Hückel Molecular Orbital theory

Consider a molecular orbital, $|\psi\rangle = |c_A\phi_A\rangle + |c_B\phi_B\rangle$; $\hat{H}|\psi\rangle = E|\psi\rangle$, where $|\phi_A\rangle$ and $|\phi_B\rangle$ are normalised atomic orbitals of atoms A and B respectively. Then,

$$\hat{H}\left(|c_A\phi_A\rangle + |c_B\phi_B\rangle\right) = E\left(|c_A\phi_A\rangle + |c_B\phi_B\rangle\right)$$

We multiply from the left by $\langle\phi_A|$ and take inner product, the gives us (for convenience, assume real functions):

$$c_A\alpha_{AA} + c_B\beta_{AB} = Ec_A + Ec_B S; \text{ where } \alpha_{AA} = \langle\phi_A|\hat{H}|\phi_A\rangle; \ \beta_{AB} = \langle\phi_A|\hat{H}|\phi_B\rangle; \ S = \langle\phi_A|\phi_B\rangle$$

$$\text{or, } \left(\alpha_{AA} - E\right)c_A + \left(\beta_{AB} - ES\right)c_B = 0$$

A similar equation is obtained by multiplying from the left by $\langle\phi_B|$ and taking inner product,

$$\left(\beta_{AB} - ES\right)c_A + \left(\alpha_{BB} - E\right)c_B = 0$$

Together the above two equations are called the secular equations.

Alternatively, we can obtain the these equations using variation theorem as follows:

Consider

$$E = \langle\hat{H}\rangle = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\langle c_A\phi_A + c_B\phi_B|\hat{H}|c_A\phi_A + c_B\phi_B\rangle}{\langle c_A\phi_A + c_B\phi_B|c_A\phi_A + c_B\phi_B\rangle} = \frac{c_A^2\alpha_{AA} + 2c_A c_B\beta_{AB} + c_B^2\alpha_{BB}}{c_A^2 + 2c_A c_B S + c_B^2}$$

The Variation theorem states that the for the exact solution, energy must be a minimum with respect to variation of parameters, in this case c_A and c_B.

$$\frac{\partial E}{\partial c_A} = \frac{\partial E}{\partial c_B} = 0$$

If we implement the above varational conditions, we will get the secular equations.

In case the atoms A and B are identical and the orbitals $|\phi_A\rangle$ and $|\phi_B\rangle$ are also identical, (for instance, a $2p_x$ orbital of C atom A and a $2p_y$ orbital of C atom A, then we can avoid the subscripts on α (called the Coulomb integral) and β (called the Resonance integral) .

Then, the secular equations may be written as:

$$\begin{pmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

This has a non-trivial solution provided,

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

The determinant on the left is called the secular determinant.

We will see applications of this to unsaturated organic compounds.

For this, we invoke the following approximations,

1. separation of σ and π electrons: This helps us to discuss the unsaturated part of the system separately from the sigma skelelton.

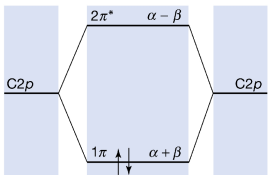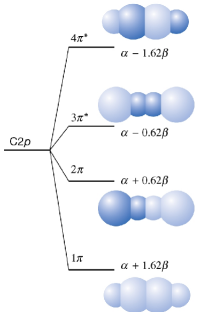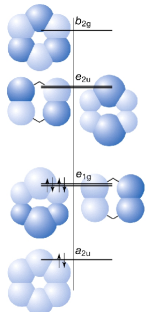2. We will ignore the overlap integral, S since it is very small. This reduces the system to

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

This could now be applied to a compound like ethene. We can divide each element by β and obtain

$$
\begin{vmatrix}
x & 1 \\
1 & x
\end{vmatrix} = 0; \text{ where } x = \frac{\alpha - E}{\beta} \implies E = \alpha + x\beta
$$

3. For more then two atoms, we also ignore the β. Thus, for butadiene, we will get,

$$
\begin{vmatrix}
x & 1 & 0 & 0 \\
1 & x & 1 & 0 \\
0 & 1 & x & 1 \\
0 & 0 & 1 & x
\end{vmatrix} = 0
$$

Ethylene	Butadiene	Benzene

Benzene:

since this is a cyclic conjugated system, with $\alpha =$ the Coulomb integral and $\beta =$ the resonance integral, and $x = \frac{\alpha - E}{\beta}$, the secular equation from HMO is:

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

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

$$\Rightarrow x \left[x \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 0 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} \right] - \left[\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 0 & 0 & 0 \\ x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \end{vmatrix} \right] + \left[\begin{vmatrix} 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \\ 0 & 0 & 0 & 1 \end{vmatrix} - \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} \right] =$$

0 and so on...giving finally

$$\Rightarrow (x^2 - 4)(x^2 - 1)^2 = 0$$

$$\Rightarrow x^2 = 4 \text{ or } x^2 = 1 \Rightarrow x = \pm 2, x = \pm 1, x = \pm 1$$

$$\Rightarrow E = \alpha \pm 2\beta; \; \alpha \pm \beta; \; \alpha \pm \beta$$

for hexatriene, there is no cyclic conjugation. Hence, it is effectively a system of three ethylenes.

For ethylene, the secular equation is:

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

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

$$\Rightarrow x \pm 1 \Rightarrow E = \alpha \pm \beta$$

Comparing the total energy of the benzene system:

$$E_{benzne} = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

with three ethylene systems:

$$3 \times E_{ethylene} = 3.2(\alpha + \beta) = 6\alpha + 6\beta$$

we find an additional stability of 2β for benzene. This is the stability due to delocalization of the electron density over the skeleton.