



Fig. 10.37 The bonding and antibonding π molecular orbitals of ethene and their energies.

orbitals perpendicular to the σ -framework (ψ_A and ψ_B), each of which is occupied by a single electron, are then used to construct molecular orbitals (Fig. 10.37):

$$\psi = c_A\psi_A + c_B\psi_B \quad (10.11)$$

We show in the following *Justification* that to find the energies and coefficients of the two molecular orbitals that can be formed from these two atomic orbitals we need to solve the following simultaneous equations:

$$\begin{aligned} (H_{AA} - ES_{AA})c_A + (H_{AB} - ES_{AB})c_B &= 0 \\ (H_{BA} - ES_{BA})c_A + (H_{BB} - ES_{BB})c_B &= 0 \end{aligned} \quad \text{Secular equations for ethene} \quad (10.12)$$

In the context of MO theory, these simultaneous equations are called **secular equations**. The H_{JK} are expressions that include various contributions to the energy, including the repulsion between electrons and their attractions to the nuclei; the S_{JK} are the overlap integrals between orbitals on atoms J and K.

Justification 10.3 The secular equations

We begin by substituting eqn 10.11 into the Schrödinger equation written in the form $\hat{H}\psi = E\psi$:

$$c_A\hat{H}\psi_A + c_B\hat{H}\psi_B = c_A E\psi_A + c_B E\psi_B$$

Then we multiply both sides by ψ_A

$$c_A\psi_A\hat{H}\psi_A + c_B\psi_A\hat{H}\psi_B = c_A\psi_A E\psi_A + c_B\psi_A E\psi_B$$

and integrate over all space (with the term $d\tau$ denoting an infinitesimal volume element in three dimensions; in cartesian coordinates, $d\tau = dx dy dz$):

$$c_A \int \psi_A \hat{H} \psi_A d\tau + c_B \int \psi_A \hat{H} \psi_B d\tau = c_A E \int \psi_A \psi_A d\tau + c_B E \int \psi_A \psi_B d\tau$$

E is a constant, so we have been able to take it outside the integral. Now we write

$$H_{AA} = \int \psi_A \hat{H} \psi_A d\tau \quad H_{AB} = \int \psi_A \hat{H} \psi_B d\tau \quad S_{AA} = \int \psi_A \psi_A d\tau \quad S_{AB} = \int \psi_A \psi_B d\tau$$

The preceding equation then becomes

$$c_A H_{AA} + c_B H_{AB} = c_A E S_{AA} + c_B E S_{AB}$$

which is easy to rearrange into the first of eqn 10.12. If instead of multiplying through by ψ_A we multiply by ψ_B , we obtain the second of eqn 10.12.

To simplify the solution of the secular equations Hückel introduced the following drastic approximations:

- All H_{JJ} are set equal to a single quantity α called the **Coulomb integral**.
- All H_{JK} are set equal to zero unless atoms J and K are adjacent, when it is set equal to a single quantity β (a negative quantity) called the **resonance integral**.
- All S_{JJ} are set equal to 1 and all S_{JK} are set equal to 0 whether or not J and K are adjacent.

Mathematical toolbox 10.1 Simultaneous equations and determinants

Two simultaneous equations of the form

$$ax + by = 0$$

$$cx + dy = 0$$

have solutions only if the 'determinant' of the coefficients is equal to zero. In this case we write

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = 0$$

where the term on the left is the determinant and has the following meaning:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

Three simultaneous equations of the form

$$ax + by + cz = 0$$

$$dx + ey + fz = 0$$

$$gx + hy + iz = 0$$

have a solution only if

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = 0$$

This 3×3 determinant expands as follows:

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix}$$

Note the alternation in signs for successive columns. The 2×2 determinants then expand like the one above.

With these 'Hückel approximations' the secular equations become

$$(\alpha - E)c_A + \beta c_B = 0$$

$$\beta c_A + (\alpha - E)c_B = 0$$

Hückel approximation for ethene (10.13a)

As set out in Mathematical toolbox 10.1, these two simultaneous equations have a solution only if the **secular determinant** vanishes:

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0$$

Hückel secular determinant for ethene (10.13b)

This condition is satisfied if

$$E = \alpha \pm \beta$$

Hückel energies for ethene (10.13c)

When each value is substituted into eqn 10.13a, we find:

$$\text{For } E = \alpha + \beta \quad c_A = c_B, \text{ so } \psi = c_A(\psi_A + \psi_B)$$

$$\text{For } E = \alpha - \beta \quad c_A = -c_B, \text{ so } \psi = c_A(\psi_A - \psi_B)$$

(Remember that $\beta < 0$, so $E = \alpha + \beta$ is the lower energy of the two.) These energies and orbitals are represented in Fig. 10.37: they will be recognized as the bonding and antibonding combinations of the $C2p_z$ atomic orbitals. The value of the one unknown, c_A , is found by ensuring that each orbital is normalized, but we do not need its explicit value.

Because there are two electrons to be accommodated, both enter the lower energy orbital and contribute $2\alpha + 2\beta$ to the energy of the molecule. We can also infer that the energy needed to excite a π electron to the antibonding combination is $2|\beta|$. A typical value of β in hydrocarbons is about -2.4 eV, or -230 kJ mol $^{-1}$.