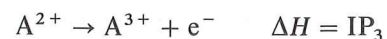
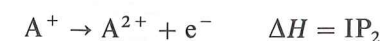


Finally one can define a second,  $IP_2$ , (or third,  $IP_3$ , etc.) ionization potential which represents the smallest amount of energy needed to detach an electron from the singly charged cation (or doubly charged cation etc.) produced after the first (or second etc.) ionization.



etc.

The second IP is always larger than the first, in spite of the fact that the electron often comes from the same sub-shell, since the outermost electron in the ion is less effectively shielded than in the neutral atom. For example in the carbon atom the effective charge seen by a  $2p$  electron is equal to 3.25 in the neutral species but 3.60 in the singly charged cation. The six ionization potentials for carbon are:

$$IP_1 = 11.3 \text{ eV} \quad IP_3 = 47.9 \text{ eV} \quad IP_5 = 392.1 \text{ eV}$$

$$IP_2 = 24.4 \text{ eV} \quad IP_4 = 64.5 \text{ eV} \quad IP_6 = 490.0 \text{ eV}$$

$$2p \text{ electrons} \quad 2s \text{ electrons} \quad 1s \text{ electrons}$$

### (b) Electron affinity

The *electron affinity* (EA) measures the capacity of an atom to accept an extra electron. The production of a stable anion is an exothermic process ( $\Delta H < 0$ ), but conventionally, values of the electron affinity are reported after reversing the sign. The larger the value of the EA the greater the stability of the anion  $A^-$  relative to a neutral atom  $A$  plus an electron



By analogy with our analysis of the variations found for the IPs we can correlate the values of the EAs with the properties of the orbital that receives the extra electron. So for the case of chlorine, with a valence electron configuration  $3s^2 3p^5$ , this electron has to occupy the last free place in the set of  $3p$  orbitals whose orbital energy is  $-13.7 \text{ eV}$ . On the most naïve level the gain in energy associated with the electron capture process should therefore be close to this value, i.e., the EA should then be close to  $+13.7 \text{ eV}$ . However the value measured experimentally ( $3.6 \text{ eV}$ ) is far from this figure. This is a very general result as may be seen by a comparison of the EA values given in Table 2.7 with the orbital energy values of Table 2.4. A part of the solution to this problem is immediately apparent once we realize that the electron affinity of an atom is identical to the ionization potential of its singly charged negative ion.

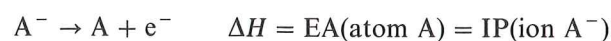


Table 2.7: Electron affinities expressed in eV.

1							18
H 0.75							He 0.0
Li 0.62	2 Be 0.0	13 B 0.28	14 C 1.26	15 N 0.0	16 O 1.46	17 F 3.40	Ne 0.0
Na 0.55	Mg 0.0	Al 0.44	Si 1.39	P 0.75	S 2.08	Cl 3.62	Ar 0.0
K 0.50	Ca 0.0	Ga 0.30	Ge 1.23	As 0.81	Se 2.02	Br 3.37	Kr 0.0
Rb 0.49	Sr 0.0	In 0.30	Sn 1.11	Sb 1.07	Te 1.97	I 3.06	Xe 0.0

Thus our arguments above concerning the difference in first and second ionization potentials of neutral atoms are applicable to this case too. For carbon, for example the three ionization potentials to consider are:

$$IP \text{ of } C^- (=EA \text{ of } C) = 1.26 \text{ eV}$$

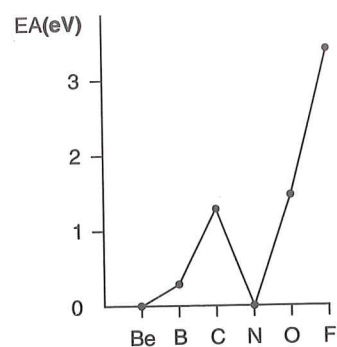
$$IP \text{ of } C (IP_1) = 11.3 \text{ eV}$$

$$IP \text{ of } C^+ (IP_2) = 24.4 \text{ eV}$$

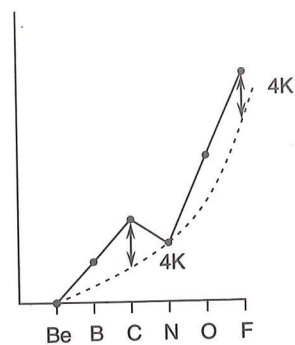
Each time the number of valence electrons changes by one, the corresponding ionization potential varies by around 10 eV for carbon.  $Z^*$  for the three species are 2.90 ( $C^-$ ), 3.25 ( $C$ ) and 3.60 ( $C^+$ ).

A second observation concerning the figures of Table 2.7 are the zero values of the EA for some atoms. Thus for Be, N and Ne no stable anion exists. For Be and Ne this result is easy to understand. The added electron would have to occupy the next highest sub-shell since both of these species have full sub-shells. This costs energy and the overall process of electron attachment is unfavorable. As a result all of the elements of groups 2 (valence configuration  $ns^2$ ) and 18 (valence configuration  $ns^2 np^6$ ) have zero electron affinities.

The realization that the EA of  $A$  is just the IP of  $A^-$  enables a further correlation with our earlier discussion. 2-19a shows a plot of the observed EAs for the  $2p^n$  series. Notice that it has the same saw-tooth behavior as that seen in 2-18a for the ionization potentials of the neutral atoms. The EA drops between carbon and nitrogen in just the same way that the IP drops between nitrogen and oxygen. From Table 2.6 we can construct a qualitative prediction of the variation across the  $p^n$  series by adding to a sloping background, increasing with increasing  $Z$ , the effect of the difference in exchange energy between anion and neutral atom (2-19b). The critical electron count associated with the saw-tooth discontinuity is different by one electron from that



2-19a



2-19b

found in 2-18 for the IPs since there we were concerned with the difference in exchange energy between neutral atom and cation. In general, given the exceptions associated with the  $ns^2$ ,  $ns^2np^3$  and  $ns^2np^6$  valence configurations we have described how EA tends to increase on going from left to right across the table.

The general ideas of this chapter would predict an increase in the electron affinities on moving from the bottom to the top of a column of the periodic table mirroring such predictions found experimentally for the ionization potentials. This is in general true but with the exceptions that the elements of the second row of the table (B-F) have smaller values than those of the third row (Al-Cl). To summarize, *the electron affinity has a tendency to increase on moving from left to right across a row of the periodic table from column 13 to column 17 and on moving from bottom to top with a reversal of this order between second row and third rows. The halogens have the largest electron affinities.*

### 2.6.3. Electronegativity scales

As we indicated in the first chapter, it is important to have an idea, albeit qualitative, of the way an atom polarizes the electron cloud within a molecule, that is to say its capacity to attract electron density. The quantity which we use to characterize this property is the electronegativity. It is not feasible to measure experimentally the polarization created by the presence of given atoms in molecules, but it is very useful to employ an electronegativity scale which allows a qualitative feeling for the concept.

There are three scales commonly in use. The first two are defined using some of the atomic properties which we have just described.

- (i) Mulliken's scale. The electronegativity,  $\chi(A)$  of an element A is proportional to the sum of the ionization potential (IP) and the electron affinity (EA).

$$\chi(A) = K[\text{IP}(A) + \text{EA}(A) + C]$$

where  $K$  and  $C$  are constants.

- (ii) The Allred-Rochow scale. Here the electronegativity is proportional to the attractive force exerted on the outermost electron by the nucleus, via the

following relationship

$$\chi(A) = KZ^*/r^2 + C$$

Here  $K$  and  $C$  are constants (different from those in (i)) and  $r$  is defined as the covalent radius of the atom. The values of this parameter for atoms of interest come from experimental data on the bond lengths in molecules containing the atom concerned. The covalent radius for chlorine, for example, is just half the Cl-Cl distance in the  $\text{Cl}_2$  molecule. In practice the values for  $r$  are close to those found for  $\rho$ , the atomic radius we defined earlier (Section 2.5.3).

- (iii) Pauling's scale. The third scheme is defined using some molecular properties. Pauling noticed that the bond dissociation energy,  $D_{AB}$ , of a heteronuclear diatomic molecule AB is generally larger than that of each of the AA and BB bond dissociation energies. For example the dissociation energy of HF is  $570 \text{ kJ mole}^{-1}$  but those of  $\text{H}_2$  and  $\text{F}_2$  are  $436$  and  $159 \text{ kJ mol}^{-1}$  respectively.

Table 2.8: Three electronegativity scales, (a) Mulliken, (b) Allred-Rochow, and (c) Pauling.

	H 3.1						
a	Li	Be	B	C	N	O	F
	1.3	2.0	1.8	2.7	3.1	3.2	4.4
	Na	Mg	Al	Si	P	S	Cl
	1.2	1.6	1.4	2.0	2.4	2.7	3.5

	H 2.2						
b	Li	Be	B	C	N	O	F
	1.0	1.5	2.0	2.5	3.1	3.5	4.1
	Na	Mg	Al	Si	P	S	Cl
	1.0	1.2	1.5	1.7	2.1	2.4	2.8

	H 2.2						
c	Li	Be	B	C	N	O	F
	1.0	1.6	2.0	2.6	3.0	3.4	4.0
	Na	Mg	Al	Si	P	S	Cl
	0.9	1.3	1.6	1.9	2.2	2.6	3.2

In Pauling's scale the difference in electronegativity between A and B is determined by the values of the diatomic dissociation energies.

$$[\chi(A) - \chi(B)]^2 = K(D_{AB} - \sqrt{D_{AA} \times D_{BB}})$$

Pauling set the value for fluorine at 4.0.

The variations in electronegativity across the periodic table are very similar and independent of the scale which is used. Table 2.8 shows values for the first three rows. We notice that the electronegativity increases on moving from left to right across the periodic table and from bottom to top.

In Table 2.8 the most electronegative element is fluorine and the least electronegative is sodium. For the first two scales the variation in  $\chi$  across the periodic table is easy to understand given our earlier discussion of the concepts of IP, EA,  $Z^*$  and  $\rho$ . Pauling's scale though, is perhaps the one most commonly used. We note though that there is no value of the electronegativity for the noble gases (column 18) since there are no diatomic molecules for these atoms. The Mulliken and Allred-Rochow scales do not suffer from this problem.

#### 2.6.4. Electronegativity, orbital energy and orbital radius

A result which we will often use in the rest of this book relies on the comparison between Tables 2.4 and 2.8. This is that *the valence s and p orbital energies vary in a way which is paralleled by the variation in atomic electronegativity*. Thus the steady increase in electronegativity in the series boron (2.0), carbon (2.6), nitrogen (3.0), oxygen (3.4) and fluorine (4.0), corresponds with a steady lowering of the 2p orbital energy; -5.7 (B), -10.7 (C), -12.9 (N), -15.9 (O) and -18.6 eV (F). In the same way, the more electronegative the atom, the more contracted the orbitals (Table 2.3).

## EXERCISES

### Single-electron atoms

- 2.1 Consider the hydrogen atom in the 3p excited state
- Which electronic transitions are possible with emission of energy?
  - Calculate the wavelengths of light associated with these transitions. (In SI units,  $Ry = 2.18 \times 10^{-18} \text{ J}$ ;  $h = 6.62 \times 10^{-34} \text{ J s}$ ;  $c = 3 \times 10^8 \text{ m s}^{-1}$ .) Recall that wavelength and frequency are related via the expression  $\lambda\nu = c$ .
  - Determine the ionization potential for hydrogen in this excited state in eV and in  $\text{kJ mol}^{-1}$ . Recall  $N_A$  (Avogadro's number) =  $6.02 \times 10^{23}$ .
- 2.2
- Calculate (in eV) the IPs of the ions  $\text{He}^+$  and  $\text{C}^{5+}$  in their ground electronic state. ( $Ry = 13.6 \text{ eV}$ .)
  - Consider the  $\text{Li}^{2+}$  cation in its second excited state. What is the degeneracy of the wavefunctions describing this state? What is the ionization potential (in eV) of the ion in this state?

### Many-electron atoms

- 2.3 Consider the sulfur atom ( $Z = 16$ )
- Give the electronic configuration of the lowest energy state.
  - Calculate the radii of the different occupied AOs for this atom (equation (41)).
- 2.4 Calculate the radii of the atoms of fluorine ( $Z = 9$ ), chlorine ( $Z = 17$ ) and bromine ( $Z = 35$ ). Which is the most, and which the least, polarizable?
- 2.5 Give the electronic configuration for platinum (Pt,  $Z = 78$ ) which is in accord with Klechkowsky's rule. Knowing that the 6s and 5d levels are very close in energy, suggest two other configurations which should be close in energy to this.
- 2.6 Consider all the atoms with  $Z$  less than or equal to 20. In their electronic ground state
- Which of them are diamagnetic?
  - Which of them have a single unpaired electron?
  - Which of them have two unpaired electrons?

*Analytic calculation of the orbital radius*

2.7 Recalling that the radial probability density  $dS/dr$  of an atomic orbital is defined as:  $dS/dr = R_{n,l}^2(r)r^2$  calculate the position of the maximum in this density for the 1s, 2s and 2p orbitals of the hydrogen atom. The analytical expressions for the different functions are given by equations (28)–(30).

2.8 An approximate expression for the radial part of the orbital wavefunctions of many-electron atoms was proposed by Slater.

$$R_{n,l}(r) = N(r/a_0)^{n-1} \exp(-Z^*r/na_0)$$

where  $N$  is a normalization constant. Calculate the radius of an orbital of this type. You should recover equation (41).

*Orthonormalization of the hydrogen wavefunctions*

2.9 Show that the 1s function (equation (28)) of the hydrogen atom is normalized, given that the volume element  $d\tau$  expressed in spherical polar coordinates is  $d\tau = r^2 \sin \theta dr d\theta d\phi$  ( $r$  goes from 0 to infinity,  $\theta$  from 0 to  $\pi$  and  $\phi$  from 0 to  $2\pi$ ). Show that the radial and angular parts of the wavefunction are normalized independently of each other. Note that

$$\int_0^\infty x^2 \exp(-ax) dx = 2/a^3$$

2.10 (i) Show that the 1s and 2s functions are both orthogonal to the three 2p functions. This result will be able to be established using the angular parts only of the respective analytic functions given by equations (28)–(30).  
(ii) Show that the 1s and 2s functions are also orthogonal. Use the relationships

$$\int_0^\infty x^2 \exp(-ax) dx = 2/a^3 \quad \int_0^\infty x^3 \exp(-ax) dx = 6/a^4.$$

## Part II

# Building up molecular orbitals and electronic structure

### 3 Interaction of two atomic orbitals on different centers

The attempt to use quantum mechanics to provide an electronic description of molecules raises a number of difficulties, some of which have already been encountered in the treatment of the isolated atom. Others are directly connected with the polyatomic nature of the molecule. The Schrödinger equation, which in principle allows the calculation of the molecular wavefunction, is much more difficult to solve than in the case of the many-electron atom. (The exception to this statement concerns molecules with a single electron such as  $\text{H}_2^+$ .) The most usual resolution of this problem makes use of a number of simplifying assumptions. The picture which results provides an excellent approximation to the real state of affairs.

#### 3.1. Basic approximations

Three approximations are frequently used to calculate the molecular wavefunction.

##### 3.1.1. The Born–Oppenheimer approximation

In a molecule the nuclei move together as a block during the displacements associated with translation and rotation, and move relative to each other during vibrations. All of these motions carry a contribution to the total energy of the molecule and have to be taken into account in the determination of the total wavefunction of the system since it depends both upon the nuclear coordinates ( $\mathbf{R}$ ) and the electronic coordinates ( $\mathbf{r}$ ).

The *Born–Oppenheimer approximation* writes the total wavefunction  $\Psi(\mathbf{r}, \mathbf{R})$  as a product of two parts; one  $\Xi(\mathbf{R})$  which describes the nuclei and the other  $\Phi_{\text{el}}(\mathbf{r})$  the electrons

$$\Psi(\mathbf{r}, \mathbf{R}) = \Phi_{\text{el}}(\mathbf{r})\Xi(\mathbf{R}) \quad (1)$$

The justification for this is that since the nuclei are so much heavier than the electrons, they move much more slowly. Thus equation (1) represents a description of a set of mobile electrons moving in the field of frozen nuclei. Within the framework of this approximation the Schrödinger equation as a function of the coordinates of all the particles, nuclei and electrons, is replaced by one which still contains the electron coordinates as variables but uses a fixed geometry for the nuclear ones. The problem

is thus reduced to solution of  $\Phi_{el}(r)$  at a given molecular (i.e., nuclear) geometry. In this way the energy of the system may be calculated as a function of geometry by performing a series of computations at different values of the set of coordinates,  $R$ . In what follows we will restrict ourselves to the study of the molecular electronic wavefunction  $\Phi_{el}(r)$ .

### 3.1.2. The orbital approximation

We described the use of this approximation in Chapter 2 when studying the electronic situation in many-electron atoms. It is used both for atoms of this type and also for molecules since it is not possible to find an exact analytic solution for the electronic wavefunction for systems containing more than a single electron. An approximate solution is found by writing the many-electron wavefunction as a product of one-electron functions

$$\Phi_{el}(e_1, e_2, \dots, e_n) = \phi_1(e_1)\phi_2(e_2) \dots \phi_n(e_n) \quad (2)$$

The one-electron functions  $\phi_i$  are called the *molecular orbitals* (MOs) of the system under consideration.

The molecular case poses another problem however. Remember that for atoms the one-electron functions are the atomic orbitals  $\chi_i$ , whose mathematical form is derived from those found for the hydrogen atom. These, of course, are known exactly. It is not at all clear though how to choose the form of the molecular orbitals,  $\phi_1, \phi_2, \dots, \phi_n$ , but one approach is almost universally used in chemistry.

### 3.1.3. The form of the MOs: the LCAO approximation

The simplest form used for describing molecular orbitals is the *linear combination of atomic orbitals (LCAO) approximation*. We write the molecular orbital ( $\phi_i$ ) as a linear sum of contributions from the atomic orbitals of the molecule  $\chi_j$

$$\phi_i = \sum_j c_{ij}\chi_j \quad (3)$$

In this expression the  $c_{ij}$  are the coefficients or the weights of the AO  $\chi_j$  in the molecular orbital  $\phi_i$ . A simple justification for the validity of the approach, is that in the interior of the molecule an atom does not completely lose its identity and retains many of the characteristics of the isolated atom. For example the elements having a large electron affinity and a large ionization potential, are the most electronegative elements, and those which have a tendency to attract electrons in the molecule. In equation (3) the AOs,  $\chi_j$  are supposedly known and we just have to determine the coefficients  $c_{ij}$ . In principle there are an infinite number of functions  $\chi_j$  (1s, 2s, 2p, 3s, 3p, etc.) for each atom, but in order for the problem to be manageable we need to truncate the summation in expression (3) by selecting a reasonable number of AOs. Two simplifications narrow this choice.

(i) Orbitals describing core electrons are ignored. This is understandable in part

from the contraction of these orbitals. Their amplitude is only large close to the nucleus and they play a negligible role in the formation of chemical bonds. Although it is not a quantum mechanical approach, we recall here too that Lewis' theory only considered the valence electrons when viewing bond formation (Chapter 1).

(ii) Included for each atom in the sum of equation (3) are all the occupied valence orbitals and also those orbitals, which might be empty in the isolated atom but have the same value of the principal quantum number. For example for carbon ( $1s^2 2s^2 2p^2$ ) only the 2s and 2p orbitals are included, for hydrogen ( $1s^2$ ) the 1s orbital and for helium ( $1s^2$ ) the 1s orbital. For lithium ( $1s^2 2s^1$ ) we use both 2s and 2p orbitals. (Some variations on this are used for transition metal systems.)

The LCAO theory is not an approximation in itself. If it were possible, the calculation using an infinite set of AOs should lead to an exact solution for the MO. It is the restriction that the set of AOs included is limited to a small number which introduces the approximation. In fact it works well for much of the periodic table but it is often necessary to increase the 'basis set' to be able to calculate the MOs and properties of several molecules.

Determination of the form of the MOs,  $\phi_i$ , reduces to finding the set of coefficients  $c_{ij}$  which characterize it. In practice these may be calculated using a result from the variation theorem. Essentially this theorem states that if we have a wavefunction such as that of equation (3), then the best approximation to the energy can be achieved by minimizing the analytical expression for the energy with respect to all of the  $c_{ij}$ . This leads to a direct determination of these coefficients. When the coefficients are known, the calculation of the energy of the orbital ( $\epsilon_i$ ) follows via a relationship of the type used for the many-electron atom in Chapter 2 (equation (38)). However in this book we will follow a different path. We shall show that the orbital problem may be analyzed in a very qualitative way and one which relies on a number of simple rules, based on symmetry, electronegativity and on the relative energies of the AOs of the isolated atoms. In this chapter we will treat the simplest cases one could imagine, namely MOs which are linear combinations of only two atomic orbitals.

## 3.2. Construction of MOs

Let us consider two atoms A and B each carrying a single atomic orbital,  $\chi_1$  and  $\chi_2$  respectively (3-1). We shall see that this in fact is not the great restriction it appears



at first sight. The MOs of the molecule AB are simply the linear combinations of the AOs  $\chi_1$  and  $\chi_2$ . In current parlance we say that the AOs  $\chi_1$  and  $\chi_2$  *interact* to give the MOs of the AB molecule. The simplest situation of this type corresponds to real systems such as  $H_2$  or  $H_2^+$  ( $\chi_1 = \chi_2 = 1s_H$ ),  $He_2^+$  or  $He_2^{2+}$  ( $\chi_1 = \chi_2 = 1s_{He}$ ) and

HeH<sup>+</sup> ( $\chi_1 = 1s_{\text{He}}$ ,  $\chi_2 = 1s_{\text{H}}$ ). Although an analysis of this problem will be quite sufficient to understand the structure of these small molecules, the principal motivation is the generation of a set of general rules which may be applied to the more complex systems which we will discuss later.

### 3.2.1. Interaction of two identical AOs

In the homonuclear diatomics, such as H<sub>2</sub>, H<sub>2</sub><sup>+</sup>, He<sub>2</sub><sup>+</sup> or He<sub>2</sub><sup>2+</sup>, the two atoms, A and B, are the same. We will call them A<sub>1</sub> and A<sub>2</sub>. The two AOs  $\chi_1$  and  $\chi_2$  are identical with the same form and the same energy, but they are centered at two different points in space,  $\chi_1$  on A<sub>1</sub> and  $\chi_2$  on A<sub>2</sub>. The formation of the MOs in these systems therefore results from the interaction of *two degenerate atomic orbitals*.

#### (a) Study of the electron density

Within the framework of the LCAO approximation, each MO may be written as a simple linear combination of the two AOs

$$\phi = c_1\chi_1 + c_2\chi_2 \quad (4)$$

So for each MO there are two coefficients to calculate,  $c_1$  and  $c_2$ . We can see how various restrictions on their relative values arise by study of the probability density for an electron located in a given MO. As described earlier (Section 2.1.1) the probability density is given by the square of the wavefunction:

$$\phi^2 = (c_1\chi_1 + c_2\chi_2)^2 = c_1^2\chi_1^2 + c_2^2\chi_2^2 + 2c_1c_2\chi_1\chi_2 \quad (5)$$

This expression may be divided into three parts. The first,  $c_1^2\chi_1^2$ , is only important in those regions of space where  $\chi_1$  itself is large, namely in the vicinity of atom A<sub>1</sub>. The integral  $\int c_1^2\chi_1^2 d\tau$  may be written as  $c_1^2\langle\chi_1|\chi_1\rangle$  using the notation introduced in Chapter 2. It represents, approximately, the probability of finding the electron close to atom A<sub>1</sub>. In the same way, the integral of the second term  $c_2^2\langle\chi_2|\chi_2\rangle$  gives the probability of finding the electron close to atom A<sub>2</sub>. The last term  $2c_1c_2\langle\chi_1|\chi_2\rangle$  is only important when *both*  $\chi_1$  and  $\chi_2$  are non-negligible, namely in the region between the two atoms A<sub>1</sub> and A<sub>2</sub>.

#### (b) Some mathematical descriptions of the MOs

Some very important results may be derived from the symmetry properties of the A<sub>2</sub> diatomics. Since the molecule is symmetrical about the A—A bond, the two nuclei are completely equivalent. Put another way, the electrons in the molecule have the same probability of being close to atom A<sub>1</sub> as they do of being close to atom A<sub>2</sub>. This means that the two terms describing the electron probability from the quantum mechanical description must be equal i.e.

$$c_1^2\langle\chi_1|\chi_1\rangle = c_2^2\langle\chi_2|\chi_2\rangle \quad (6)$$

Since  $\chi_1$  and  $\chi_2$  are normalized ( $\langle\chi_1|\chi_1\rangle = \langle\chi_2|\chi_2\rangle = 1$ ) the result puts strong restrictions on the values of the coefficients, namely;

$$c_1^2 = c_2^2 \quad \therefore c_1 = \pm c_2 \quad (7)$$

This is a very important result. It means that starting from two AOs,  $\chi_1, \chi_2$  one can construct two MOs which in fact only contain one unknown, the normalization constant  $N_+, N_-$ .

$$\phi_+ = N_+(\chi_1 + \chi_2) \quad \phi_- = N_-(\chi_1 - \chi_2) \quad (8)$$

To obtain  $N_{\pm}$  we must normalize these functions. For  $\phi_+$

$$\begin{aligned} \langle\phi_+|\phi_+\rangle &= 1 \\ N_+^2(\langle\chi_1|\chi_1\rangle + \langle\chi_2|\chi_2\rangle + 2\langle\chi_1|\chi_2\rangle) &= 1 \end{aligned} \quad (9)$$

$\langle\chi_1|\chi_2\rangle$  is the overlap integral,  $S$ , between the two AOs  $\chi_1$  and  $\chi_2$  (Section 2.1.2b). The orbitals are normalized so that

$$\begin{aligned} N_+^2(1 + 1 + 2S) &= 1 \\ N_+ &= 1/[2(1 + S)]^{1/2} \end{aligned} \quad (10)$$

An analogous calculation for the orbital  $\phi_-$  leads to

$$N_- = 1/[2(1 - S)]^{1/2} \quad (11)$$

The two MOs for the homonuclear diatomic molecule thus become

$$\phi_+ = \frac{1}{[2(1 + S)]^{1/2}}(\chi_1 + \chi_2) \quad \phi_- = \frac{1}{[2(1 - S)]^{1/2}}(\chi_1 - \chi_2) \quad (12)$$

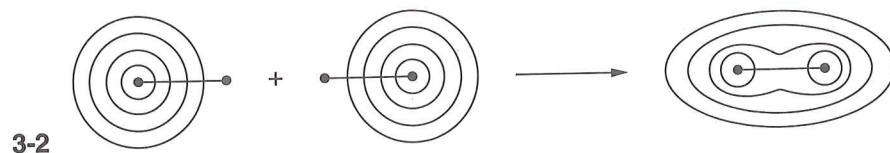
So, starting off from two AOs,  $\chi_1$  and  $\chi_2$ , we have obtained two MOs  $\phi_+$  and  $\phi_-$ . This relationship between the number of AOs and the number of MOs they generate is a general one, even in more complex systems;  $n$  AOs give rise to  $n$  MOs. If we calculate the overlap between the MOs we get

$$\begin{aligned} \langle\phi_+|\phi_-\rangle &= \frac{1}{2(1 - S^2)^{1/2}}(\langle\chi_1|\chi_1\rangle + \langle\chi_1|\chi_2\rangle - \langle\chi_1|\chi_2\rangle - \langle\chi_2|\chi_2\rangle) \\ &= \frac{1}{2(1 - S^2)^{1/2}}(1 + S - S - 1) \\ &= 0 \end{aligned} \quad (13)$$

Thus, just as atomic orbitals on the same atom are orthogonal, so molecular orbitals are orthogonal to each other.

### (c) The form of the MOs

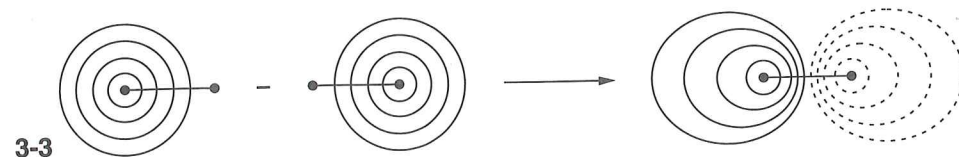
In the orbital  $\phi_+$  the atomic orbital coefficients have the same sign, and thus they add together, a condition which we describe as being in phase. If we consider a point outside the region of space between the two nuclei, close to  $A_1$  and therefore far from  $A_2$ , the form of the wavefunction shows that the amplitude of  $\chi_2$  is small but that of  $\chi_1$  large. Thus in this region the MO  $\phi_+$  has practically the same form as the AO  $\chi_1$ . Correspondingly, in the region close to  $A_2$  and far from  $A_1$ ,  $\phi_+$  resembles the AO  $\chi_2$ . It is in the internuclear region where  $\phi_+$  is distinctly different from either  $\chi_1$  or  $\chi_2$  alone. In fact  $\chi_1$  and  $\chi_2$  have similar contributions in the internuclear region and neither is negligible. The in-phase addition of  $\chi_1$  and  $\chi_2$  in this region leads to an amplitude of  $\phi_+$  which is clearly larger than that from  $\chi_1$  or  $\chi_2$  alone. This characteristic appears in the schematic contour diagram for the  $\phi_+$  function shown in 3-2. Thus the function  $\phi_+$  is characterized by a large amplitude in the internuclear region.



In contrast the amplitudes of the two functions  $\chi_1$  and  $\chi_2$  are subtracted in the  $\phi_-$  orbital where the coefficients of  $\chi_1$  and  $\chi_2$  are opposite in sign, or out of phase. As before, close to the nuclei the wavefunction strongly resembles  $\chi_1$  or  $\chi_2$  but in the internuclear region, the subtraction of the two functions leads to a small amplitude of  $\phi_-$ . If we consider a point, M, equidistant between the two nuclei, then by symmetry at this point the contributions from  $\chi_1$  and  $\chi_2$  are exactly equal but opposite in sign. The result is simple

$$\phi_-(M) = \chi_1(M) - \chi_2(M) = 0 \quad (14)$$

The plane which bisects the A—A axis is thus a *nodal plane*. A contour diagram is shown in 3-3, and just as for the atomic orbital case the change in sign of the function is shown by the use of dashed lines. Thus the MO  $\phi_-$  is characterized by a small amplitude in the internuclear region.



Conventionally we describe MOs in terms of the contributions from the AOs from which they are derived. The signs of the AOs are indicated by the conventions adopted

in Chapter 2 (2-4). When the function is positive the orbital is hatched and when the function is negative it is unhatched. Additionally the size of the AO used reflects the magnitude of its coefficient in the LCAO expansions; the larger the coefficient, the larger the orbital size. In  $\phi_+$  (3-4) the AO coefficients are equal in absolute size (circles of the same radius) and are of the same sign (circles which are either both hatched or both unhatched since  $\phi_+$  and  $-\phi_+$  have the same physical significance.) In  $\phi_-$  (3-5) the coefficients are again equal in absolute value (same radius) but now different in sign (opposite hatching characteristics). The schematic representation of a molecular orbital gives the relative signs and relative weights of the coefficients.



### (d) Bonding and antibonding orbitals

Let us return to the probability density functions associated with the two MOs  $\phi_+$  and  $\phi_-$ .

$$\phi_+^2 = \frac{1}{2(1+S)} (\chi_1^2 + \chi_2^2 + 2\chi_1\chi_2) \quad (15)$$

$$\phi_-^2 = \frac{1}{2(1-S)} (\chi_1^2 + \chi_2^2 - 2\chi_1\chi_2) \quad (16)$$

Ignoring the normalization term the two density functions differ only in the sign of the cross term  $2\chi_1\chi_2$ , which we recall, is only important in the region between the nuclei. In  $\phi_+$  this density adds to that already associated with the nuclei ( $\chi_1^2 + \chi_2^2$ ) and an electron occupying this orbital has an increased probability, relative to the atoms of finite separation, of being between the nuclei. An electron in this orbital lies at a lower energy than one in an isolated AO. Although the detailed breakdown of the energy is beyond the scope of our approach, both the kinetic and potential energy of the electron are reduced. We can see that the electron between the two nuclei is attracted to both, rather than just a single nucleus, and in this orbital, where the internuclear probability is enhanced via the term  $2\chi_1\chi_2$ , this is important. Because of this energetic stabilization this orbital is called a *bonding orbital*.

The converse is true in  $\phi_-$ . Here the electron density  $2\chi_1\chi_2$  is subtracted from the terms associated with the density around the nuclei ( $\chi_1^2 + \chi_2^2$ ). There is now a reduced probability of finding the electron between the nuclei, and the stabilization described above for the bonding orbital is absent. In fact the electron is less stable in this orbital than in an isolated orbital. Such an orbital is called an *antibonding orbital*.

The term  $2\chi_1\chi_2$  clearly plays an important role in determining the energetics here.



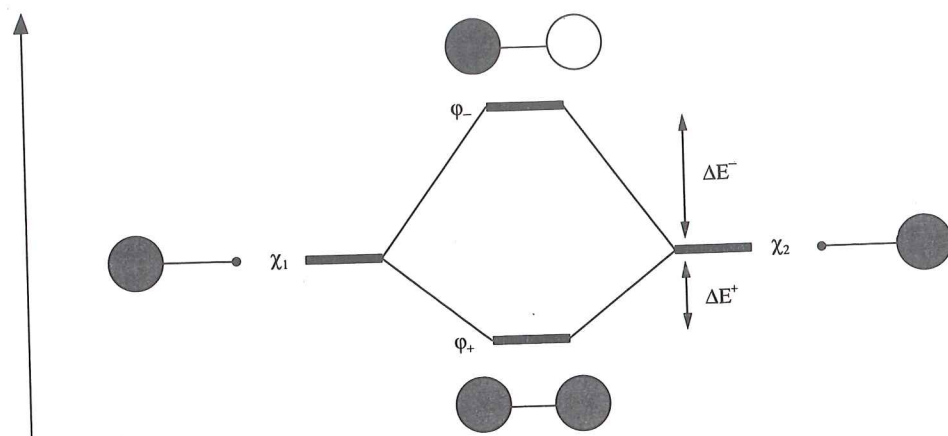


Figure 3.1. Molecular orbital diagram showing the interaction between two identical atomic orbitals in a homonuclear molecule.

Its integral over all space  $2\langle\chi_1|\chi_2\rangle$  is twice the overlap integral between  $\chi_1$  and  $\chi_2$ . This overlap controls the way molecular orbitals are constructed and is a crucial ingredient in the formation of a bond between two atoms.

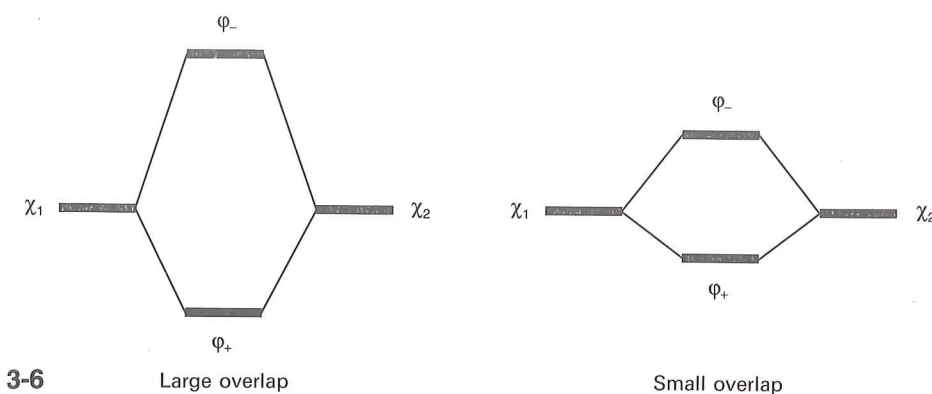
#### (e) Molecular orbital energies: interaction diagrams

The energies of the two MOs  $\phi_+$  and  $\phi_-$ , in contrast to the energies of the AOs from which they are derived, are not equal. Summarizing the discussion above, *the bonding orbital  $\phi_+$  is stabilized and the antibonding orbital  $\phi_-$  destabilized with respect to the energies of the starting AOs.*

Let us call  $\Delta E^+$  the stabilization energy of the bonding orbital ( $\Delta E^+ = \varepsilon(\chi_1) - \varepsilon(\phi_+)$ ) and  $\Delta E^-$  the destabilization of the antibonding MO ( $\Delta E^- = \varepsilon(\phi_-) - \varepsilon(\chi_1)$ ). These two quantities are thus, by definition, positive, and a general result connecting the two is that *the stabilization of the bonding orbital ( $\Delta E^+$ ) is smaller than the destabilization of the antibonding orbital ( $\Delta E^-$ ).*

It is now possible to construct an interaction diagram between the two atomic orbitals  $\chi_1$  and  $\chi_2$  in Figure 3.1. The atomic and molecular levels are represented by horizontal lines arranged in order of increasing energy. Since the AOs  $\chi_1$  and  $\chi_2$  are degenerate they lie at the same level on the diagram. Reading the diagram is made easier by including the graphical description of the orbitals. (In fact we have simplified the diagram a little here. Since the normalization constants, equations (10) and (11) include  $S (> 0)$  the coefficients for the bonding orbitals are smaller than those for the antibonding ones.)

The strength of the interaction between the AOs is measured by the stabilization  $\Delta E^+$ , or the destabilization  $\Delta E^-$ , of the bonding or antibonding orbital respectively. As we have noted these depend upon the size of the overlap integral ( $S$ ) between the two AOs. The larger the overlap the larger those energies  $\Delta E^+$  and  $\Delta E^-$ , as shown in 3-6. *The two quantities  $\Delta E^+$  and  $\Delta E^-$  are proportional to the overlap integral  $S$ .*



3-6

Large overlap

Small overlap

#### 3.2.2. Interaction of two different AOs

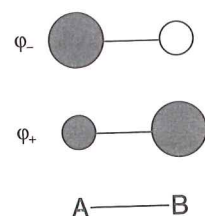
Let us consider the case of a diatomic heteronuclear molecule AB, in which the two atoms are not the same. We assume once again that each atom only has a single AO ( $\chi_1$  on A and  $\chi_2$  on B) and that their energies are different (the energy of  $\chi_2$  will be chosen to lie deeper than that of  $\chi_1$ ). An example of a molecule of this type is the ion  $\text{HHe}^+$  where A = H, B = He,  $\chi_1 = 1s_{\text{H}}$ ,  $\chi_2 = 1s_{\text{He}}$ ,  $\varepsilon_1 = -13.6 \text{ eV}$  and  $\varepsilon_2 = -24.6 \text{ eV}$ .

#### (a) Expression for the MOs

The determination of the details of the molecular orbitals is more complex than in the homonuclear case. In effect the symmetry arguments used before which allowed us to find expressions for  $\phi_+$  and  $\phi_-$  do not hold here. The two AOs,  $\chi_1$  and  $\chi_2$  are different and the electron densities associated with A and B need not be equal. In practice we need to perform a calculation to uncover the nature of the orbitals, but there are two rules which apply in general.

- (i) The interaction of two AOs ( $\chi_1$  and  $\chi_2$ ) which are non-degenerate leads to a bonding orbital ( $\phi_+$ ) and an antibonding orbital ( $\phi_-$ ).
- (ii) In the bonding orbital the larger coefficient is associated with the AO which started off at lower energy and in the antibonding orbital the opposite is true, the larger coefficient is associated with the AO which started off at higher energy.

In other words when  $\varepsilon_2 < \varepsilon_1$  *the bonding orbital is largely located on  $\chi_2$  and the antibonding orbital largely localized on  $\chi_1$ .* Using our pictorial scheme the two orbitals look as in 3-7. The antibonding orbital,  $\phi_-$ , in which the coefficients are of different signs, has a nodal surface. Since the absolute values of the atomic orbital coefficients are not equal this does not lie midway between A and B as in the symmetric case. It lies closer to atom B.



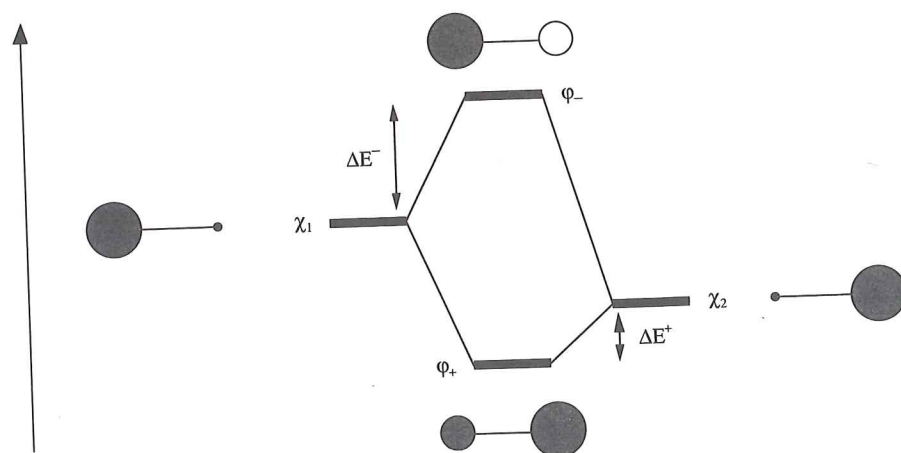
3-7

**(b) The interaction diagram**

Just as in the degenerate case, the important electron density lies between the nuclei in the bonding orbital  $\phi_+$  where the two AOs are in phase. Contrariwise this density is extruded from this region in the antibonding orbital  $\phi_-$ . As a consequence the bonding orbital is stabilized below the initial level of the deeper-lying AO and the antibonding orbital is destabilized above the higher energy AO. We can profitably define  $\Delta E^+$  ( $=\epsilon(\chi_2) - \epsilon(\phi_+)$ ) and  $\Delta E^-$  ( $=\epsilon(\phi_-) - \epsilon(\chi_1)$ ) just as in the symmetric case. Just as before  $\Delta E^+ < \Delta E^-$ . This collection of results is shown in the orbital diagram of Figure 3.2.

As before the interaction between the two AOs depends upon the overlap integral  $S$ . The larger  $S$  the larger the interaction. For the non-degenerate case we can show that it is proportional to the square of the overlap integral. Another factor which is important here is the energy separation between the two orbitals. The largest interaction between the two orbitals is found for small values of  $\Delta\epsilon = \epsilon_1 - \epsilon_2$ . In general the two quantities  $\Delta E^+$  and  $\Delta E^-$  are proportional to the function  $S^2/\Delta\epsilon$ . This formula is only applicable for the case where  $\Delta\epsilon$  is large enough. For  $\Delta\epsilon = 0$  or close to zero then, as described earlier the interaction energy is proportional to  $S$  alone.

Now it is possible to qualitatively justify the approximation which involved neglect of the core orbitals in the construction of the molecular orbital diagrams.



**Figure 3.2.** Molecular orbital diagram showing the interaction between two different atomic orbitals in a heteronuclear molecule.

These orbitals lie so deep in energy that there is a large energy separation between them and the valence orbitals (large  $\Delta\epsilon$ ). In addition they are strongly contracted, have small orbital radii and thus have extremely small overlap with orbitals (of any type) on adjacent atoms (small  $S$ ). These two factors both contribute to negligibly small interactions between these two sets of orbitals and are usually ignored.

**3.2.3. Orbitals with zero overlap**

Recall that when two orbitals interact, the stabilization of the bonding MO which is formed is proportional to  $S$  if the starting orbitals have the same energy and to  $S^2/\Delta\epsilon$  if they don't. In both cases if the overlap integral between two orbitals centered on different atoms is zero (i.e., orthogonal orbitals) then there will be no interaction between them. This apparently trivial result is, in fact, quite important. Since formation of a bonding molecular orbital results in deformation of the electronic cloud and allows an electron simultaneously to interact with both nuclei, if  $S = 0$  then there will be no such deformation and no resulting stabilization.

**3.3. Application to some simple diatomic molecules**

We will limit these examples to those ions and molecules formed from those atoms with a single valence orbital, namely H and He. In what follows we will describe the electronic energy in a molecule  $E_e$  as a simple sum of the energies of the individual electrons;  $E_e = \sum_i n_i \epsilon_i$  where  $n_i$  is the number of electrons occupying the MO  $\phi_i$  with energy  $\epsilon_i$ .

**3.3.1. Level filling rules**

Once the MOs have been constructed from the AOs we must now put electrons into them to generate the electronic structure for the molecule. The orbital filling rules are just the same as for AOs.

- (i) The MOs are filled in order of increasing energy.
- (ii) Each MO cannot accommodate more than two electrons. These two have opposite spins.

In some systems, more complex than those envisaged here, fewer electrons will be present than needed to fill a given set of degenerate orbitals and we will need to place these electrons in different orbitals with their spins parallel according to Hund's rule. In molecules, contrary to the success of the rule in atoms, Hund's rule sometimes breaks down. However the exceptions are infrequent and will not be discussed here.

**3.3.2. Systems with two or four electrons**

The general result, derived above, is that when two orbitals, degenerate or not, interact a bonding orbital is formed which is lower in energy than either of the AOs, and an antibonding orbital formed, which is higher in energy than either of the AOs.