

# Quantum Chemistry

## Lecture 14

### Semi-empirical methods

**NC State University**

# Hückel theory introduction

Hückel theory is an example of semi-empirical approaches to the solution of the linear equations that represent combinations of atomic orbitals. In the Hückel approach, one assumes that the coulomb integral for a p-orbital in a  $\pi$ -system has energy  $\alpha$  and the resonance integral between any two adjacent carbon atoms is  $\beta$ . The overlap integral  $S$  is often ignored.

We have seen the initial steps of an electronic structure calculation in the formation of symmetry-adapted linear combinations of atomic orbitals (LCAOs). The application of group theory can also be used to simplify the determinant used to calculate the energy. The theory that uses this approach most extensively is known as Hückel theory.

# Hückel theory implementation

The following steps can be employed in Hückel theory.

- Determine the molecular point group.
- Determine the normalized symmetry adapted linear combinations (SALCs) using the projection operator method.
- Use the SALCs to determine the elements of the Hückel secular determinant  $\det|H_{ij} - S_{ij}E_0| = 0$

- Simplify the mathematical formalism by letting  $H_{ii} = \alpha$  and  $H_{ij} = \beta$ . Divide each element by  $\beta$  and let  $x = (\alpha - E)/\beta$
- For each eigenvalue solve for the eigenvectors (coefficients). These are the contributions of each SALC to the MO.

$$\sum_{j=1}^N |H_{ij} - S_{ij}E_0| C_{ij} = 0$$

The coefficients must obey the normalization condition.

$$\sum_{j=1}^N C_{ij}^2 = 1$$

# Hückel treatment of ethene

We can start with ethene, which can be treated using the following determinant.

$$\det \begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} = 0$$

Thus,

$$(\alpha - E)^2 - \beta^2 = 0$$

By inspection we can see that the answer is,

$$E_{\pm} = \alpha \pm \beta$$

According to the semi-empirical aspect of the model, the transition energy between the HOMO and the LUMO is  $2\beta$ . Thus, one can compare with experiment and obtain a value for  $\beta$ .

# Hückel treatment of butadiene

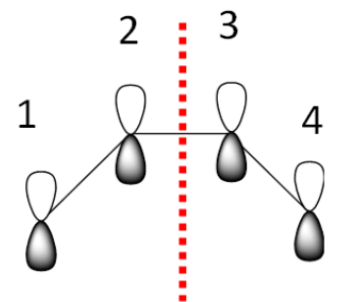
The practical limitation to Hückel theory is that the matrices rapidly become too large to solve analytically. For this reason group theory became an important part of the Hückel procedure. To illustrate this we will examine the case of butadiene. There are four p-orbitals in butadiene. Therefore, the determinant we need to solve is

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix}$$

This 4 x 4 determinant cannot be solved analytically.

# Application of group theory

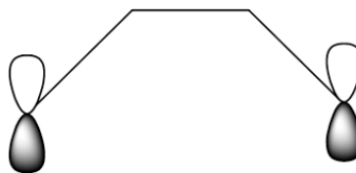
However, we can solve this problem using group theory. For the present purpose we will assume that butadiene is in the cis form as shown in the Figure . We can assign butadiene to the  $C_{2v}$  point group and use the principles of group theory to recast the 4x4 matrix of the secular equations into symmetry adapted matrices. First, we identify the atoms in butadiene that are related by symmetry. The Figure shows that the  $C_2$  rotation relates two symmetry related groups of atoms (2,3) and (1,4). Moreover both of these groups have shown in the Figure.



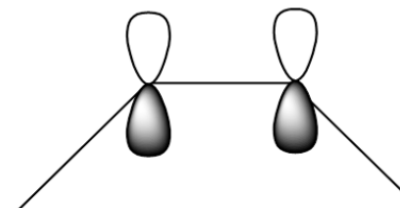
Determine appropriate sets:  
 2 and 3 are symmetry related  
 1 and 4 are symmetry related

Both transform as

	E	$C_{2v}$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma$	2	0	-2	0



Set 1  
 Carbons 1 and 4



Set 2  
 Carbons 2 and 3

The structure of cis-butadiene and the division of the molecule into sets of atoms that are related by symmetry.

## Decompose into irreps

	E	C <sub>2v</sub>	σ(xz)	σ(yz)		E	C <sub>2v</sub>	σ(xz)	σ(yz)
Γ	2	0	-2	0	Γ	2	0	-2	0
A <sub>1</sub>	1	1	1	1	A <sub>2</sub>	1	1	-1	-1
Total	2	+ 0	+ -2	+ 0 = 0	Total	2	+ 0	+ 2	+ 0 = 4
	E	C <sub>2v</sub>	σ(xz)	σ(yz)		E	C <sub>2v</sub>	σ(xz)	σ(yz)
Γ	2	0	-2	0	Γ	2	0	-2	0
B <sub>1</sub>	1	-1	1	-1	B <sub>2</sub>	1	-1	-1	1
Total	2	+ 0	- 2	+ 0 = 0	Total	2	+ 0	+ 2	+ 0 = 4

The order is 4 so the character sums are divided by 4.

The irreducible representations are:

$$\Gamma = a_2 + b_2$$

Decomposition of reducible representation into the basis vectors of the C<sub>2v</sub> point group.

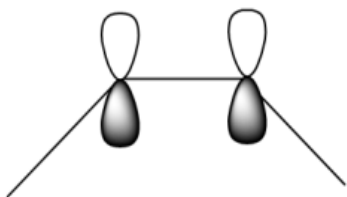
# Projection operators for butadiene

One is symmetric ( $a_2$ ) and one is anti-symmetric ( $b_2$ ) with respect to  $C_2$  rotation. We use the method of projection operators to construct symmetry adapted linear combinations (SALCs) of atomic orbitals. This procedure uses symmetry to create a LCAO.

## Apply projection operators

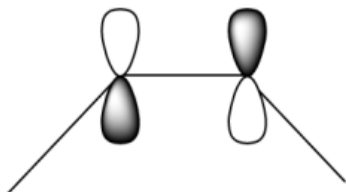
$$\text{SALC}_{23}(b_2) = p_2 + p_3 + p_3 + p_2$$

$$\text{SALC}_{23}(b_2) = \frac{1}{\sqrt{2}}(p_2 + p_3)$$



$$\text{SALC}_{23}(a_2) = p_2 - p_3 - p_3 + p_2$$

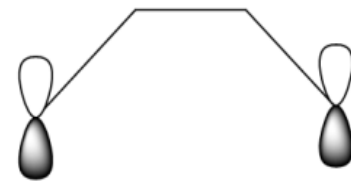
$$\text{SALC}_{23}(a_2) = \frac{1}{\sqrt{2}}(p_2 - p_3)$$



## Apply projection operators

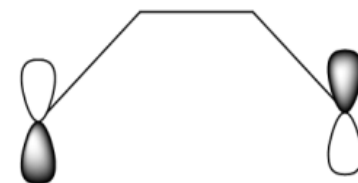
$$\text{SALC}_{14}(b_2) = p_1 + p_4 + p_1 + p_4$$

$$\text{SALC}_{14}(b_2) = \frac{1}{\sqrt{2}}(p_1 + p_4)$$



$$\text{SALC}_{14}(a_2) = p_1 - p_4 - p_4 + p_1$$

$$\text{SALC}_{14}(a_2) = \frac{1}{\sqrt{2}}(p_1 - p_4)$$





# Symmetry Adapted Linear Combinations

The importance of this method is that it greatly expands the number of problems that can be treated with Hückel theory without the use of a computer. Finally, we need to combine the SALCs in each symmetry block. The total wave functions are:

$$\Psi_4 = SALC_{14}(a_2) - SALC_{23}(a_2)$$

$$\Psi_3 = SALC_{14}(b_2) - SALC_{23}(b_2)$$

$$\Psi_2 = SALC_{14}(a_2) + SALC_{23}(a_2)$$

$$\Psi_1 = SALC_{14}(b_2) + SALC_{23}(b_2)$$

# Evaluation of the integrals

The secular determinant can be calculated using the SALCs as the basis.

$$H_{11} = \frac{1}{2} \int (p_1 + p_4) H (p_1 + p_4) d\tau$$

$$\begin{aligned} H_{11} &= \frac{1}{2} \left( \int p_1 H p_1 d\tau + \int p_4 H p_1 d\tau + \int p_1 H p_4 d\tau + \int p_4 H p_4 d\tau \right) \\ &= \alpha \end{aligned}$$

$$H_{22} = \frac{1}{2} \int (p_2 + p_3) H (p_2 + p_3) d\tau$$

$$\begin{aligned} H_{22} &= \frac{1}{2} \left( \int p_2 H p_2 d\tau + \int p_2 H p_3 d\tau + \int p_3 H p_2 d\tau + \int p_3 H p_3 d\tau \right) \\ &= \alpha + \beta \end{aligned}$$

# Evaluation of the integrals

$$H_{12} = \frac{1}{2} \int (p_1 + p_4) H(p_2 + p_3) d\tau$$

$$H_{12} = \frac{1}{2} \left( \int p_1 H p_2 d\tau + \int p_1 H p_3 d\tau + \int p_4 H p_2 d\tau + \int p_4 H p_3 d\tau \right) = \beta$$

$$H_{21} = H_{12}$$

$$H_{33} = \frac{1}{2} \int (p_1 - p_4) H(p_1 - p_4) d\tau$$

$$H_{33} = \frac{1}{2} \left( \int p_1 H p_1 d\tau - \int p_4 H p_1 d\tau - \int p_1 H p_4 d\tau + \int p_4 H p_4 d\tau \right) = \alpha$$

# Evaluation of the integrals

$$H_{44} = \frac{1}{2} \int (p_2 - p_3) H(p_2 - p_3) d\tau$$

$$H_{44} = \frac{1}{2} \left( \int p_2 H p_2 d\tau - \int p_2 H p_3 d\tau - \int p_3 H p_2 d\tau + \int p_3 H p_3 d\tau \right) \\ = \alpha - \beta$$

$$H_{34} = \frac{1}{2} \int (p_1 - p_4) H(p_2 - p_3) d\tau$$

$$H_{34} = \frac{1}{2} \left( \int p_1 H p_2 d\tau - \int p_1 H p_3 d\tau - \int p_4 H p_2 d\tau + \int p_4 H p_3 d\tau \right) = \beta$$

$$H_{43} = H_{34}$$

# The secular determinant

The secular determinant is:

$$\begin{vmatrix} H_{11} - E & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} - E & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} - E & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} - E \end{vmatrix}$$

Based on the foregoing analysis we see that there are Two 2x2 blocks. Terms such as  $H_{14} = H_{24} = H_{23} = 0$

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha + \beta - E & 0 & 0 \\ 0 & 0 & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - \beta - E \end{vmatrix}$$

Divide by  $\beta$  and let  $\mathbf{x} = \frac{\alpha - E}{\beta}$

# The Hückel simplification

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x+1 & 0 & 0 \\ 0 & 0 & x & 1 \\ 0 & 0 & 1 & x-1 \end{vmatrix}$$

The upper determinant is:  $x(x+1) - 1 = 0$

$$x^2 + x - 1 = 0$$

$$x = \frac{-1 \pm \sqrt{1+4}}{2} = \frac{-1 \pm \sqrt{5}}{2}$$

The lower determinant is:  $x(x-1) - 1 = 0$

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

$$x = \frac{1 \pm \sqrt{1+4}}{2} = \frac{1 \pm \sqrt{5}}{2}$$

If we assume that the average energy is  $\alpha = 0$ , i.e. the energy of an isolated carbon p-orbital is our reference, then energy energies of the MOs relative to that value are given in the diagram below.

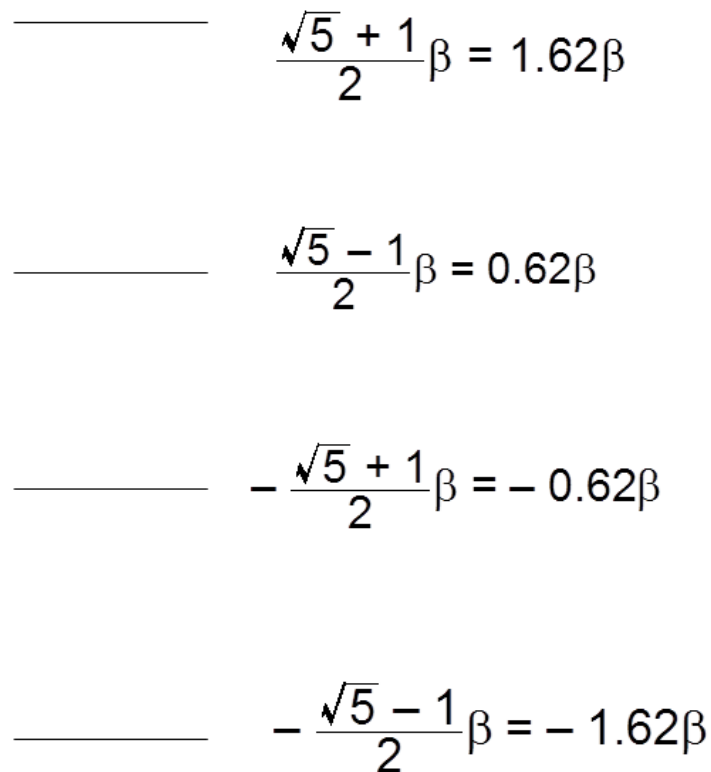


Figure. Energy levels derived from the Hückel theory analysis of cis-butadiene.

# Determination of the eigenvectors

We see that there are two bonding orbitals with energies more negative than 0 and two anti-bonding orbitals with more positive energies.

The Hückel method can be used to obtain the coefficients for the wave functions. Once the eigenvalues (i.e. the energies) have been determined, these values are substituted back into the matrix and then the coefficients are determined.

For the  $b_2$  block, the eigenvalues are  $-1.62\beta$  and  $0.62\beta$ . In units of  $\beta$  the matrix is:

$$\begin{pmatrix} x & 1 \\ 1 & x + 1 \end{pmatrix} \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix}$$

$$\begin{pmatrix} -1.62 & 1 \\ 1 & -0.62 \end{pmatrix} \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix}$$



The matrix equation can only provide a relationship between the coefficients between set 1 ( $p_1$  and  $p_4$ ) and set 2 ( $p_2$  and  $p_3$ ).

$$-1.62 c_{11} + c_{21} = 0$$

$$c_{21} = 1.62 c_{11}$$

The values can be established by including normalization:

$$c_{11}^2 + c_{21}^2 = 1$$

$$c_{11}^2 + (1.62c_{11})^2 = 1$$

$$c_{11}^2 = \frac{1}{3.624}$$

$$c_{11} = 0.5252$$

$$c_{21} = 0.8509$$

The lowest energy MO is given by:

$$\Psi_1 = \frac{c_{11}(p_1 + p_4) + c_{21}(p_2 + p_3)}{\sqrt{2}}$$

$$\Psi_1 = 0.37p_1 + 0.60p_2 + 0.60p_3 + 0.37p_4$$

The other root ( $0.62\beta$ ) gives

$$\begin{pmatrix} 0.62 & 1 \\ 1 & 1.62 \end{pmatrix} \begin{pmatrix} c_{13} \\ c_{23} \end{pmatrix}$$

$$0.62 c_{13} + c_{23} = 0$$

$$c_{23} = -0.62 c_{13}$$

Using the normalization condition:

$$c_{13}^2 + (-0.62c_{13})^2 = 1$$

$$c_{13}^2 = \frac{1}{1.384}$$

$$c_{13} = 0.8500$$

$$c_{23} = -0.5269$$

The lowest energy MO is given by:

$$\Psi_3 = \frac{c_{13}(p_1 + p_4) + c_{23}(p_2 + p_3)}{\sqrt{2}}$$

$$\Psi_3 = 0.60p_1 - 0.37p_2 - 0.37p_3 + 0.60p_4$$

Using the same method, starting with the matrix of the  $a_2$  block, we have:

$$\begin{pmatrix} x & 1 \\ 1 & x - 1 \end{pmatrix} \begin{pmatrix} c_{12} \\ c_{22} \end{pmatrix}$$

$$\begin{pmatrix} -0.62 & 1 \\ 1 & -1.62 \end{pmatrix} \begin{pmatrix} c_{12} \\ c_{22} \end{pmatrix}$$

$$-0.62 c_{12} + c_{22} = 0$$

$$c_{22} = 0.62 c_{12}$$

Using the normalization condition:

$$c_{12}^2 + (0.62c_{12})^2 = 1$$

$$c_{12} = 0.8500$$

$$c_{22} = 0.5269$$

$$\Psi_2 = \frac{c_{12}(p_1 - p_4) + c_{22}(p_2 - p_3)}{\sqrt{2}}$$

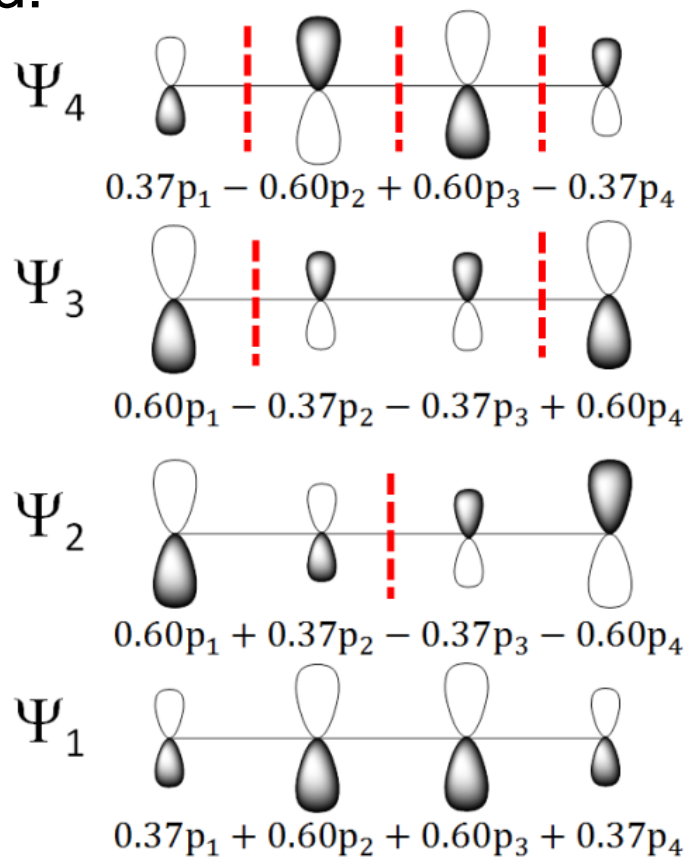
$$\Psi_2 = 0.60p_1 + 0.37p_2 - 0.37p_3 - 0.60p_4$$

# Butadiene MOs

Using a similar approach for the  $1.62\beta$  eigenvalue, we find:

$$\Psi_4 = 0.37p_1 - 0.60p_2 + 0.60p_3 - 0.37p_4$$

Plotting these wave functions using appropriate coefficient weighting, we find:



# Butadiene Energy

Hückel theory is known as a semi-empirical method. The HOMO-LUMO transition energy is determined to be  $1.24\beta$ . The value of the resonance integral,  $\beta$ , can be obtained from experiment using the measured HOMO-LUMO transition energy.

The energy of the system can be obtained from the calculation of the energies of the occupied levels. The total  $\pi$ -electron binding energy is given by:

$$E_{\text{binding}} = \sum_{k=1}^{N_{\text{occ}}} n_k E_k$$

For butadiene, we find that

$$\begin{aligned} E_{\text{binding}} &= (2)(-1.62\beta) + (2)(-0.62\beta) \\ &= -4.48\beta \end{aligned}$$

# Wolfsberg-Helmholtz approximation

Hückel theory is usually applied to the solution of  $\pi$ -systems. It can be extended to include the  $\sigma$ -bonding framework of the molecule. This approach pioneered Dr. Roald Hoffman is known as extended Hückel theory. The diagonal matrix elements,  $H_{ii}$ , can be estimated from ionization potentials. However, the off-diagonal matrix elements or resonance integrals must be determined in some manner. One common method is to invoke the Wolfsberg-Helmholtz approximation.

$$H_{ij} = KS_{ij} \frac{(H_{ii} + H_{jj})}{2}$$

The parameter  $K$  is called the Wolfsberg-Helmholtz parameter and it is usually set equal to 1.75.