

# 2 Atomic and Molecular Orbitals

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## 2.1 Atomic Orbitals

According to quantum mechanics, an electron bound to an atom cannot possess any arbitrary *energy* or occupy any *position* in space. These characteristics can be determined by solving the time-independent Schrödinger equation:

$$\mathbf{H}\varphi = E\varphi \quad (2.1)$$

where  $\mathbf{H}$  is the *Hamiltonian operator* of the atom. We obtain a set of functions  $\varphi$ , which are termed *atomic orbitals* (AOs). Their mathematical equations are shown in Table 2.1, for the 1s to the 3d orbitals inclusive. With each electron is associated an atomic orbital, whose equation allows the position (or more precisely the probability  $dP$  of finding the electron within a given volume  $dV$ ) and the energy of the electron to be calculated:

$$dP = \varphi\varphi^* dV \quad (2.2)$$

$$E = \int \varphi\mathbf{H}\varphi^* dV = \langle \varphi | \mathbf{H} | \varphi \rangle \quad (2.3)$$

In the above equations,  $\varphi^*$  is the complex conjugate of  $\varphi$ . In the cases which we will cover, it is always possible to choose atomic orbitals which are mathematically real, so we will do this systematically.

### Don't panic!

To *use* frontier orbital theory efficiently, we have to understand its approximations, which define its limitations. This is not really complicated and requires more common sense than mathematical skills. So, don't worry about words like *operator* or about maths that we do not need to use.<sup>1</sup> Just to prove how little maths is in fact required, let us re-examine the previous section point by point.

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<sup>1</sup>Chemistry is like any other science, in that the more we understand maths, the better things are. This does not mean that we have to employ maths continually: after all, a computer is not necessary for a simple sum. Maths is only a tool which allows us to make complicated deductions in the same way that computers allow us to do long calculations: quickly and without mistakes. Remember, though, the computing adage: *garbage in, garbage out*. If a theory is chemically wrong, no amount of mathematics will put it right.

1. In this course, we do not need to know how to solve the Schrödinger equation. In fact, after this chapter, we shall not even use the equations in Table 2.1. Just remember that orbitals are mathematical functions – solutions of Equation (2.1) – which are *continuous* and *normalized* (i.e. the square of  $\psi$  is 1 when integrated over all space).

Equation (2.1) cannot be solved exactly for a polyelectronic atom A because of complications resulting from interelectronic repulsions. We therefore use approximate solutions which are obtained by replacing A with a fictitious atom having the same nucleus but only one electron. For this reason, atomic orbitals are also called *hydrogen-like orbitals* and the orbital theory the *monoelectronic approximation*.

**Table 2.1** Some real atomic orbitals:  $Z$  is the atomic number and  $a$  is the Bohr radius ( $a = \hbar^2/4\pi^2me^2 = 0.53 \times 10^{-8}$  cm)

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a} \right)^{\frac{3}{2}} e^{-Zr/a}$$

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a} \right)^{\frac{3}{2}} \left( 2 - \frac{Zr}{a} \right) e^{-Zr/2a}$$

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a} \right)^{\frac{5}{2}} r e^{-Zr/2a} \cos \theta$$

$$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a} \right)^{\frac{5}{2}} r e^{-Zr/2a} \sin \theta \cos \varphi$$

$$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a} \right)^{\frac{5}{2}} r e^{-Zr/2a} \sin \theta \sin \varphi$$

$$\psi_{3s} = \frac{1}{81\sqrt{3\pi}} \left( \frac{Z}{a} \right)^{\frac{3}{2}} \left( 27 - 18 \frac{Zr}{a} + 2 \frac{Z^2 r^2}{a^2} \right) r e^{-Zr/3a}$$

$$\psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left( \frac{Z}{a} \right)^{\frac{5}{2}} \left( 6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \cos \theta$$

$$\psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left( \frac{Z}{a} \right)^{\frac{5}{2}} \left( 6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \sin \theta \cos \varphi$$

$$\psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left( \frac{Z}{a} \right)^{\frac{5}{2}} \left( 6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \sin \theta \sin \varphi$$

$$\psi_{3d_z^2} = \frac{1}{81\sqrt{6\pi}} \left( \frac{Z}{a} \right)^{\frac{7}{2}} \left( \frac{Z}{a} \right) r^2 e^{-Zr/3a} (3 \cos^2 \theta - 1)$$

**Table 2.1** (Continued)

$$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a}\right)^{\frac{7}{2}} r^2 e^{-Zr/3a} \sin \theta \cos \theta \cos \varphi$$

$$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a}\right)^{\frac{7}{2}} r^2 e^{-Zr/3a} \sin \theta \cos \theta \sin \varphi$$

$$\psi_{3d_{x^2-y^2}} = \frac{\sqrt{2}}{81\sqrt{2\pi}} \left(\frac{Z}{a}\right)^{\frac{7}{2}} r^2 e^{-Zr/3a} \sin^2 \theta \cos 2\varphi$$

$$\psi_{3d_{xy}} = \frac{\sqrt{2}}{81\sqrt{2\pi}} \left(\frac{Z}{a}\right)^{\frac{7}{2}} r^2 e^{-Zr/3a} \sin^2 \theta \sin 2\varphi$$

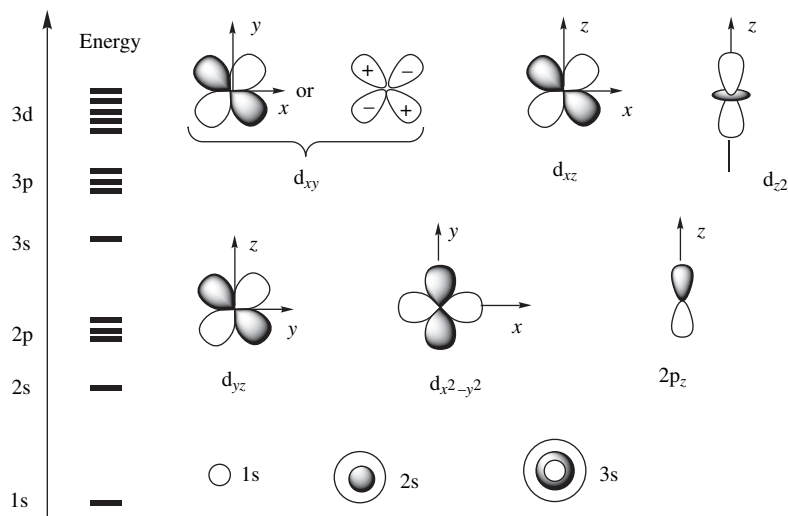
2. An *operator* is merely a symbol which indicates that a mathematical operation must be carried out upon the expression which follows it. Thus:  
3 is the operator ‘multiply by 3’;  
d/dx is the operator ‘total differentiation with respect to x’.

Each quantum mechanical operator is related to one physical property. The Hamiltonian operator is associated with *energy* and allows the energy of an electron occupying orbital  $\varphi$  to be calculated [Equation (2.3)]. We will never need to perform such a calculation. In fact, in perturbation theory and the Hückel method, the mathematical expressions of the various operators are never given and calculations cannot be done. *Any expression containing an operator is treated merely as an empirical parameter.*

If  $a$  is a number and  $x$  and  $y$  are variables, then an operator  $f$  is said to be *linear* if  $f(ax) = af(x)$  and  $f(x + y) = f(x) + f(y)$ . We will often employ the linearity of integrals in Hückel and perturbation calculations because it allows us to rewrite the integral of a sum as a sum of integrals.

By extension, *atomic orbital* has also come to mean a volume, limited by an equiprobability surface, wherein we have a high probability (let us say a 90% chance) of finding an electron. Figure 2.1 depicts the shapes of some atomic orbitals and a scale showing their relative energies. It deserves a few comments:

1. The energy scale is approximate. We only need remember that for a *polyelectronic* atom, the orbital energy within a given shell increases in the order s, p, d and that the first three shells are well separated from each other. However, the 4s and 3d orbitals have very similar energies. As a consequence, the 3d, 4s and 4p levels in the first-row transition metals all function as valence orbitals. The p orbitals are *degenerate* (i.e. the three p AOs of the same shell all have the same energy), as are the five d orbitals.
2. The orbitals of the same shell have more or less the same size. However, size increases with the principal quantum number. Thus a 3p orbital is more diffuse than a 2p orbital.



**Figure 2.1** Shapes and approximate energies of some atomic orbitals.

3. The sign shown inside each orbital lobe is the sign of the function  $\phi$  within that region of space. Taken on its own, this sign has no physical meaning, because the electron probability density is given by the square of  $\phi$  [Equation (2.2)]. For this reason, we often distinguish between two different lobes by hatching or shading one of them, rather than using the symbols + or - (cf. the two representations of the  $d_{xy}$  orbital in Figure 2.1). However, we will see (p. 12) that the *relative signs* of two neighboring atomic orbitals *do* have an important physical significance.

Let us now compare a 1s and a 2s orbital. If we start at the nucleus and move away, the 1s orbital always retains the same sign. The 2s orbital passes through a null point and changes sign afterwards (Figure 2.1). The surface on which the 2s orbital becomes zero is termed a *nodal surface*. The number of nodal surfaces increases with increasing energy: thus the 1s orbital has none, the 2s orbital has one, the 3s has two, etc.

4. Orbitals having the same azimuthal quantum number  $l$  have the same shape: all s orbitals have spherical symmetry and all p orbitals have cylindrical symmetry. The  $d_z^2$  orbital is drawn differently from the other d orbitals but, being a linear combination of  $d_{x^2-x^2}$  and  $d_{x^2-y^2}$  orbitals, it is perfectly equivalent to them. (This statement may be checked, using Table 2.1). The whole field of *stereochemistry* is founded upon the directional character of p and d orbitals.
5. Obviously, an orbital boundary surface defines an interior and an exterior. Outside the boundary, the function  $\phi$  has very small values because its square, summed over all space from the boundary wall to infinity, has a value of only 0.1. Recognizing this fact allows the LCAO approximation to be interpreted in physical terms. When we say that a molecular orbital is a linear combination of AOs, we imply that it is almost indistinguishable from  $\phi_k$  in the neighbourhood of atom  $k$ . This is because we are then inside the boundary of  $\phi_k$  and outside the boundary of  $\phi_l$  ( $l \neq k$ ), so that  $\phi_k$  has finite values and contributions from  $\phi_l$  are negligible. Therefore, an MO is broadly a series of AOs, the size of each AO being proportional to its LCAO coefficient.

Once the AOs are known, their occupancy is determined by:

1. The *Pauli exclusion principle*: each orbital can only contain one electron of any given spin.
2. The *Aufbau principle*: in the ground state (i.e. the lowest energy state), the lowest energy orbitals are occupied first.
3. *Hund's rules*: when *degenerate orbitals* (orbitals having the same energy) are available, as many of them as possible will be filled, using electrons of like spin.

Each electronic arrangement is known as a *configuration* and represents (more or less well) an *electronic state* of the atom.

## 2.2 Molecular Orbitals

All that we have just seen for atoms applies to molecules. Thus the *molecular orbitals* (MOs) of a given compound are the solutions of the Schrödinger equation for a fictitious molecule having the same nuclear configuration but only one electron. Once an MO's expression is known, the energy of an electron occupying it and the probability of finding this electron in any given position in space can be calculated. By extension, the term molecular orbital has also come to mean a volume of space wherein we have a 90% probability of finding an electron. Once the MOs are known, the electrons are distributed among them according to the Aufbau and Pauli principles and, eventually, Hund's rules. Each electronic configuration represents (more or less well) an electronic state of the molecule.<sup>2</sup>

The definitions above are rather abstract. Their meaning will be clarified in the examples given in the following sections. While working through these examples, we will be more concerned with the chemical implications of our results than with the detail of the calculations themselves. It would be a mistake to think that the diatomics we will study are theoreticians' molecules, too simple to be of any interest to an organic chemist. On the contrary, *the results in the next sections are important* because there is no significant conceptual difference between the interaction of two atoms to give a diatomic molecule and the interaction of two molecules to give a transition state, which may be regarded as a 'supermolecule'. Formally, the equations are identical in both cases, and we can obtain the transition state MOs by just taking the diatomic MOs and replacing the atomic orbitals by the reactants' MOs, rather than having to start again from scratch. Hence the study of diatomic molecules provides an understanding of bimolecular reactions. Furthermore, the same general approaches can be used to investigate unimolecular reactions or conformations in isolated molecules. In these cases, it is only necessary to split the molecule into two appropriate fragments, and to treat their recombination as a bimolecular reaction.

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<sup>2</sup>Electronic configurations are the MO equivalents of resonance structures. Sometimes a molecular state cannot adequately be represented by a single configuration, just as benzene or an enolate ion cannot be represented by only one Kekulé structure. The molecular state is then better described by a linear combination of several electronic configurations (*configuration interaction method*).

## 2.3 The MOs of a Homonuclear Diatomic Molecule

### 2.3.1 Calculations

Consider a homonuclear diatomic molecule  $A_2$ , whose two atoms A are identical. For the sake of simplicity, we will assume that each atom uses one (and only one) valence AO to form the bond. These interacting AOs, which we will call  $\varphi_1$  and  $\varphi_2$ , are chosen so as to be mathematically *real*. The following procedure is used to calculate the resulting MOs:

1. The two nuclei are held at a certain fixed distance from each other (i.e. we apply the Born–Oppenheimer approximation).
2. The time-independent Schrödinger Equation (2.4) is written for the molecule, multiplied on the left-hand side by  $\Psi$ , and integrated over all space [Equation (2.5)]:

$$\mathbf{H}\Psi = E\Psi \quad (2.4)$$

$$\langle \Psi | \mathbf{H} | \Psi \rangle = E \langle \Psi | \Psi \rangle \quad (2.5)$$

3. Each MO is expressed as a linear combination of atomic orbitals (LCAOs):

$$\Psi = c_1\varphi_1 + c_2\varphi_2 \quad (2.6)$$

In Equation (2.6), we know  $\varphi_1$  and  $\varphi_2$ . Calculating an MO  $\Psi_i$  therefore involves evaluating its associated energy  $E_i$  and the coefficients  $c_{i1}$  and  $c_{i2}$  of its LCAO expansion. Incorporating Equation (2.6) in Equation (2.5) gives

$$\langle c_1\varphi_1 + c_2\varphi_2 | \mathbf{H} | c_1\varphi_1 + c_2\varphi_2 \rangle = E \langle c_1\varphi_1 + c_2\varphi_2 | c_1\varphi_1 + c_2\varphi_2 \rangle \quad (2.7)$$

The linearity of integrals (p. 7), allows the left-hand side of Equation (2.7) to be expressed as

$$\begin{aligned} \langle c_1\varphi_1 + c_2\varphi_2 | \mathbf{H} | c_1\varphi_1 + c_2\varphi_2 \rangle &= \langle c_1\varphi_1 | \mathbf{H} | c_1\varphi_1 \rangle + \langle c_1\varphi_1 | \mathbf{H} | c_2\varphi_2 \rangle + \dots \\ &= c_1^2 \langle \varphi_1 | \mathbf{H} | \varphi_1 \rangle + c_2^2 \langle \varphi_2 | \mathbf{H} | \varphi_2 \rangle + \dots \end{aligned}$$

To express this more simply, let us set

$$\langle \varphi_i | \mathbf{H} | \varphi_i \rangle = \alpha_i$$

$$\langle \varphi_i | \mathbf{H} | \varphi_j \rangle = \beta_{ij}$$

$$\langle \varphi_i | \varphi_j \rangle = S_{ij}$$

where  $\alpha_i$  is termed the *Coulomb integral*,  $\beta_{ij}$  the *resonance integral* and  $S_{ij}$  the *overlap integral*. We are using normalized AOs, so  $S_{ii} = 1$ . Furthermore, the two atoms are identical,<sup>3</sup> so

$$\alpha_1 = \alpha_2 \quad \text{and} \quad \beta_{12} = \beta_{21}$$

<sup>3</sup>In physical terms,  $\beta_{12} = \beta_{21}$  simply means that the force binding atom 1 to atom 2 is the same as the force binding 2 to 1.

Thus, Equation (2.7) can be written as

$$(c_1^2 + c_2^2)\alpha + 2c_1c_2\beta - E(c_1^2 + c_2^2 + 2c_1c_2S) = 0 \quad (2.8)$$

where  $\alpha$ ,  $\beta$  and  $S$  are parameters and  $c_1$ ,  $c_2$  and  $E$  are unknowns.

4. Let us now choose  $c_1$  and  $c_2$  so as to minimize  $E$  (*variational method*). To do this, we differentiate Equation (2.8), and set the partial derivatives to zero:

$$\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0$$

thus obtaining the *secular equations*:

$$\begin{aligned} (\alpha - E)c_1 + (\beta - ES)c_2 &= 0 \\ (\beta - ES)c_1 + (\alpha - E)c_2 &= 0 \end{aligned} \quad (2.9)$$

These equations are homogeneous in  $c_i$ . They have a nontrivial solution if the *secular determinant* (i.e. the determinant of the coefficients of the secular equations) can be set to zero:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0 \quad (2.10)$$

The solutions to Equation (2.10) are

$$E_1 = \frac{\alpha + \beta}{1 + S} \quad \text{and} \quad E_2 = \frac{\alpha - \beta}{1 - S} \quad (2.11)$$

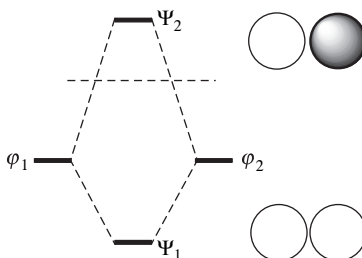
$E_1$  and  $E_2$  are the only energies which an electron belonging to the diatomic molecule  $A_2$  can have. Each energy level  $E_i$  is associated with a molecular orbital  $\Psi_i$ , whose coefficients may be obtained by setting  $E = E_i$  in Equation (2.9) and solving these equations, taking into account the normalization condition:

$$\langle \Psi_i | \Psi_i \rangle = c_{i1}^2 + c_{i2}^2 + 2c_{i1}c_{i2}S = 1 \quad (2.12)$$

The solutions are

$$\Psi_1 = \frac{1}{\sqrt{2(1+S)}}(\varphi_1 + \varphi_2) \quad \text{and} \quad \Psi_2 = \frac{1}{\sqrt{2(1-S)}}(\varphi_1 - \varphi_2) \quad (2.13)$$

Figure 2.2 gives a pictorial representation of Equation (2.11) and (2.13).



**Figure 2.2** The MOs of the homonuclear diatomic  $A_2$ .  $\varphi_1$  and  $\varphi_2$  are arbitrarily drawn as orbitals. Note that the destabilization of  $\Psi_2$  is greater than the stabilization of  $\Psi_1$ .

### 2.3.2 A Physical Interpretation

#### Molecular Orbitals

As we can see from Figure 2.2, the approach of two atoms to form a molecule is accompanied by the mixing of their two AOs to form two MOs. One,  $\Psi_1$ , lies at lower energy than the isolated AOs whereas the other,  $\Psi_2$ , is at higher energy.

The destabilization of  $\Psi_2$  with respect to the parent atomic orbitals is greater than the stabilization of  $\Psi_1$ , so the stability of the product will depend on the number of its electrons. When the molecule has one or two electrons, the Aufbau principle states that they will occupy  $\Psi_1$ , which has a lower energy than the orbitals in the separated atoms. Hence the molecule is stable with respect to the atoms. This analysis explains the phenomenon of *covalent bonds*.<sup>4</sup>

If the system contains three electrons, the two occupying  $\Psi_1$  will be stabilized, and the other one, localized in  $\Psi_2$ , destabilized. Here, the stability of the molecule depends upon the relative energies of  $\Psi_1$ ,  $\Psi_2$  and the AOs: thus, HHe dissociates spontaneously, but the three-electron bond in  $\text{He}_2^+$  is moderately robust. Note that, in contradiction with Lewis theory, a covalent bond may be formed with one or three electrons. Electron-deficient bonds (where there are fewer than two electrons per bond) are particularly prevalent amongst boron compounds.

If the system contains four electrons, two will be stabilized but the other two are destabilized to a greater extent. The molecule is then unstable with respect to the separated atoms. This is why the inert gases, where all the valence orbitals are doubly occupied, exist as atoms rather than behaving like hydrogen, oxygen or nitrogen and combining to give diatomic molecules. The mutual repulsion which occurs between filled shells is the MO description of *steric repulsion*.

Let us now turn to the LCAO expansions of  $\Psi_1$  and  $\Psi_2$ . In  $\Psi_1$ , the AOs are in phase (they have the same sign). Thus,  $\Psi_1$  has its greatest amplitude in the region between the two nuclei, where the AOs reinforce each other. An electron occupying  $\Psi_1$  therefore has a high chance of being found in this internuclear region. Having a negative charge, it attracts the two (positive) nuclei and holds them together.<sup>5</sup> Hence, orbitals such as  $\Psi_1$  are termed *bonding orbitals*.

In  $\Psi_2$ , the AOs have opposite phases, so  $\Psi_2$  has different signs on  $A_1$  and  $A_2$ .  $\Psi_2$  is continuous, so it must pass through zero between  $A_1$  and  $A_2$ . Consequently, an electron occupying  $\Psi_2$  has only a small chance of being localized in the internuclear region where it can produce a bonding contribution. In fact, such an electron tends to break the bond: in the process, it can leave  $\Psi_2$  for a lower lying AO. Hence the name *antibonding orbitals* is given to orbitals like  $\Psi_2$ .

These results will be used frequently in this book in the following form:

<sup>4</sup>Note that this kind of bond cannot be explained by classical physics. Two atoms will only form a bond if an attractive force holds them together. Newtonian gravitational forces are too weak, and Coulombian interactions require that the atoms have opposite charges, which is difficult to accept when the atoms are identical.

<sup>5</sup>Kinetic energy terms, which are more favorable in an MO than in an AO, also play a significant role in promoting bonding (Kutzelnigg W., *Angew. Chem. Int. Ed. Engl.*, 1973, **12**, 546).



An in-phase overlap is bonding and lowers the MO energy, whereas an out-of-phase overlap is antibonding and raises the MO energy.

### The Parameters

#### The Coulomb Integral $\alpha$

To a first approximation, the Coulomb integral  $\alpha_A$  gives the energy of an electron occupying the orbital  $\varphi_A$  in the isolated atom A. Therefore, its absolute value represents the energy required to remove an electron from  $\varphi_A$  and place it at an infinite distance from the nucleus where, by convention, its energy is zero. Consequently,  $\alpha_A$  is always negative and its absolute value increases with the *electronegativity* of A.

#### The Resonance Integral $\beta$

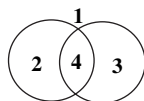
The absolute value of the resonance integral gives a measure of the  $A_1A_2$  bond strength.<sup>6</sup> It increases with increasing overlap. We will see that  $S_{12}$  measures the volume common to  $\varphi_1$  and  $\varphi_2$ , which encloses the electrons shared by  $A_1$  and  $A_2$ . Large values of  $S_{12}$  thus imply strong bonding between  $A_1$  and  $A_2$ . When  $S_{12}$  is zero,  $\beta_{12}$  is also zero. It follows that two orthogonal orbitals cannot interact with each other. Conversely, the more two orbitals overlap, the more they interact. *Stereoelectronic control* results from this *principle of maximum overlap*: the best trajectory is that corresponding to the best overlap between the reagent and the substrate. The principle of maximum overlap is often expressed in terms of the *Mulliken approximation*:

$$\beta_{12} \approx kS_{12} \quad (2.14)$$

where the proportionality constant  $k$  is negative. Basis AOs are generally chosen with the same sign, so the overlap integrals are positive and the resonance integrals negative.

#### The Overlap Integral

Consider two overlapping orbitals  $\varphi_i$  and  $\varphi_j$ . They define four regions in space:



- Region **1** lies outside  $\varphi_i$  and  $\varphi_j$ , where both orbitals have small values. The product  $\varphi_i \varphi_j$  is negligible.
- Region **2** (enclosed by  $\varphi_i$  but outside  $\varphi_j$ ) and region **3** (enclosed by  $\varphi_j$  but outside  $\varphi_i$ ) also have negligible values for  $\varphi_i \varphi_j$ : one component is appreciable, but the other is very small.
- Region **4**, where both  $\varphi_i$  and  $\varphi_j$  are finite. The value of  $S_{ij}$  comes almost exclusively from this region where the two orbitals overlap (hence the term 'overlap integral').

<sup>6</sup> $\beta_{12}$  is sometimes said to represent the coupling of  $\varphi_1$  with  $\varphi_2$ . This originates in the mathematical analogy between the interaction of two AOs and the coupling of two pendulums. The term resonance integral has similar roots (Coulson C. A., *Valence*, Oxford University Press, Oxford, 2nd edn, p. 79).

### Mulliken Analysis

The MOs in the diatomic molecules discussed above have only two coefficients, so their chemical interpretation poses few problems. The situation becomes slightly more complicated when the molecule is polyatomic or when each atom uses more than one AO. *Overlap population* and *net atomic charges* can then be used to give a rough idea of the electronic distribution in the molecule.

#### Overlap Population

Consider an electron occupying  $\Psi_1$ . Its probability density can best be visualized as a cloud carrying an overall charge of one electron. To obtain the shape of this cloud, we calculate the square of  $\Psi_1$ :

$$\langle \Psi_1 | \Psi_1 \rangle = c_{11}^2 \langle \phi_1 | \phi_1 \rangle + 2c_{11}c_{12}S_{12} + c_{12}^2 \langle \phi_2 | \phi_2 \rangle = 1 \quad (2.15)$$

Equation (2.15) may be interpreted in the following way. Two portions of the cloud having charges of  $c_{11}^2$  and  $c_{12}^2$  are essentially localized within the orbitals  $\phi_1$  and  $\phi_2$  and 'belong' to  $A_1$  and  $A_2$ , respectively. The remainder has a charge of  $2c_{11}c_{12}S$  and is concentrated within the zone where the two orbitals overlap. Hence this last portion is termed the *overlap population* of  $A_1A_2$ . It is positive when the AOs overlap in phase (as in  $\Psi_1$ ) and negative when they are out of phase (as in  $\Psi_2$ ). The overlap population gives the fraction of the electron cloud shared by  $A_1$  and  $A_2$ . A positive overlap population strengthens a bond, whereas a negative one weakens it. We can therefore take  $2c_{11}c_{12}S$  as a rough measure<sup>7</sup> of the  $A_1A_2$  bond strength.

#### Net Atomic Charges

It is often useful to assign a net charge to an atom. This allows the nuclei and electron cloud to be replaced by an ensemble of point charges, from which the dipole moment of the molecule can be easily calculated. It also allows the reactive sites to be identified: positively charged atoms will be preferentially attacked by nucleophiles, whereas negatively charged atoms will be favored sites for electrophiles.<sup>8</sup>

The *net charge* on an atom is given by the algebraic sum of its nuclear charge  $q_n$  and its electronic charge  $q_e$ . The latter is usually evaluated using the Mulliken partition scheme, which provides a simple way of dividing the electron cloud among the atoms of the molecule. Consider an electron occupying the molecular orbital  $\Psi_1$  of the diatomic  $A_1A_2$ . The contribution of this electron to the electronic charge of  $A_1$  is then  $c_{11}^2$  plus half of the overlap population. In the general case:

$$q_e(\text{A}) = \sum_{i,j} n_i c_{i\text{A}} c_{j\text{A}} S_{ij} \quad (2.16)$$

<sup>7</sup>In a polyelectronic molecule, it is necessary to sum over all electrons and calculate the total overlap population to obtain a measure of the bond strength.

<sup>8</sup>This rule is not inviolable. See pp. 87, 96 and 175.

where  $S_{Aj}$  is the overlap integral of  $\varphi_A$  and  $\varphi_j$ ,  $n_i$  is the number of electrons which occupy  $\Psi_i$  and  $c_{iA}$  and  $c_{ij}$  are the coefficients of  $\varphi_A$  and  $\varphi_j$  in the same MO. The summation takes in all of the MOs  $\Psi_i$  and all of the atoms  $j$  in the molecule.

## 2.4 MOs of a Heteronuclear Diatomic Molecule

### 2.4.1 Calculations

A heteronuclear diatomic molecule is comprised of two different atoms A and B. For simplicity, we will again assume that only one AO on each atom is used to form the bond between A and B. The two relevant AOs are then  $\varphi_A$  of energy  $\alpha_A$  and  $\varphi_B$  of energy  $\alpha_B$ . The calculation is completely analogous to the case of the homonuclear diatomic given above. For a heteronuclear diatomic molecule AB, Equation (2.10) – where the secular determinant is set to zero – becomes

$$(\alpha_A - E)(\alpha_B - E) - (\beta - ES)^2 = 0 \quad (2.17)$$

Equation (2.17) is a second-order equation in  $E$  which can be solved exactly. However, the analogs of expressions Equation (2.11) and (2.13) are rather unwieldy. For qualitative applications, they can be approximated as follows:

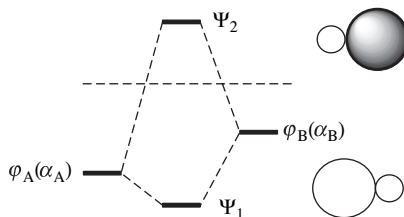
$$E_1 \approx \alpha_A + \frac{(\beta - \alpha_A S)^2}{\alpha_A - \alpha_B} \quad E_2 \approx \alpha_B + \frac{(\beta - \alpha_B S)^2}{\alpha_B - \alpha_A} \quad (2.18)$$

$$\Psi_1 \approx N_1 \left( \varphi_A + \frac{\beta - \alpha_A S}{\alpha_A - \alpha_B} \varphi_B \right) \quad \Psi_2 \approx N_2 \left( \varphi_B + \frac{\beta - \alpha_B S}{\alpha_B - \alpha_A} \varphi_A \right) \quad (2.19)$$

where  $N_1$  and  $N_2$  are normalization coefficients. Equations (2.18) assume that  $E_1$  and  $E_2$  are not very different from  $\alpha_A$  and  $\alpha_B$ , respectively. Using this approximation, it is possible to rewrite Equation (2.17) in the form

$$\alpha_A - E_1 = \frac{(\beta - E_1 S)^2}{\alpha_B - E_1} \approx \frac{(\beta - \alpha_A S)^2}{\alpha_B - \alpha_A} \quad (2.20)$$

which is equivalent to Equations (2.18). Equations (2.18) and (2.19) are shown pictorially in Figure 2.3.



**Figure 2.3** MOs of a heteronuclear diatomic molecule.  $\varphi_A$  and  $\varphi_B$  are arbitrarily shown as s orbitals.

## 2.4.2 A Physical Interpretation

Figure 2.3 shows that combination of the two AOs  $\phi_A$  and  $\phi_B$  (having energies  $\alpha_A < \alpha_B$ ) produces two MOs: one,  $\Psi_1$ , has lower energy than  $\alpha_A$ , whereas the other,  $\Psi_2$ , has higher energy than  $\alpha_B$ . The destabilization of  $\Psi_2$  with respect to  $\alpha_B$  is always larger than the stabilization of  $\Psi_1$  with respect to  $\alpha_A$ . The bonding MO  $\Psi_1$  comprises mainly  $\phi_A$ , with a small contribution from an in-phase mixing with  $\phi_B$ ; the antibonding orbital  $\Psi_2$  is mainly  $\phi_B$ , with a small out-of-phase contribution from  $\phi_A$ . Hence we can consider  $\Psi_1$  as the  $\phi_A$  orbital slightly perturbed by  $\phi_B$  and  $\Psi_2$  as the  $\phi_B$  orbital perturbed by  $\phi_A$ . This is the physical meaning of the right-hand side of Equations (2.18) and (2.19), which is why they appear as a main term and a correction. It is convenient to write the denominator of the correction in the form (energy of the perturbed orbital minus the energy of the perturbing orbital). The correction will then have a positive sign.

The stabilization of  $\Psi_1$  with respect to  $\alpha_A$  and the destabilization of  $\Psi_2$  with respect to  $\alpha_B$  increase as the  $\alpha_A - \alpha_B$  energy gap decreases, the maximum being attained when the two AO's are degenerate ( $\alpha_A = \alpha_B$ ), i.e. as in a homonuclear diatomic molecule. Comparison with Equations (2.11) and (2.13) shows that Equations (2.18) and (2.19) are only valid when

$$|\alpha_A - \alpha_B| > |\beta - \alpha_A S| \quad (2.21)$$

The physical meaning of this inequality is obvious: the correction can never be larger than the principal term. We will return to this point in the next chapter.

## 2.5 $\pi$ MOs of Polyatomic Molecules

### 2.5.1 The Hückel Method for Polyatomic Molecules

In many exercises where only  $\pi$  systems are considered, we will employ Hückel calculations.<sup>9</sup> For polyenes, these simple calculations reproduce *ab initio* energies and coefficients fairly well.

#### *The Hückel Method Applied to the Allyl System*

We use the same approach as for diatomic molecules and begin with the Schrödinger Equation (2.22), which we multiply by  $\Psi$  on the left-hand side and integrate over all space [Equation (2.23)]. After replacing  $\Psi$  by its LCAOs [Equation (2.24)], we obtain Equation (2.25):

$$\mathbf{H}\Psi = E\Psi \quad (2.22)$$

$$\langle \Psi | H | \Psi \rangle = E \langle \Psi | \Psi \rangle \quad (2.23)$$

<sup>9</sup>For details on the different types of calculations (*ab initio*, semi-empirical, etc.), see Chapter 8.

$$\Psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 \quad (2.24)$$

$$\begin{aligned} & \langle c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 | \mathbf{H} | c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 \rangle \\ & = E \langle c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 | c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 \rangle \end{aligned} \quad (2.25)$$

The Hückel treatment assumes that:<sup>10</sup>

- (a) each Coulomb integral has the same value:

$$\alpha_1 = \alpha_2 = \alpha_3 = \alpha \quad (2.26)$$

- (b) the resonance integral is the same for any two neighboring atoms and zero for any two atoms not directly bound to each other:

$$\begin{aligned} \beta_{13} &= 0 \\ \beta_{12} &= \beta_{23} = \beta \end{aligned} \quad (2.27)$$

- (c) the overlap integrals  $S_{ij}$  are zero when  $i \neq j$  and 1 when  $i = j$ :

$$S_{ij} = \delta_{ij} \quad (\delta_{ij} = \text{Kronecker symbol}) \quad (2.28)$$

Equation (2.25) then becomes

$$(\alpha - E)(c_1^2 + c_2^2 + c_3^2) + 2\beta(c_1c_2 + c_2c_3) = 0 \quad (2.29)$$

Differentiating Equation (2.29) and zeroing each partial derivative of  $E$  with respect to  $c_i$ , we obtain the secular equations:

$$\begin{aligned} (\alpha - E)c_1 + \beta c_2 &= 0 \\ \beta c_1 + (\alpha - E)c_2 + \beta c_3 &= 0 \\ \beta c_2 + (\alpha - E)c_3 &= 0 \end{aligned} \quad (2.30)$$

Writing  $x = (\alpha - E) / \beta$  and setting the secular determinant to zero, this gives

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x(x^2 - 2) = 0 \quad (2.31)$$

whose roots are  $x = 0$  and  $x = \pm \sqrt{2}$ . Hence an electron may have one of three possible energies:

$$\begin{aligned} E_1 &= \alpha + \sqrt{2}\beta \\ E_2 &= \alpha \\ E_3 &= \alpha - \sqrt{2}\beta \end{aligned} \quad (2.32)$$

which increase down the page. Substituting these energies into Equation (2.30) and normalizing according to

<sup>10</sup>The validity of these approximations is discussed in Anh N. T., *Introduction à la Chimie Moléculaire*, Ellipses, Paris, 1994, p. 200.

$$\langle \Psi_i | \Psi_i \rangle = c_{i1}^2 + c_{i2}^2 + c_{i3}^2 = 1 \quad (2.33)$$

we find that:

$$\begin{aligned} \Psi_1 &= 0.5(\varphi_1 + \varphi_3) + 0.707\varphi_2 \\ \Psi_2 &= 0.707(\varphi_1 - \varphi_3) \\ \Psi_3 &= 0.5(\varphi_1 + \varphi_3) - 0.707\varphi_2 \end{aligned} \quad (2.34)$$

Any electrons found in  $\Psi_2$  have the same energy  $\alpha$  as an electron in an isolated carbon atom. Hence they neither stabilize nor destabilize the allyl system. For this reason,  $\Psi_2$  is termed a *nonbonding orbital*.

### Coulson Formulae for Linear Polyenes

*Linear polyenes* are unbranched, open-chain conjugated hydrocarbons having the general formula  $C_n H_{n+2}$ . Coulson<sup>11</sup> has shown that the energy levels of a linear polyene having  $N$  atoms are given by Equation (2.35), with MOs labeled in order of increasing energy:

$$E_p = \alpha + 2\beta \cos\left(\frac{p\pi}{N+1}\right) \quad (2.35)$$

The coefficient  $c_{pk}$  of  $\varphi_k$  in the  $\Psi_p$  MO is given by

$$c_{pk} = \sqrt{\frac{2}{N+1}} \sin\left(\frac{pk\pi}{N+1}\right) \quad (2.36)$$

With respect to the median plane of a rectilinear polyene, atoms  $k$  and  $N - k + 1$  are symmetrical. Now, the coefficient of atom  $(N - k + 1)$  is given by

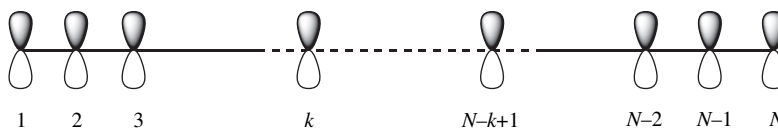
$$c_{p,N-k+1} = \sqrt{\frac{2}{N+1}} \sin\left[\frac{p(N-k+1)\pi}{N+1}\right] = \sqrt{\frac{2}{N+1}} \sin\left(p\pi - \frac{pk\pi}{N+1}\right)$$

Since

$$\sin(p\pi - x) = \sin x \quad \text{if } p \text{ is odd}$$

$$\sin(p\pi - x) = -\sin x \quad \text{if } p \text{ is even}$$

it follows that *all odd-numbered MOs are symmetrical*, i.e. the coefficients at  $C_1$  and  $C_N$ , at  $C_2$  and  $C_{N-1}$ , etc., are identical. *All even-numbered MOs are antisymmetrical*, i.e. these coefficients are equal, but have opposite signs.



<sup>11</sup>Coulson C. A., *Proc. R. Soc. London*, 1939, **A169**, 413; Coulson C. A., Longuet-Higgins H. C., *Proc. Ry. Soc. London*, 1947, **A192**, 16; Coulson C. A., *Proc. Ry. Soc. London*, 1938, **A164**, 383.

We have just seen that coefficients at  $C_1$  and  $C_n$  are either identical or opposite. According to formula Equation (2.36), they vary as

$$\sin\left(\frac{p\pi}{N+1}\right) \text{ with } p = 1, 2, 3, \dots, N$$

Therefore, *the coefficients at the terminal atoms rise steadily, reaching a maximum in the HOMO and the LUMO, and then decline.* These properties will be useful for the derivation of the selection rules of pericyclic reactions.

### Bond Orders and Net Charges

The overlap population is always zero in a Hückel calculation ( $S_{ij} = 0$ ), so we employ a *bond order*  $p_{rs}$  to estimate the strength of a  $\pi$  bond between two atoms  $r$  and  $s$ . It is defined as

$$p_{rs} = \sum_j n_j c_{jr} c_{js} \quad (2.37)$$

where  $n_j$  represents the number of electrons and  $c_{jr}$  and  $c_{js}$  the coefficients of  $r$  and  $s$ , respectively, in  $\Psi_j$ . The summation includes all of the occupied orbitals (the vacant orbitals can be neglected, because  $n_j = 0$ ). Therefore, the bond index  $p_{rs}$  is simply an overlap population obtained using Hückel coefficients and an arbitrary value of 0.5 for  $S_{rs}$ .<sup>12</sup> The electronic charge on the atom  $r$  is given by

$$q_e^{(r)} = \sum_j n_j c_{jr}^2 \quad (2.38)$$

and its *net charge* is the sum of  $q_e^{(r)}$  and its nuclear charge  $q_n^{(r)}$ .

#### \*Exercise 1 (E)<sup>13</sup>

- Use Coulson's equations to derive the  $\pi$  molecular orbitals of butadiene.
- Calculate the bond orders  $p_{12}$ ,  $p_{23}$ ,  $p_{34}$ . These results are a great success for Hückel theory. Why?

#### Answer

$$\begin{aligned} (1) \quad \Psi_1 &= 0.37(\varphi_1 + \varphi_4) + 0.60(\varphi_2 + \varphi_3) & E_1 &= \alpha + 1.618\beta \\ \Psi_2 &= 0.60(\varphi_1 - \varphi_4) + 0.37(\varphi_2 - \varphi_3) & E_2 &= \alpha + 0.618\beta \\ \Psi_3 &= 0.60(\varphi_1 + \varphi_4) - 0.37(\varphi_2 + \varphi_3) & E_3 &= \alpha - 0.618\beta \\ \Psi_4 &= 0.37(\varphi_1 - \varphi_4) - 0.60(\varphi_2 - \varphi_3) & E_4 &= \alpha - 1.618\beta \end{aligned}$$

- In the ground state, only  $\Psi_1$  and  $\Psi_2$  are occupied. Each contains two electrons. Using formula Equation (2.37), we see that

<sup>12</sup>A bond order for two nonbonded atoms is meaningless, as  $S_{rs}$  is then zero.

<sup>13</sup>For the meaning of asterisks, (E), (M), etc., see the Preface.

$$p_{12} = p_{34} = 2(0.37 \times 0.60) + 2(0.60 \times 0.37) = 0.89$$

$$p_{23} = 2(0.60 \times 0.60) - 2(0.37 \times 0.37) = 0.45$$

The  $p_{23}$  index is smaller than the others, which suggests that the central bond is weaker. Thus the calculation reproduces the alternating single and double bonds, even though the same resonance integral was used for all of them.

### Exercise 2 (M)

- (1) Calculate the bond orders for ethylene in (a) the ground state and (b) the first excited state ( $\pi \rightarrow \pi^*$ ). What are the chemical consequences of these results?
- (2) Introduce overlap [using Equation (2.13) and Figure 2.2]. What conformation would the ethylene excited state have if it were sufficiently long-lived to reach equilibrium?

### Answer

- (1) According to Coulson's equations, the  $\pi$  MOs of ethylene are:

$$\Psi_1 = 0.707(\varphi_1 + \varphi_2) \quad \text{with} \quad E_1 = \alpha + \beta$$

$$\Psi_2 = 0.707(\varphi_1 - \varphi_2) \quad \text{with} \quad E_2 = \alpha - \beta$$

In the ground state  $\Psi_1$  contains two electrons. The bond order is given by

$$p_{12} = 2 \times 0.707^2 = 1$$

$\Psi_1$  and  $\Psi_2$  both contain one electron in the excited state, so the bond order becomes

$$p_{12} = 0.707^2 - 0.707^2 = 0$$

and the  $\pi$  bond disappears. Since only a  $\sigma$  bond links the carbon atoms, they can rotate freely about the C–C axis. Hence alkenes can be isomerized by irradiation. It is worth remembering that one of the key steps in vision involves the photochemical isomerization of *cis*- to *trans*-rhodopsin.

- (2) If overlap is neglected, the destabilization due to the antibonding electron is exactly equal to the stabilization conferred by the bonding electron. However, the destabilizing effects become greater when overlap is introduced [cf. Equations (2.11) and (2.14)]. When the p orbitals are orthogonal, the overlap is zero and the destabilization disappears. As a result, this conformation is adopted in the ethylene excited state.

### \* Exercise 3 (E)

Calculate the net atomic charges in the allyl cation.

### Answer

In the allyl cation, the two electrons are both found in  $\Psi_1$ . The charges are:

$$q_1 = q_3 = 2 \times 0.5^2 = 0.5 \quad \text{net charge: } 0.5$$

$$q_2 = 2 \times 0.707^2 = 1 \quad \text{net charge: } 0$$

So, the positive charge is divided equally between the terminal atoms.



## 2.5.2 How to Calculate Hückel MOs

Why should we use Hückel calculations in some exercises, when it is now so easy to do semi-empirical or *ab initio* calculations? There are two reasons. First, experimentalists often need only rapid 'back of an envelope' solutions, which can be readily obtained with Hückel calculations. Second, there is a close analogy between the formalisms of Hückel and perturbation methods. Understanding Hückel calculations will help you master perturbation theory.

Most modern Hückel programs will accept the molecular structure as the input. In older programs, the input requires the *kind of atoms* present in the molecule (characterized by their Coulomb integrals  $\alpha_i$ ) and the way in which they are *connected* (described by the resonance integrals  $\beta_{ij}$ ). These are fed into the computer in the form of a *secular determinant*. Remember that the Coulomb and resonance integrals cannot be calculated (the mathematical expression of the Hückel Hamiltonian being unknown) and must be treated as empirical parameters.

### Choosing the Parameters $\alpha$ and $\beta$

#### Heteroatoms

Theoreticians call any non-hydrogen atom a *heavy* atom, and any heavy atom other than carbon a *heteroatom*. In the Hückel model, all carbon atoms are assumed to be the same. Consequently, their Coulomb and resonance integrals never change from  $\alpha$  and  $\beta$ , respectively. However, heteroatom X and carbon have different electronegativities, so we have to set  $\alpha_X \neq \alpha$ . Equally, the C-X and C-C bond strengths are different, so that  $\beta_{CX} \neq \beta$ . Thus, for heteroatoms, we employ the modified parameters

$$\begin{aligned}\alpha_X &= \alpha + k\beta \\ \beta_{CX} &= h\beta\end{aligned}\tag{2.39}$$

When  $i$  and  $j$  are both heteroatoms, we can take  $\beta_{ij} = h_i h_j \beta$ . The recommended values for X = O, N, F, Cl, Br and Me are given in Table 2.2. The exact numerical values of these parameters are not crucially important but it is essential that values of  $\alpha_i$  appear in the correct order of electronegativity and  $\beta_{ij}$  in the correct order of bond strength.<sup>14</sup>

#### Alkyl Substituents

Hückel calculations are very approximate, so it is pointless to use oversophisticated models. Therefore, all alkyl substituents can be treated as methyl groups.

The methyl group is represented as a doubly occupied orbital of energy  $\alpha + \beta$  (Table 2.2). This may need some explanation. In a methyl group, the hydrogen s orbitals and the carbon valence orbitals combine to give seven three-dimensional 'fragment orbitals', which are shown on p. 188. Only two of these,  $\pi'_{\text{Me}}$  and  $\pi'^*_{\text{Me}}$  can conjugate with a neighboring  $\pi$  system: the others are orthogonal to it and cannot overlap. Hence, in

<sup>14</sup>Minot C., Anh N. T., *Tetrahedron*, 1977, **33**, 533.

**Table 2.2** Some Hückel parameters for heteroatoms, after Streitwieser<sup>15</sup>

| Atom or group | Coulomb integral                         | Resonance integral              |
|---------------|--|---------------------------------|
| Oxygen        |  |                                 |
| One electron  | $\alpha_{\text{O}} = \alpha + \beta$     | $\beta_{\text{CO}} = \beta$     |
| Two electrons | $\alpha_{\text{O}} = \alpha + 2\beta$    | $\beta_{\text{CO}} = 0.8\beta$  |
| Nitrogen      |  |                                 |
| One electron  | $\alpha_{\text{N}} = \alpha + 0.5\beta$  | $\beta_{\text{CN}} = \beta$     |
| Two electrons | $\alpha_{\text{N}} = \alpha + 1.5\beta$  | $\beta_{\text{CN}} = 0.8\beta$  |
| Fluorine      | $\alpha_{\text{F}} = \alpha + 3\beta$    | $\beta_{\text{CF}} = 0.7\beta$  |
| Chlorine      | $\alpha_{\text{Cl}} = \alpha + 2\beta$   | $\beta_{\text{CCl}} = 0.4\beta$ |
| Bromine       | $\alpha_{\text{Br}} = \alpha + 1.5\beta$ | $\beta_{\text{CBr}} = 0.3\beta$ |
| Methyl        | $\alpha_{\text{Me}} = \alpha + 2\beta$   | $\beta_{\text{CMe}} = 0.7\beta$ |

calculations restricted to  $\pi$  orbitals, a methyl group can be represented *rigorously* by two orbitals: one bonding and doubly occupied the other antibonding and empty. The empty antibonding orbital is well removed from the  $\alpha$  level, so it has little effect upon the system and can be ignored.

### The Methyl Inductive Effect

Neglecting the  $\pi'^*_{\text{Me}}$  orbital amounts to assimilating the methyl group to an electron pair, in other words to consider that it has a pure  $\pi$ -donating effect. This is chemically reasonable.<sup>16</sup> In fact, a methyl is a  $\sigma$ -attracting and  $\pi$ -donating group.<sup>17</sup> This is the reason why, in the gas phase, the acidity order of amines increases with substitution as does *also their basicity order*:  $\text{Me}_3\text{N} > \text{Me}_2\text{HN} > \text{MeH}_2\text{N} > \text{H}_3\text{N}$ !

The nature of methyl inductive effect was the subject of a controversy in the 1960 and 1970s. However, a careful perusal of the literature shows in fact no contradiction, the criteria used being different with the authors. Those favoring an electron-donating effect based their arguments on the Markownikov rule, the Hammett equation and the acidity order of alcohols *in solution*. Authors advocating an electron-withdrawing effect justified their idea with NMR spectra, quantum mechanical calculations of atomic charges of molecules *in the gas phase* and acidity order of alcohols *in the gas phase*.

The inductive effect, as many other 'effects' in organic chemistry, is not an observable and cannot be defined precisely, in an objective manner. It is therefore not surprising that different criteria led to different conclusions. See Minot *et al.*<sup>16</sup> for a more detailed discussion.

<sup>15</sup>Streitwieser A., *Molecular Orbital Theory for Organic Chemists*, John Wiley & Sons, Inc., New York, 1961, p. 135

<sup>16</sup>Minot C., Eisenstein O., Hiberty P. C., Anh N. T., *Bull. Soc. Chim. Fr. II*, 1980, 119.

<sup>17</sup>A methyl is a true donor when borne by a cation, and is an apparent electron donor when borne by a double bond or an anion. By 'apparent donor', we mean that there is no real electron transfer to the double bond or the anion, but the HOMO energy is raised, compared with that of the parent unsubstituted system.

### Writing the Secular Determinant

In some Hückel packages, the input (the atoms and their connectivities) must be introduced as a secular determinant. The latter can be written merely by looking at the structural formula. Let  $a_{ij}$  be the element in row  $i$  and column  $j$ , and set

$$x = \frac{\alpha - E}{\beta} \quad (\text{in units of } \beta)$$

Using an arbitrary labeling scheme for the atoms, we then take:

- $a_{ii} = x$  if atom  $i$  is a carbon atom,  $a_{ii} = x + k$  if  $i$  is a heteroatom [for the definition of  $h$  and  $k$ , see Equation (2.39)].
- $a_{ij} = 1$  if  $i$  and  $j$  are adjacent carbon atoms, and  $a_{ij} = h$  if one of them is a heteroatom. If both are heteroatoms, we can use  $a_{ij} = h_i h_j$  as a first approximation.
- $a_{ij} = 0$  if  $i$  and  $j$  are not adjacent to each other.

### Checking the Calculations

Always check your calculations (your input may be erroneous). If your parameters are adequate, your calculations *must* reproduce the main chemical characteristics of your compound: the electronic charge should increase with the atom's electronegativity; the frontier orbitals of an electron-rich compound should be raised, etc.

*Beware:* Hückel calculations only recognize connectivities. So, for example, they are incapable of distinguishing between *cis*- and *trans*-butadiene. Care should also be taken over *degenerate orbitals*. Their *ensemble* must respect the molecular symmetries, but individual degenerate MOs may violate them. Many combinations of coefficients can be used to describe each pair of degenerate orbitals; some are more tractable than others. Thus, some program gives the following for the  $\Psi_2$  and  $\Psi_3$  MOs of the cyclopentadienyl radical:

$$\Psi_2 = 0.21\phi_1 - 0.50\phi_2 - 0.52\phi_3 + 0.18\phi_4 + 0.63\phi_5$$

$$\Psi_3 = 0.60\phi_1 + 0.38\phi_2 - 0.36\phi_3 - 0.61\phi_4 - 0.01\phi_5$$

All the coefficients are different. The MOs below are much more convenient to use:

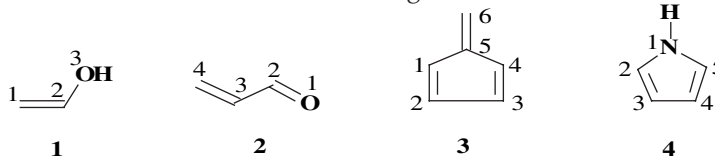
$$\Psi_2 = 0.63\phi_1 + 0.20\phi_2 - 0.51\phi_3 - 0.51\phi_4 + 0.20\phi_5$$

$$\Psi_3 = -0.60\phi_1 - 0.37\phi_2 + 0.37\phi_4 + 0.60\phi_5$$

The fivefold symmetry has been reduced to symmetry through a plane. These symmetry orbitals can be found easily, merely by redoing the calculations using slightly modified values for  $C_1$  (e.g.  $1.01\beta$  for its resonance integral).

#### \* Exercise 4 (E)

Write the secular determinant for the following molecules:



**Answer**

$$1 \quad \begin{vmatrix} x & 1 & 0 \\ 1 & x & 0.8 \\ 0 & 0.8 & x+2 \end{vmatrix}$$

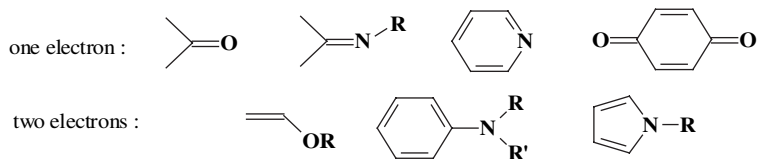
$$2 \quad \begin{vmatrix} x+1 & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix}$$

$$3 \quad \begin{vmatrix} x & 1 & 0 & 0 & 1 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 1 & 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 0 & 1 & x \end{vmatrix}$$

$$4 \quad \begin{vmatrix} x+1.5 & 0.8 & 0 & 0 & 0.8 \\ 0.8 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 0.8 & 0 & 0 & 1 & x \end{vmatrix}$$

**Electron Counting**

An accurate electron count is necessary to determine which MOs are occupied in the ground state. Halogens always provide two electrons, because they interact with a conjugated system through their lone pairs. Oxygen and nitrogen may contribute one or two electrons according to the molecule in question. Lewis structures show that a heteroatom bound by a double bond provides one electron to the  $\pi$  system, whereas a singly bound heteroatom gives two. For example:

**2.6 To Dig Deeper**

Levine I. N., *Quantum Chemistry*, 4th edn, Prentice-Hall, Englewood Cliffs, NJ, 1991. Very lucid. Contains exercises with succinct answers. The reader is taken through the proof step-by-step, which is particularly agreeable for those who have forgotten their maths.

# 3 The Perturbation Method

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## 3.1 Perturbations and Hückel Methods

A perturbation calculation requires a reference system, whose Hamiltonian  $\mathbf{H}^\circ$  and MOs  $\Psi_i^\circ$  (of energy  $E_i^\circ$ ) are known. The system we wish to study is closely related to it. In fact, it is assumed that the real system is a slightly perturbed version of the reference, so its Hamiltonian  $\mathbf{H}$  can be written as

$$\mathbf{H} = \mathbf{H}^\circ + \mathbf{P} \quad (3.1)$$

where  $\mathbf{P}$ , whose mathematical expression is *never given*, is the perturbation operator. The integrals

$$P_{ij} = \langle \Psi_i^\circ | \mathbf{P} | \Psi_j^\circ \rangle \quad (3.2)$$

being perturbations, are always small. The MOs of the perturbed system  $\Psi_i$  are expanded as linear combinations of the MOs of the reference system:

$$\Psi_i = \sum_j c_{ij} \Psi_j^\circ \quad (3.3)$$

Therefore, perturbation calculations and Hückel calculations are very similar: (a) the Hamiltonian expression is not specified and (b) the required MOs are linear combinations of known orbitals. When Equations (3.1) and (3.3) are incorporated into the time-independent Schrödinger equation:

$$\mathbf{H}_i \Psi_i = E_i \Psi_i \quad (3.4)$$

and the latter is solved by the variation method, three types of integral appear:

$$\langle \Psi_i^\circ | \mathbf{H} | \Psi_i^\circ \rangle = E_i^\circ + P_{ii} \quad (3.5)$$

$$\langle \Psi_i^\circ | \mathbf{H} | \Psi_j^\circ \rangle = P_{ij} \quad (3.6)$$

$$\langle \Psi_i^\circ | \Psi_j^\circ \rangle = S_{ij}^\circ = 0 \quad (3.7)$$

These integrals are the analogs of  $\alpha$ ,  $\beta$  and  $S$ .

## 3.2 Study of Bimolecular Reactions Using Perturbation Methods

### 3.2.1 Two-orbital Systems

Consider a reaction between two molecules A and B. For simplicity, we assume that each molecule has only one MO ( $\Psi_A^\circ$  of energy  $E_A^\circ$  and  $\Psi_B^\circ$  of energy  $E_B^\circ$ , respectively). During the reaction, the reagents evolve to produce the 'supermolecule' ( $A \cdots B$ ). As we saw in the previous section, the MOs of ( $A \cdots B$ ) can be calculated by a perturbation approach which is entirely analogous to the Hückel treatment of a diatomic molecule. In fact, we only need to take the MOs of the diatomic and replace:

- the AOs  $\phi$  by the MOs  $\Psi^\circ$  of A and B
- $\alpha$  and  $\beta$  by the expressions in Equations (3.5) and (3.6).<sup>1</sup>

We should distinguish between the two cases below:

#### **The MOs in the Starting Materials Are Degenerate**

This system is the analog of a homonuclear diatomic, with  $S = 0$ . Equations (2.11) and (2.13) indicate that the mixing of two degenerate orbitals  $\Psi_A^\circ$  and  $\Psi_B^\circ$  gives two new ones:

$$\begin{aligned} \Psi_1 &= 0.707 (\Psi_A^\circ + \Psi_B^\circ) & \text{of energy} & E_1 = E^\circ + P_{AB} \\ \Psi_2 &= 0.707 (\Psi_A^\circ - \Psi_B^\circ) & \text{of energy} & E_2 = E^\circ - P_{AB} \end{aligned} \quad (3.8)$$

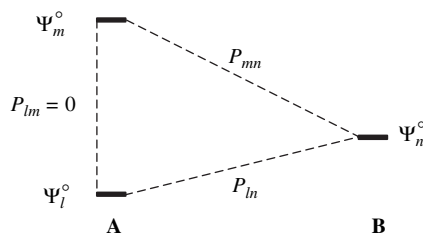
where  $P_{AB}$  represents the integral  $\langle \Psi_A^\circ | \mathbf{P} | \Psi_A^\circ \rangle$ .

#### **The MOs in the Starting Materials Are Not Degenerate**

This system is the analog of a heteronuclear diatomic (p. 15). Mixing of the two orbitals  $\Psi_A^\circ$  and  $\Psi_B^\circ$ , where  $E_A^\circ < E_B^\circ$ , will give two combinations, one of which is bonding ( $\Psi_A$ ) and the other antibonding ( $\Psi_B$ ):

$$\begin{aligned} \Psi_A &= N \left( \Psi_A^\circ + \frac{P_{AB}}{E_A^\circ - E_B^\circ} \Psi_B^\circ \right) & \text{of energy} & E_A = E_A^\circ + \frac{P_{AB}^2}{E_A^\circ - E_B^\circ} \\ \Psi_B &= N \left( \Psi_B^\circ + \frac{P_{AB}}{E_B^\circ - E_A^\circ} \Psi_A^\circ \right) & \text{of energy} & E_B = E_B^\circ + \frac{P_{AB}^2}{E_B^\circ - E_A^\circ} \end{aligned} \quad (3.9)$$

<sup>1</sup>As neither  $\mathbf{H}$  nor  $\mathbf{P}$  is specified, this amounts to a mere change in notation! We only need to replace  $\alpha_i$  by  $E_i^\circ$  and  $\beta_{ij}$  by  $P_{ij}$ . The *intramolecular* perturbation of  $\Psi_i$  by itself,  $P_{ii}$ , may be neglected, because we will only study bimolecular reactions and will invariably use the (nonperturbed) frontier orbitals of the starting materials. This point is discussed on p. 51.



**Figure 3.1** The three-orbital interaction diagram.

### Remarks

1. If we ensure that the denominators are written in the form (energy of the perturbed orbital minus energy of the perturbing orbital), the correction terms in Equations (3.9) will always have a positive sign.
2. Since  $E_A^\circ - E_B^\circ$  appears in the denominator, Equations (3.9) can only be used when  $E_A^\circ - E_B^\circ$  is greater than  $P_{AB}$ . This is the analog of the constraint in Equation (2.21). Physically, this means that the correction term must be smaller than the principal term.
3. Because  $P_{AB} < (E_A^\circ - E_B^\circ)$ , the corrections in Equations (3.8) are greater than those in Equations (3.9). In other words, the interaction between degenerate orbitals is greater than between nondegenerate orbitals.

### 3.2.2 Systems Having More Than Two Orbitals

We now consider a more realistic case where molecules A and B each have several MOs,  $n_A$  and  $n_B$ , respectively. As a first approximation, we assume that each MO on A (or B) is perturbed by all the orbitals of B (or A), which act *independently* of each other. This amounts to treating  $n_A n_B$  two-orbital problems. This number will be significantly reduced by employing the frontier orbital approximation (see below).

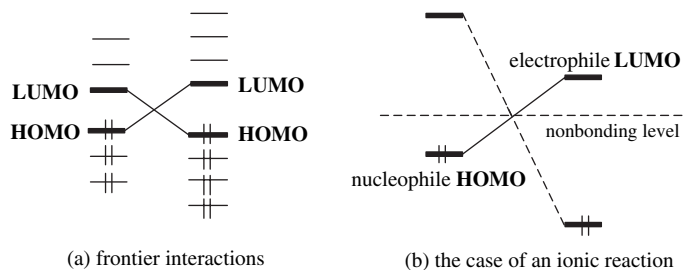
For the moment, suffice it to say that the *two-orbital perturbation* schemes give the *orbital energies* and the *sign* of the MO coefficients in the supermolecule (A  $\cdots$  B) with a reasonable degree of precision. However, *three-orbital perturbations* are needed to determine the *relative sizes* of the coefficients.

What do we mean by this? Consider the interactions between two MOs,  $\Psi_l^\circ$  and  $\Psi_m^\circ$ , of molecule A and an MO  $\Psi_n^\circ$  of molecule B (Figure 3.1).  $\Psi_l^\circ$  and  $\Psi_m^\circ$  belong to the same molecule so, *in the starting material*, they are orthogonal and cannot interact with each other. However, perturbation by B allows them to interact in the product. This interaction has little effect on the overall energy, but can markedly change the size of the MO coefficients. After reaction, orbital  $\Psi_l^\circ$  is transformed into  $\Psi_l$ , which can be written as<sup>2</sup>

$$\Psi_l = N \left[ \Psi_l^\circ + \frac{P_{ln}}{E_l^\circ - E_n^\circ} \Psi_n^\circ + \frac{P_{ln} P_{mn}}{(E_l^\circ - E_n^\circ)(E_l^\circ - E_m^\circ)} \Psi_m^\circ \right] \quad (3.10)$$

The only difference between Equations (3.10) and (3.9) lies in the last term, which mixes  $\Psi_l^\circ$  with  $\Psi_m^\circ$ , and modifies the coefficients in the A component of the supermolecule.

<sup>2</sup>A proof may be found in Anh N. T., *Introduction à la Chimie Moléculaire*, Ellipses, Paris, 1994, p. 149.



**Figure 3.2** Frontier orbital interactions.

In physical terms, this mixing means that *the electron cloud of A is distorted by the approach of B*. The mixing coefficient may look daunting, but it is not very complicated. The numerator is the product of two resonance integrals. Only three resonance integrals,  $P_{lm}$ ,  $P_{ln}$  and  $P_{mn}$ , can exist in a three-orbital system and the first, being zero (two orbitals of the same molecule), can be ignored. The denominator is the product of two energy differences: (the perturbed MO energy minus the first perturbing MO energy) multiplied by (the perturbed MO energy minus the second perturbing MO energy).

### 3.2.3 The Frontier Orbital Approximation

We saw above that  $n_A n_B$  two-orbital interactions occur during the union of A and B. In 1952, Fukui introduced the bold approximation<sup>3</sup> that, of these, only the HOMO–LUMO<sup>4</sup> interactions significantly affect the outcome of the reaction (Figure 3.2a). These MOs are termed *frontier orbitals*, because they mark the border between occupied and unoccupied orbitals. The frontier orbital (FO) approximation means that we have only consider *two* interactions for reactions between neutral molecules, irrespective of the size and complexity of A and B.

Ionic reactions are simpler still: the *only* important interaction involves the HOMO of the nucleophile and the LUMO of the electrophile (Figure 3.2b). This is because a nucleophile (or any electron-rich compound) readily donates electrons, so it will react through its HOMO, where the highest energy electrons are localized. Conversely, an electrophile (or any electron-poor compound) accepts electrons easily. These electrons can only be put into vacant orbitals. Obviously, the lower the energy of the empty orbital, the more easily it accepts electrons. Thus an electrophile generally reacts through its LUMO.

### 3.2.4 Unimolecular Systems

Theoretically, Equations (3.8) and (3.9) apply only to bimolecular processes, so we employ a trick for *unimolecular reactions*: the molecule is formally divided into two fragments whose recombination is treated as a bimolecular reaction.<sup>5</sup> This technique is also very useful for treating *structural problems* (Chapter 7).

<sup>3</sup>This approximation is justified on p. 49. Its limitations will be discussed in Chapter 8.

<sup>4</sup>HOMO = highest occupied MO; LUMO = lowest unoccupied MO.

<sup>5</sup>The selection rules for sigmatropic rearrangements were deduced in this manner (Woodward R. B., Hoffmann R., *J. Am. Chem. Soc.*, 1965, **87**, 2511).



## 3.3 Perturbation Theory: The Practical Aspects

### 3.3.1 Numerical Calculations

Let us look at the MOs of an enol, which can be modeled naturally as the combination of an ethylene fragment and a hydroxyl group, i.e. a carbon skeleton and a substituent. The carbon AOs are denoted  $\varphi_1$  and  $\varphi_2$ , the oxygen lone pair  $\varphi_3$ , the ethylene MOs  $\pi$  and  $\pi^*$  and the enol MOs  $\Psi_1$ ,  $\Psi_2$  and  $\Psi_3$ .

The interaction scheme is shown in Figure 3.3. Formally, the fragmentation process involves the breaking of one  $ij$  bond (in the present case, the  $C_2O_3$  linkage). Care should be taken to employ the *same sign* for the coefficients of  $i$  and  $j$  in the fragment orbitals. For example, when  $\varphi_3$  has a positive sign, the ethylene  $\pi^*$  orbital should be written as  $0.707(-\varphi_1 + \varphi_2)$  and not  $0.707(\varphi_1 - \varphi_2)$ . We thus ensure that  $P_{ij}$  will be negative and all correction terms which appear in Equations (3.8)–(3.10) will then have a positive sign.

The interacting orbitals ( $\pi$  of energy  $\alpha + \beta$ ,  $\pi^*$  of energy  $\alpha - \beta$  and  $\varphi_3$  of energy  $\alpha + 2\beta$ ) are not degenerate, so we can evaluate the energies  $E_i$  of the enol MOs  $\Psi_i$  using the Equations (3.9):

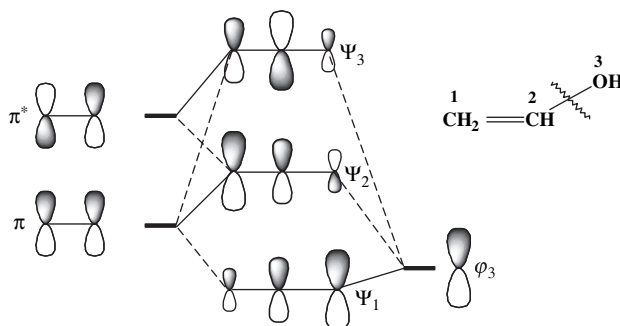
$$E_3 = E(\pi^*) + \frac{P_{\varphi_3, \pi^*}^2}{E(\pi^*) - E(\varphi_3)}$$

with

$$\begin{aligned} P_{\varphi_3, \pi^*} &= \langle \pi^* | \mathbf{P} | \varphi_3 \rangle = \langle 0.707(-\varphi_1 + \varphi_2) | \mathbf{P} | \varphi_3 \rangle \\ &= 0.707 \langle -\varphi_1 | \mathbf{P} | \varphi_3 \rangle + 0.707 \langle \varphi_2 | \mathbf{P} | \varphi_3 \rangle \end{aligned}$$

$C_1$  and  $O_3$  are not bound directly to each other, so the  $\langle -\varphi_1 | \mathbf{P} | \varphi_3 \rangle$  term is zero.  $\langle \varphi_2 | \mathbf{P} | \varphi_3 \rangle$  measures the change in the  $C_2O_3$  resonance integral during the recombination process. It is zero when the fragments are separated and  $0.8\beta$  when bound (see the parameter Table 2.2). Thus:

$$\begin{aligned} P_{\varphi_3, \pi^*} &= 0.707 \times 0.8\beta = 0.566\beta \\ E_3 &= (\alpha - \beta) + \frac{(0.566\beta)^2}{(\alpha - \beta) - (\alpha + 2\beta)} = \alpha - 1.107\beta \end{aligned}$$



**Figure 3.3** The MO diagram of an enol, built using a perturbation approach. The principal component of each MO is indicated by the unbroken line:  $\Psi_1$  is derived from  $\varphi_3$ ,  $\Psi_2$  from  $\pi$  and  $\Psi_3$  from  $\pi^*$ .

### The three perturbation schemes

To recap: splitting a molecule into fragments (Section 2.4) allows unimolecular reactions to be treated as bimolecular processes. Only one or two frontier interactions have to be considered, irrespective of the problem (Section 2.3). Two cases can be distinguished:

*The two interacting orbitals are degenerate*

The product MOs are given by:

$$\begin{aligned}\Psi_1 &= 0.707(\Psi_A^\circ + \Psi_B^\circ) & \text{with} & \quad E_1 = E^\circ + P_{AB} \\ \Psi_2 &= 0.707(\Psi_A^\circ - \Psi_B^\circ) & \text{with} & \quad E_2 = E^\circ - P_{AB}\end{aligned}\quad (3.8)$$

Equations (3.8) *must* be used when  $E_A^\circ - E_B^\circ$  is smaller than  $P_{AB}$  (see Exercise 2, p. 33)

*The two interacting orbitals are not degenerate*

This is the more usual case. The product MOs are given by

$$\begin{aligned}\Psi_A &= N \left( \Psi_A^\circ + \frac{P_{AB}}{E_A^\circ - E_B^\circ} \Psi_B^\circ \right) & \text{with} & \quad E_A = E_A^\circ + \frac{P_{AB}^2}{E_A^\circ - E_B^\circ} \\ \Psi_B &= N \left( \Psi_B^\circ + \frac{P_{AB}}{E_B^\circ - E_A^\circ} \Psi_A^\circ \right) & \text{with} & \quad E_B = E_B^\circ + \frac{P_{AB}^2}{E_B^\circ - E_A^\circ}\end{aligned}\quad (3.9)$$

These interactions are second order in  $P_{AB}$ , so they are weaker than those occurring between degenerate orbitals (first order in  $P_{AB}$ ). The more stabilized  $\Psi_A$ , the easier is the reaction between A and B. To maximize this stabilization, the numerator  $P_{AB}^2$  must be increased and/or the denominator  $(E_A^\circ - E_B^\circ)$  decreased. Since Mulliken's approximation (p. 13) takes  $P_{AB}$  proportional to the overlap between  $\Psi_A^\circ$  and  $\Psi_B^\circ$ , we can see that:

**Rule.** *Reactions are facilitated when the frontier orbitals of the reagents are close in energy and when their overlap is large.*

Except for some conformational studies, every example given in this course has been solved by applying this rule.

*Three-orbital interactions*

These are used to account for distortions in electron clouds. They are given by the equation

$$\Psi_1 = N \left[ \Psi_1^\circ + \frac{P_m}{E_l^\circ - E_n^\circ} \Psi_n^\circ + \frac{P_m P_{mn}}{(E_l^\circ - E_n^\circ)(E_l^\circ - E_m^\circ)} \Psi_m^\circ \right] \quad (3.10)$$

The correct value of  $\alpha - 1.108\beta$  is in excellent agreement with our  $E_3$ .

$$E_2 = (\alpha + \beta) + \frac{(0.566\beta)^2}{(\alpha + \beta) - (\alpha + 2\beta)} = \alpha + 0.680\beta$$

$$E_1 = (\alpha + 2\beta) + \frac{(0.566\beta)^2}{(\alpha + 2\beta) - (\alpha + \beta)} + \frac{(0.566\beta)^2}{(\alpha + 2\beta) - (\alpha - \beta)} = \alpha + 2.427\beta$$

The calculated values of  $E_2$  and  $E_1$  agree much less well with the correct values of  $\alpha + 0.773\beta$  and  $\alpha + 2.336\beta$  because we are approaching the point where second-order perturbation equations are no longer valid: the energy difference between  $\pi$  and  $\varphi_3$  is  $\beta$ , while the corresponding resonance integral is  $0.566\beta$ . Calculating the MOs using the two-orbital Equations (3.9) gives

$$\begin{aligned} \Psi_1 &= N \left( \varphi_3 + \frac{P_{\varphi_3, \pi}}{E_{\varphi_3} - E_{\pi}} \pi + \frac{P_{\varphi_3, \pi^*}}{E_{\varphi_3} - E_{\pi^*}} \pi^* \right) \\ &= N(\varphi_3 + 0.566\pi + 0.189\pi^*) = 0.23\varphi_1 + 0.46\varphi_2 + 0.86\varphi_3 \\ &\quad \text{correct solution: } 0.16\varphi_1 + 0.36\varphi_2 + 0.91\varphi_3 \end{aligned}$$

$$\begin{aligned} \Psi_2 &= N \left( \pi + \frac{P_{\varphi_3, \pi}}{E_{\pi} - E_{\varphi_3}} \varphi_3 \right) = 0.62(\varphi_1 + \varphi_2) - 0.49\varphi_3 \\ &\quad \text{correct solution: } 0.74\varphi_1 + 0.57\varphi_2 - 0.37\varphi_3 \end{aligned}$$

$$\begin{aligned} \Psi_3 &= N \left( \pi^* + \frac{P_{\varphi_3, \pi^*}}{E_{\pi^*} - E_{\varphi_3}} \varphi_3 \right) = 0.69(-\varphi_1 + \varphi_2) - 0.19\varphi_3 \\ &\quad \text{correct solution: } -0.66\varphi_1 + 0.73\varphi_2 - 0.19\varphi_3 \end{aligned}$$

These results imply that the electron density on the central carbon is higher than that on the terminal carbon.<sup>6</sup> This makes no chemical sense and also disagrees with exact calculations. The error arises because we have ignored distortions of the molecular electron clouds. When the three-orbital correction term given in Equation (3.10) is added,  $\Psi_2$  becomes

$$\begin{aligned} \Psi_2 &= N \left[ \pi + \frac{P_{\varphi_3, \pi}}{E_{\pi} - E_{\varphi_3}} \varphi_3 + \frac{P_{\varphi_3, \pi} P_{\varphi_3, \pi^*}}{(E_{\pi} - E_{\varphi_3})(E_{\pi} - E_{\pi^*})} \pi^* \right] \\ &= N(\pi - 0.566\varphi_3 - 0.16\pi^*) = 0.71\varphi_1 + 0.51\varphi_2 - 0.49\varphi_3 \end{aligned}$$

Now the electron density is higher on  $C_1$  than on  $C_2$ .

<sup>6</sup>The two lowest MOs are occupied. The  $C_2$  coefficient is greater in  $\Psi_1$ , and the  $C_1$  and  $C_2$  coefficients are equal in  $\Psi_2$ .