

Fig. 8.6 Bonding (ψ) and antibonding (ψ^*) MO formation using p orbitals: (i) HMO approach and (ii) general MO approach

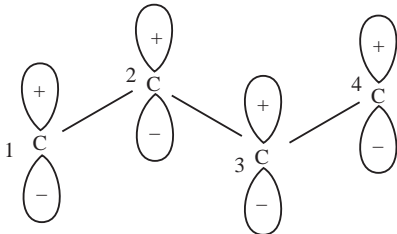
This represents the energy of an electron in an atomic orbital ϕ_μ centred at μ and is referred to as the Coulomb integral (as noted before for the hydrogen molecule). The Huckel operator is defined by the above relations (8.34) to (8.36) and is not specified in its analytical structure. The Huckel operator in effect generates the values of α , β or zero.

The Coulomb integral α is a measure of the binding energy of the $2p$ electron of carbon. Thus the value of α will vary depending on the substituents attached to the carbon atom and also the hybridization of carbon. The Coulomb integrals are sometimes approximated as the valence orbital ionization energies (VOIE). The assumption that all the values of the resonance integral β for the C—C bonds are the same in a given system, is an oversimplification. It is known that the β value varies with the bond length. Thus, two values of β should be used, for example for butadiene. However, in simple HMO method all values of α and β in a carbon system are taken as being the same.

For a π electron system containing only (skeletal) carbon atoms, all α_μ s are given the same value α and all $\beta_{\mu\nu}$ are given the value β . The quantity α corresponds approximately to the negative of the ionization energy of an electron localized in the carbon atomic orbital and is hence a negative value. The energy β describes the additional stabilization arising from the delocalization of an electron over neighbouring atomic orbitals. Accordingly β is also a negative quantity but of smaller magnitude than α .

In practice, the $H_{\mu\mu}$ and $H_{\mu\nu}$ are usually arranged as the elements of a square matrix of order n for a molecule with n $2p_z$ atomic orbitals. Therefore, $H_{\mu\mu}$ and $H_{\mu\nu}$ are termed as the matrix elements of the Huckel operator H . Use of the above conventions simplifies the Huckel determinant, for example for *s-trans*-1,3-butadiene ($\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$), the

Huckel determinant

$$\begin{vmatrix} H_{11} - E & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} - E & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} - E & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} - E \end{vmatrix} = 0$$


simplifies to

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad (8.37)$$

The other rotamer of butadiene, namely *s-cis*-butadiene (or even the linear form), yields the same secular determinant. Since the value of the determinant is zero, each element may be divided by β for simplification. Further, setting $(\alpha - E)/\beta = x$, the equation (8.37) simplifies to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \quad (8.38)$$

MO energies

The above determinant can be expanded into a polynomial of fourth degree,

$$x^4 - 3x^2 + 1 = 0 \quad (8.39)$$

On solving the equation (8.39), four roots x_j of the polynomial are obtained. They are $x_1 = 1.618$, $x_2 = 0.618$, $x_3 = -0.618$ and $x_4 = -1.618$. The one-electron HMO energies, which are the Huckel eigenvalues, are obtained from the relationship,

$$E_j = \alpha_j + x_j \beta \quad \text{since } x_j = (\alpha - E)/\beta \quad (8.40)$$

For butadiene, on substituting x_j values, the HMO energy levels obtained are shown in Fig. 8.7.

Each MO is shown as a horizontal line. The occupation of the electrons may be indicated by placing a small arrow on the line. The order of filling up of the electrons in the HMOs follows the same rules as that for the filling up of the orbitals of an atom. Thus for *trans*-butadiene in the ground state, the four electrons are placed in the two lowest energy molecular orbitals according to the aufbau principle. Two electrons occupy each molecular orbital in the