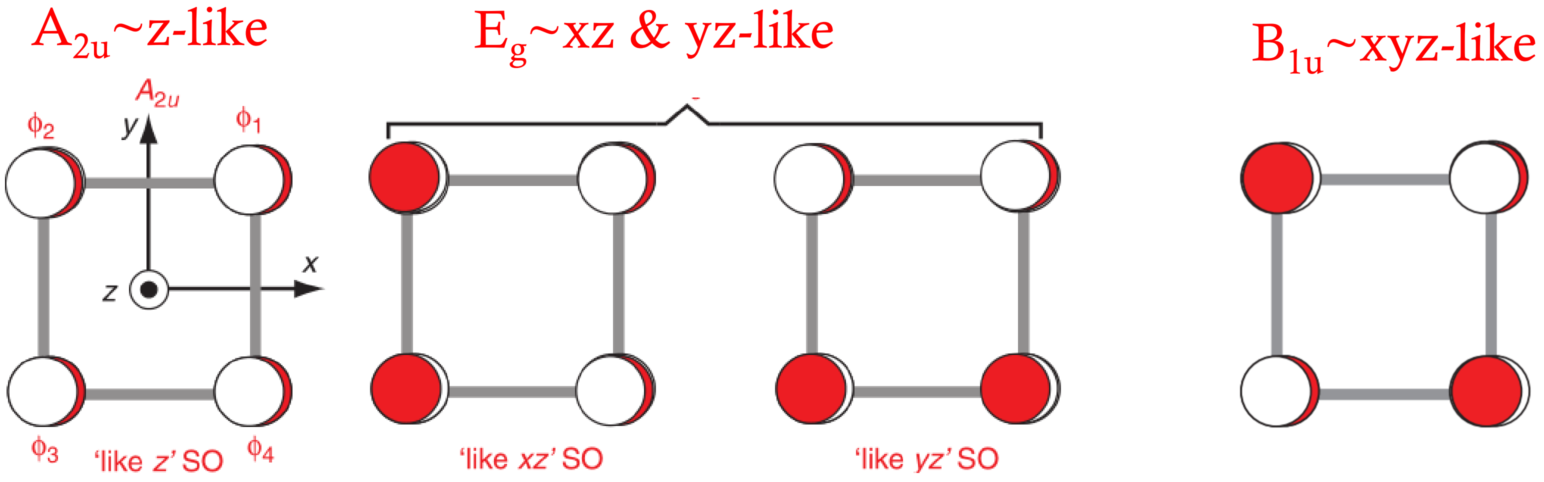
$$E_1 = H_{aa} = \int \theta_a \hat{H} \theta_a \, \mathrm{d}\tau$$

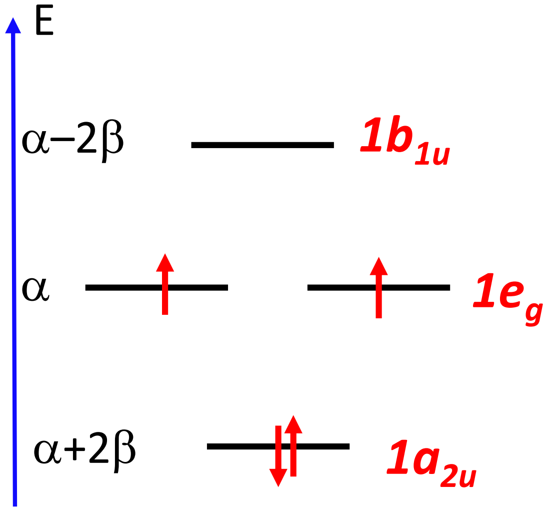
$$= \int \tfrac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)\, \hat{H}\, \tfrac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)\, \mathrm{d}\tau$$

$$= \tfrac{1}{4}(H_{11} + H_{12} + H_{13} + H_{14} + H_{21} + H_{22} + H_{23} + H_{24} + H_{31} + H_{32} + H_{33} + H_{34} + H_{41} + H_{42} + H_{43} + H_{44})$$

$$= \tfrac{1}{4}(\alpha + \beta + 0 + \beta + \beta + \alpha + \beta + 0 + 0 + \beta + \alpha + \beta + \beta + 0 + \beta + \alpha) = \alpha + 2\beta$$

6.3 Cyclobutadiene





Diradical! Anti-aromatic!

- The normalized SOs are

$$
\begin{array}{lll}
\boldsymbol{A_{2u}} & \theta_a = (\phi_1 + \phi_2 + \phi_3 + \phi_4)/2 & E_1 = H_{aa} = \alpha + 2\beta \\
\boldsymbol{E_g} \textit{ like } \boldsymbol{xz} & \theta_b = (\phi_1 - \phi_2 - \phi_3 + \phi_4)/2 & E_2 = H_{bb} = \int \theta_b \hat{H} \theta_b d\tau = \alpha \\
\boldsymbol{E_g} \textit{ like } \boldsymbol{yz} & \theta_c = (\phi_1 + \phi_2 - \phi_3 - \phi_4)/2 & E_3 = H_{cc} = \int \theta_c \hat{H} \theta_c d\tau = \alpha \\
\boldsymbol{B_{1u}} & \theta_d = (\phi_1 - \phi_2 + \phi_3 - \phi_4)/2 & E_4 = H_{dd} = \int \theta_d \hat{H} \theta_d d\tau = \alpha - 2\beta
\end{array}
$$

$$\left.\begin{array}{l} E_2 = \alpha \\ E_3 = \alpha \end{array}\right\} \text{degenerate!}$$

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

作业：

思考题1. 运用休克尔分子轨道理论推导苯分子π分子轨道的能量和组成，画出能级图，并推算其离域能。

思考题2. 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 ($k = 1,2,3,\dots n$)

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

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

思考题3. 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，$k = 0, 1, 2, \dots, (n-1)/2$ (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*.

6.4 Summary

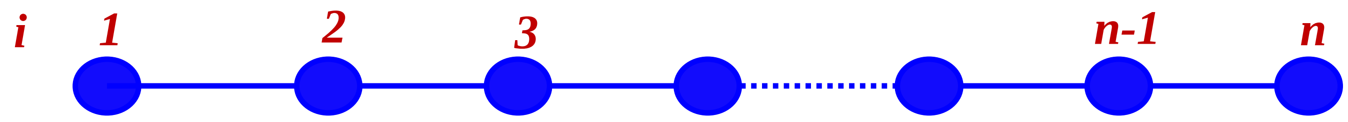
- The ***secular equations*** are of the form:

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

- ***The solution to the secular equations is 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!!!!!!!!!!)***
- 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 = (α-E)/β***) :

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

(cyclic formula)

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

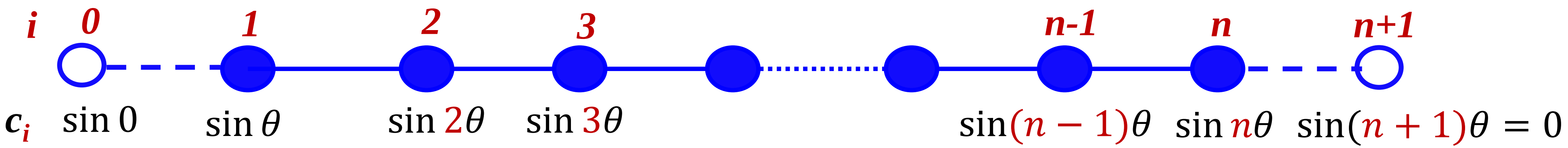
$$\sin A + \sin B = 2\sin\frac{A+B}{2}\cos\frac{A-B}{2}$$

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

$$then\ \ x = -2\cos\theta$$

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

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

$xc_1 + c_2 = 0;$

$c_1 + xc_2 + c_3 = 0;$ ……

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

(cyclic formula)

……; $c_{n-1} + xc_n = 0$

$$\xrightarrow[c_1 = \sin\theta]{\text{set } x = -2\cos\theta} \left\{ \begin{array}{l} c_2 = \sin 2\theta \\ c_3 = \sin 3\theta \\ \cdots \\ c_i = \sin i\theta \\ \cdots \\ c_n = \sin n\theta \end{array} \right.$$

Boundary condition:

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

$\theta_k = 2k\pi/(n+1) \quad (k=1,\ldots,n)$

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

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

(***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)

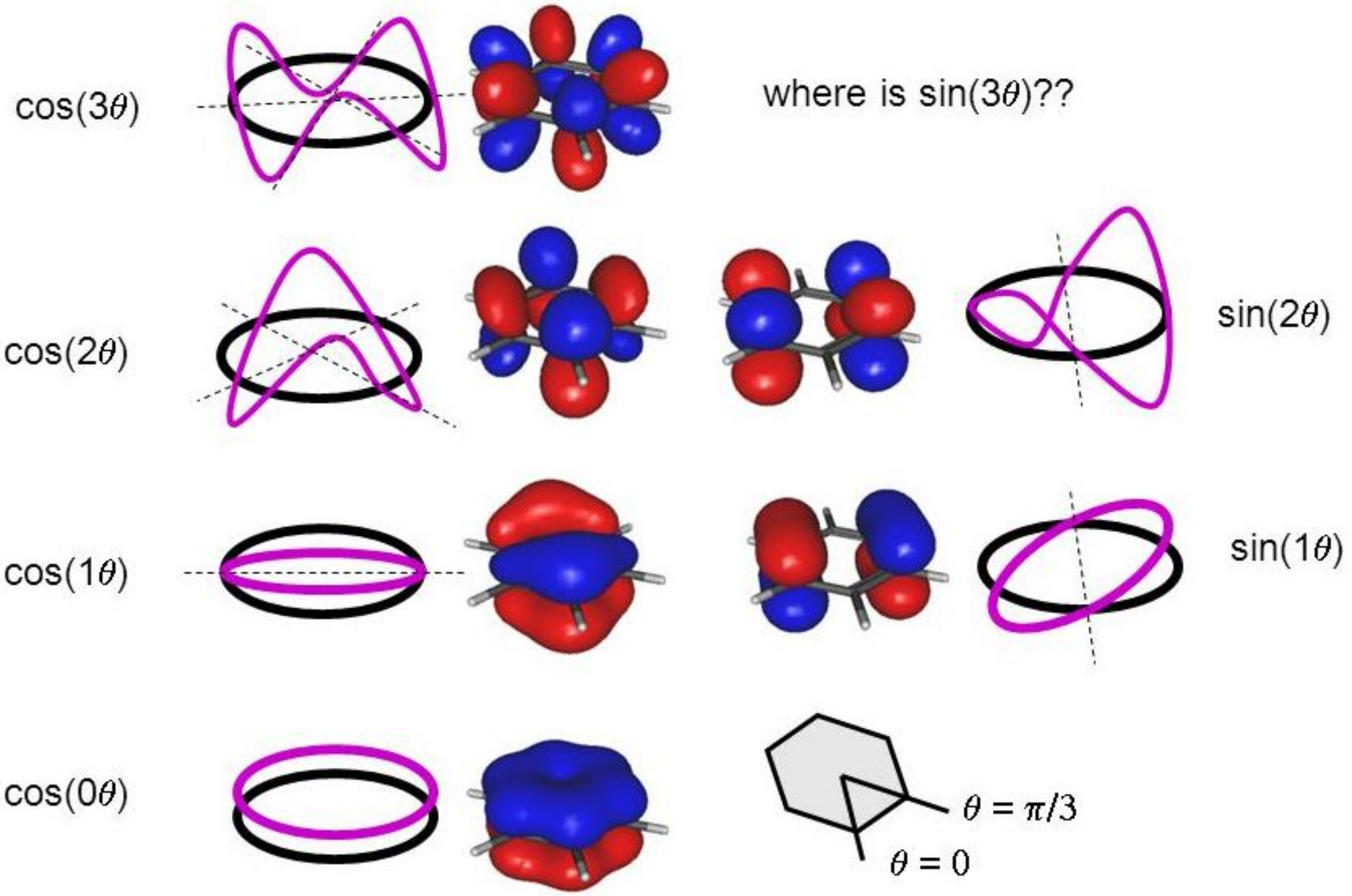
$$E_k = \alpha + 2\beta\cos(k\theta)$$

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

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

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

π MOs of Benzene



where is sin(3θ)??

- 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.

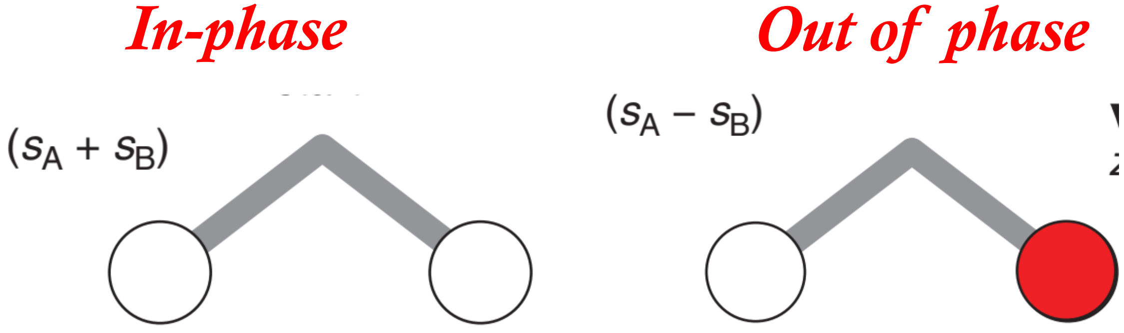
(https://pubs.acs.org/doi/full/10.1021/ed500376q)

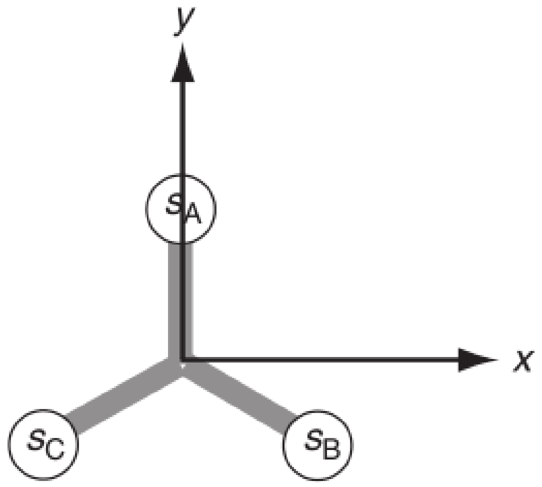
Work out SOs quickly by inspection & using trends!

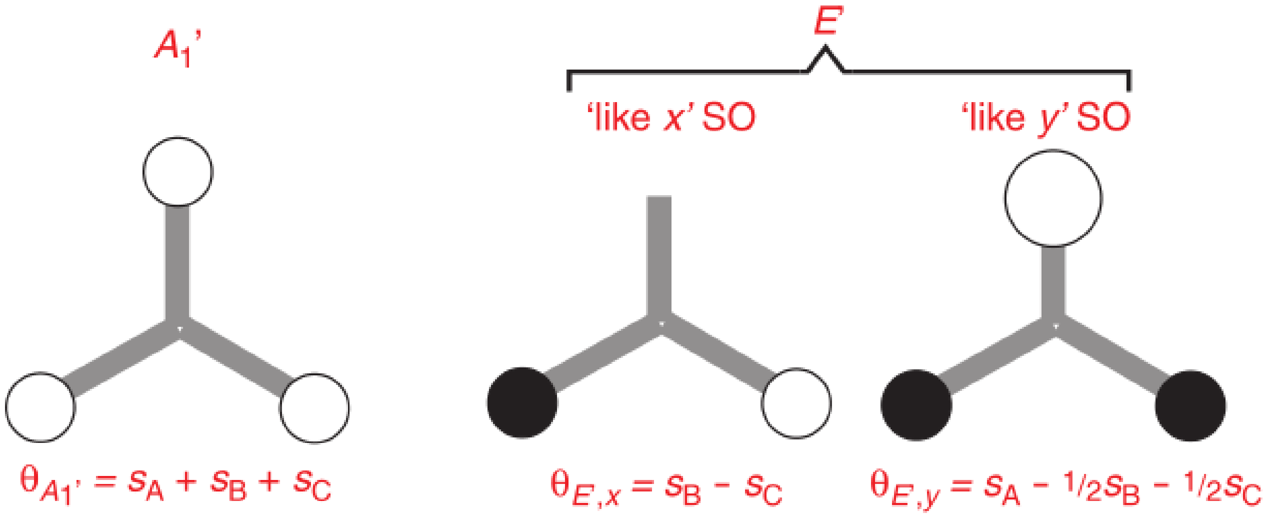
Trend in SOs arising from

i) 2 equivalent AOs

ii) 3 equivalent AOs



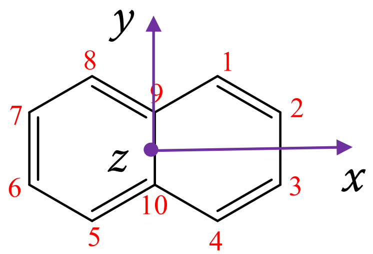




- The aforementioned trend in the SOs arising from 2, 3,4-equivalent functions can be used to quickly work out the SOs as well as the corresponding IRs by inspection.

Work out SOs quickly by inspection & using trends!

- Example: Naphthalene (D_{2h})



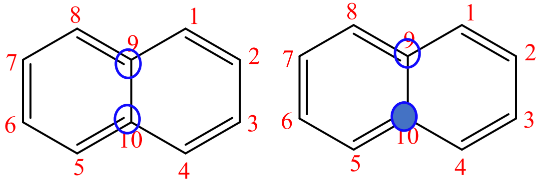
- 10 p_z AOs:

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

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	

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

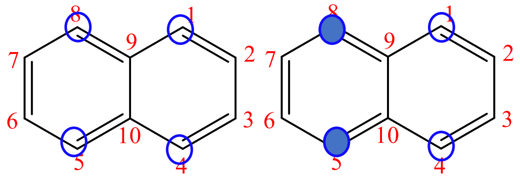
(9,10):



z-like, B_{1u} *yz-like*, B_{3g}

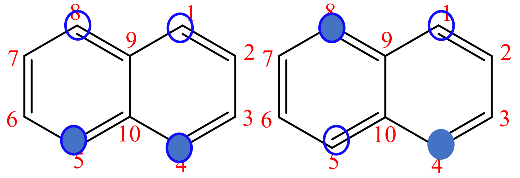
$\theta_a=(\phi_9+\phi_{10})/\sqrt{2}$ $\theta_b=(\phi_9-\phi_{10})/\sqrt{2}$

(1,4,5,8):



z-like, B_{1u} *xz-like*, B_{2g}

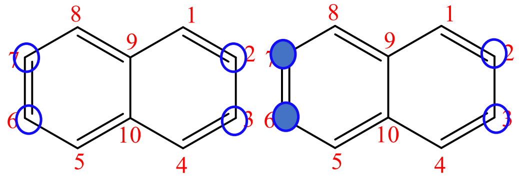
$\theta_c=(\phi_1+\phi_4+\phi_5+\phi_8)/2$ $\theta_d=(\phi_1+\phi_4-\phi_5-\phi_8)/2$



yz-like, B_{3g} *xyz-like*, A_u

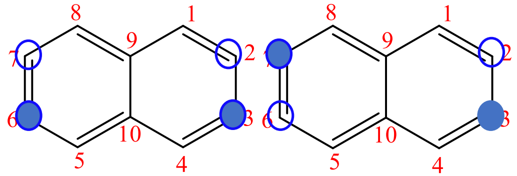
$\theta_e=(\phi_1-\phi_4-\phi_5+\phi_8)/2$ $\theta_f=(\phi_1-\phi_4+\phi_5-\phi_8)/2$

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

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

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

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

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

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

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

………