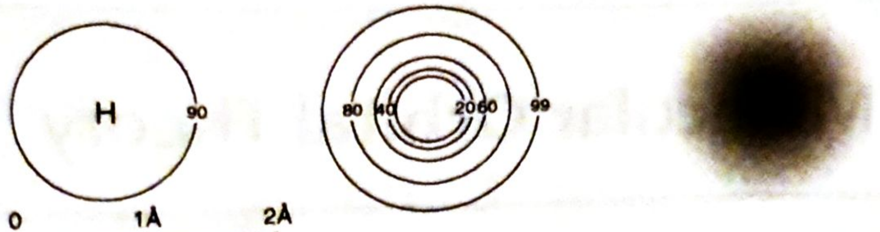
# 1 Molecular Orbital Theory

## 1.1 The Atomic Orbitals of a Hydrogen Atom

The spatial distribution of the electron in a hydrogen atom is usually expressed as a *wave function* $\phi$, where $\phi^2 d\tau$ is the probability of finding the electron in the volume $d\tau$, and the integral of $\phi^2 d\tau$ over the whole of space is 1. The wave function is the underlying mathematical description, and it may be positive or negative. Only when squared does it correspond to anything with physical reality—the probability of finding an electron in any given space. Quantum theory gives us a number of permitted wave equations, but the one that matters here is the lowest in energy, in which the electron is in a 1s orbital. This is spherically symmetrical about the nucleus, with a maximum at the centre, and falling off rapidly, so that the probability of finding the electron within a sphere of radius 1.4 Å is 90% and within 2 Å better than 99%. This orbital is calculated to be 13.60 eV lower in energy than a completely separated electron and proton.

We need pictures to illustrate the electron distribution, and the most common is simply to draw a circle, Fig. 1.1a, which can be thought of as a section through a spherical contour, within which the electron would be found, say, 90% of the time. Fig. 1.1b is a section showing more contours and Fig. 1.1c is a section through a cloud, where one imagines blinking one's eyes a very large number of times, and plotting the points at which the electron was at each blink. This picture contributes to the language often used, in which the electron population in a given volume of space is referred to as the electron density. Taking advantage of the spherical symmetry, we can also plot the fraction of the electron population outside a radius *r* against *r*, as in Fig. 1.2a, showing the rapid fall off of electron population with distance. The van der Waals radius at 1.2 Å has no theoretical significance—it is an empirical measurement from solid-state structures, being one-half of the distance apart of the hydrogen atoms in the C—H bonds of adjacent molecules. It is an average of several measurements. Yet another way to appreciate the electron distribution is to look at the radial density, where we plot the probability of finding the electron between one sphere of radius *r* and another of radius $r + dr$. This has the form, Fig. 1.2b, with a maximum 0.529 Å from the nucleus, showing that, in spite of the wave function being at a maximum at the

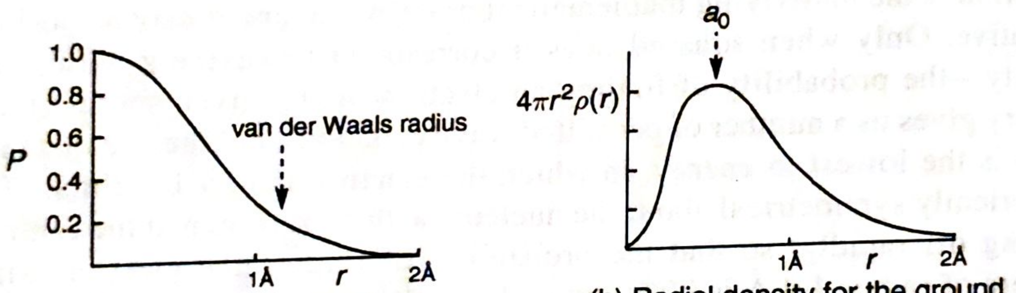
*Molecular Orbitals and Organic Chemical Reactions: Student Edition* Ian Fleming



(a) One contour (b) Several contours (c) An electron cloud

**Fig. 1.1** The 1s atomic orbital of a hydrogen atom

nucleus, the chance of finding an electron precisely there is very small. The distance 0.529 Å proves to be the same as the radius calculated for the orbit of an electron in the early but untenable planetary model of a hydrogen atom. It is called the Bohr radius $a_0$, and is often used as a unit of length in molecular orbital calculations.



(a) Fraction of charge-cloud outside a sphere of radius *r*

(b) Radial density for the ground state hydrogen atom

**Fig. 1.2** Radial probability plots for the 1s orbital of a hydrogen atom

## 1.2 Molecules made from Hydrogen Atoms

### 1.2.1 The $H_2$ Molecule

To understand the bonding in a hydrogen molecule, we have to see what happens when the atoms are close enough for their atomic orbitals to interact. We need a description of the electron distribution over the whole molecule. We accept that a first approximation has the two atoms remaining more or less unchanged, so that the description of the molecule will resemble the sum of the two isolated atoms. Thus we combine the two atomic orbitals in a linear combination expressed in Equation 1.1, where the function which describes the new electron distribution, the *molecular orbital*, is called $\sigma$ and $\phi_1$ and $\phi_2$ are the atomic 1s wave functions on atoms 1 and 2.

$$\sigma = c_1\phi_1 + c_2\phi_2 \qquad 1.1$$

The coefficients, $c_1$ and $c_2$, are a measure of the contribution which the atomic orbital is making to the molecular orbital. They are of course equal in magnitude in this case, since the two atoms are the same, but they may be positive or negative. To obtain the electron distribution, we square the function in Equation 1.1, which is written in two ways in Equation 1.2.

$$\sigma^2 = (c_1\phi_1 + c_2\phi_2)^2 = (c_1\phi_1)^2 + (c_2\phi_2)^2 + 2c_1\phi_1c_2\phi_2 \qquad 1.2$$

Taking the expanded version, we can see that the molecular orbital $\sigma^2$ differs from the superposition of the two atomic orbitals $(c_1\phi_1)^2+(c_2\phi_2)^2$ by the term $2c_1\phi_1c_2\phi_2$. Thus we have two solutions (Fig. 1.3). In the first, both $c_1$ and $c_2$ are positive, with orbitals of the same sign placed next to each other; the electron population *between* the two atoms is increased (shaded area), and hence the negative charge which these electrons carry *attracts* the two positively charged nuclei. This results in a lowering in energy and is illustrated in Fig. 1.3, where the bold horizontal line next to the drawing of this orbital is placed low on the diagram. Alternatively, $c_1$ and $c_2$ are of opposite sign, and we represent the sign change by shading one of the orbitals, calling the plane which divides the function at the sign change a node. If there were any electrons in this orbital, the reduced electron population between the nuclei would lead to repulsion between them and a raised energy for this orbital. In summary, by making a bond between two hydrogen atoms, we create two new orbitals, $\sigma$ and $\sigma^*$, which we call the molecular orbitals; the former is *bonding* and the latter *antibonding* (an asterisk generally signifies an antibonding orbital). In the ground state of the molecule, the two electrons will be in the orbital labelled $\sigma$. There is, therefore, when we make a bond, a lowering of energy equal to twice the value of $E_\sigma$ in Fig. 1.3 (*twice* the value, because there are two electrons in the bonding orbital).

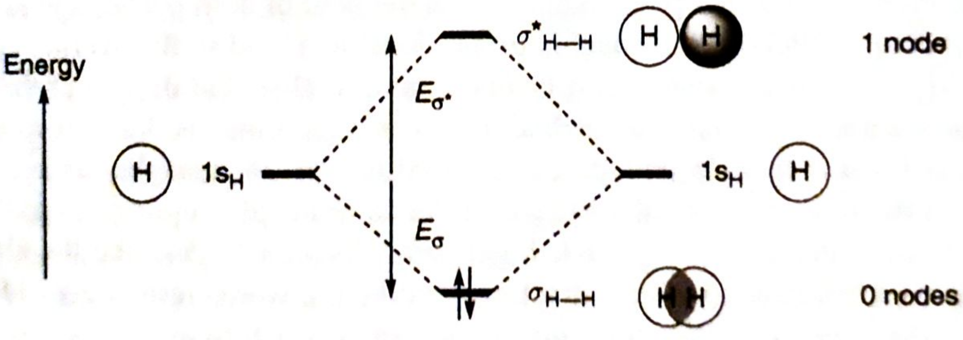


**Fig. 1.3** The molecular orbitals of the hydrogen molecule

The force holding the two atoms together is obviously dependent upon the extent of the overlap in the bonding orbital. If we bring the two 1s orbitals from a position where there is essentially no overlap at 2.5 Å through the bonding arrangement to superimposition, the extent of overlap steadily increases. The mathematical description of the overlap is an integral $S_{12}$ (Equation 1.3) called the *overlap integral*, which, for a pair of 1s orbitals rises from 0 at infinite separation to 1 at superimposition (Fig. 1.4).

$$S_{12} = \int \phi_1\phi_2 d\tau \qquad 1.3$$

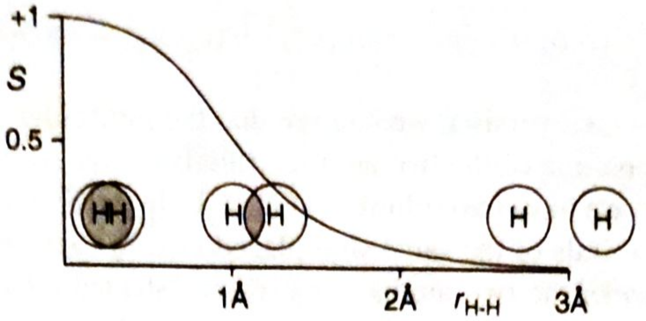


**Fig. 1.4** The overlap integral $S$ for two $1s_H$ orbitals as a function of internuclear distance

The mathematical description of the effect of overlap on the electronic energy is complex, but some of the terminology is worth recognising. The energy $E$ of an electron in a bonding molecular orbital is given by Equation 1.4 and for the antibonding molecular orbital is given by Equation 1.5:

$$E = \frac{\alpha + \beta}{1 + S} \tag{1.4}$$

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$$E = \frac{\alpha - \beta}{1 - S} \tag{1.5}$$

denominator

in which the symbol $\alpha$ represents the energy of an electron in an isolated atomic orbital, and is called a *Coulomb integral*. The function represented by the symbol $\beta$ contributes to the energy of an electron in the field of both nuclei, and is called the *resonance* integral. It is roughly proportional to $S$, and so the overlap integral appears in the equations twice. It is important to realise that the use of the word resonance does not imply an oscillation, nor is it the same as the 'resonance' of valence bond theory. In both cases the word is used because the mathematical form of the function is similar to that for the mechanical coupling of oscillators. We also use the words *delocalised* and *delocalisation* to describe the electron distribution enshrined in the $\beta$ function—unlike the words resonating and resonance, these are not misleading, and are the better words to use.

The function $\beta$ is a negative number, lowering the value of $E$ in Equation 1.4 and raising it in Equation 1.5. In this book, $\beta$ will not be given a sign on the diagrams on which it is used, because the sign can be misleading. The symbol $\beta$ should be interpreted as $|\beta|$, the positive absolute value of $\beta$. Since the diagrams are always plotted with energy upwards and almost always with the $\alpha$ value visible, it should be obvious which $\beta$ values lead to a lowering of the energy below the $\alpha$ level, and which to raising the energy above it.

The overall effect on the energy of the hydrogen molecule relative to that of two separate hydrogen atoms as a function of the internuclear distance is given in Fig. 1.5. If the bonding orbital is filled, the energy derived from the electronic contribution (Equation 1.4) steadily falls as the two hydrogen atoms are moved from infinity towards one another (curve A). At the same time the nuclei repel each other ever more strongly, and the nuclear contribution to the energy goes steadily up (curve B).

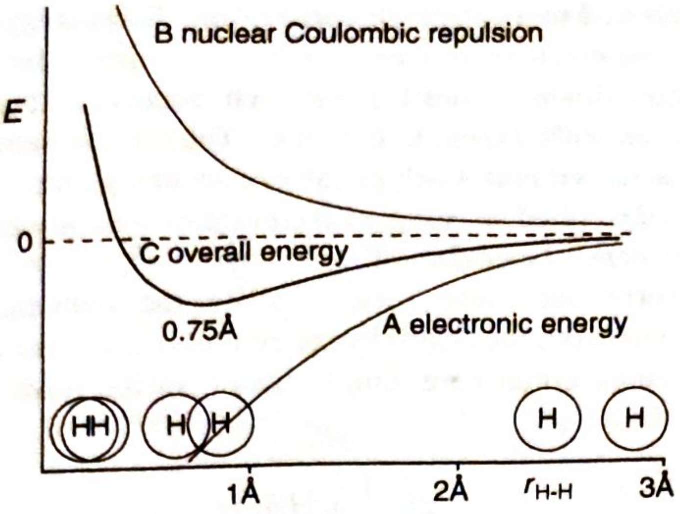

**Fig. 1.5** Electronic attraction, nuclear repulsion and the overall effect as a function of internuclear distance for two $1s_H$ atoms

The sum of these two is the familiar Morse plot (curve C) for the relationship between internuclear distance and energy, with a minimum at the bond length. If we had filled the antibonding orbital instead, the resultant curve would be a steady increase in energy as the nuclei are pushed together. The characteristic of a bonding orbital is that the nuclei are held together, whereas the characteristic of an antibonding orbital, if it were to be filled, is that the nuclei would fly apart unless there are enough compensating filled bonding orbitals. In hydrogen, having both orbitals occupied is overall antibonding, and there is no possibility of compensating for a filled antibonding orbital.

We can see from the form of Equations 1.4 and 1.5 that the term $\alpha$ relates to the energy levels of the isolated atoms labelled $1s_H$ in Fig. 1.3, and the term $\beta$ to the drop in energy labelled $E_\sigma$ (and the rise labelled $E_{\sigma^*}$). Equations 1.4 and 1.5 show that, since the denominator in the bonding combination is $1 + S$ and the denominator in the antibonding combination is $1 - S$, the bonding orbital is not as much lowered in energy as the antibonding is raised. In addition, putting *two* electrons into a bonding orbital does not achieve exactly twice the energy-lowering of putting *one* electron into it. We are *allowed* to put two electrons into the one orbital if they have opposite spins, but they still repel each other, because they have the same sign and have to share the same space; consequently, in forcing a second electron into the $\sigma$ orbital, we lose some of the bonding we might otherwise have gained. For this reason too, the value of $E_\sigma$ in Fig. 1.3 is smaller than that of $E_{\sigma^*}$. This is why two helium atoms do not combine to form an $He_2$ molecule. There are four electrons in two helium atoms, two of which would go into the $\sigma$-bonding orbital and two into the $\sigma^*$-antibonding orbital. Since $2E_{\sigma^*}$ is greater than $2E_\sigma$, we would need extra energy to keep the two helium atoms together. Two electrons in the same orbital can keep out of each other's way, with one electron on one side of the orbital, while the other is on the other side most of the time, and so the energetic penalty for having a second electron in the orbital is not large. This synchronisation of the electrons'

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movements is referred to as *electron correlation*. The energy-raising effect of the repulsion of one electron by the other is automatically included in calculations based on Equations 1.4 and 1.5, but each electron is treated as having an average distribution with respect to the other. The effect of electron correlation is often not included, without much penalty in accuracy, but when it is included the calculation is described as being with *configuration interaction*, a bit of fine tuning added to a careful calculation.

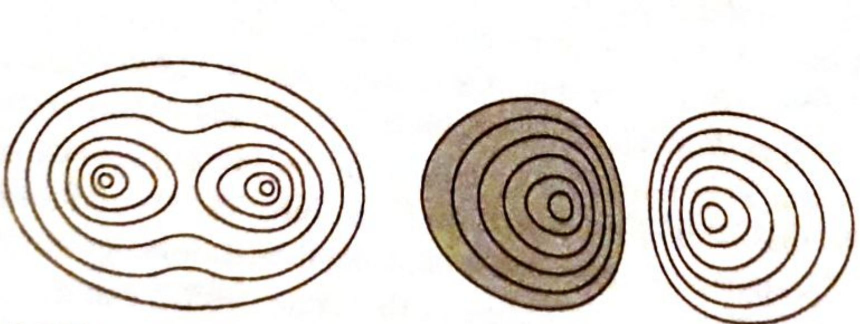
The detailed form that $\alpha$ and $\beta$ take is where the mathematical complexity appears. They come from the Schrödinger equation, and they are integrals over all coordinates, represented here simply by $d\tau$, in the form of Equations 1.6 and 1.7:

$$\alpha = \int \phi_1 H \phi_1 d\tau \qquad 1.6$$

$$\beta = \int \phi_1 H \phi_2 d\tau \qquad 1.7$$

where $H$ is the energy operator known as a Hamiltonian. Even without going into this in more detail, it is clear how the term $\alpha$ relates to the atom, and the term $\beta$ to the interaction of one atom with another.

As with atomic orbitals, we need pictures to illustrate the electron distribution in the molecular orbitals. For most purposes, the conventional drawings of the bonding and antibonding orbitals in Fig. 1.3 are clear enough—we simply make mental reservations about what they represent. In order to be sure that we do understand enough detail, we can look at a slice through the two atoms showing the contours (Fig. 1.6). Here we see in the bonding orbital that the electron population close in to the nucleus is pulled in to the midpoint between the nuclei (Fig. 1.6a), but that further out the contours are an elliptical envelope with the nuclei as the foci. The antibonding orbital, however, still has some dense contours between the nuclei, but further out the electron population is pushed out on the back side of each nucleus. The node is halfway between the nuclei, with the change of sign in the wave function symbolised by the shaded contours on the one side. If there were electrons in this orbital, their distribution on the outside would pull the nuclei apart—the closer the atoms get, the more the electrons are pushed to the outside.

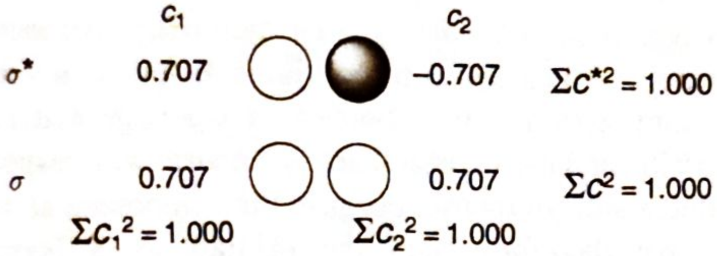


(a) The $\sigma$-bonding orbital

(b) The $\sigma^*$-antibonding orbital

**Fig. 1.6** Contours of the wave function of the molecular orbitals of $H_2$

The coefficients $c_1$ and $c_2$ in Equation 1.1 are a measure of the contribution which each atomic orbital is making to the molecular orbital. When there are electrons in the orbital, the squares of the $c$-values are a measure of the electron population in the neighbourhood of the atom in question. Thus *in each orbital* the sum of the squares of all the $c$-values must equal one, since only one electron in each spin state can be in the orbital. Since $|c_1|$ must equal $|c_2|$ in a homonuclear diatomic like $H_2$, we have defined what the values of $c_1$ and $c_2$ in the bonding orbital must be, namely $1/\sqrt{2} = 0.707$:



If all molecular orbitals were filled, then there would have to be one electron in each spin state on each atom, and this gives rise to a second criterion for $c$-values, namely that the sum of the squares of all the $c$-values *on any one atom* in *all* the molecular orbitals must also equal one. Thus the $\sigma^*$-antibonding orbital of hydrogen will have $c$-values of 0.707 and −0.707, because these values make the whole set fit both criteria.

### 1.2.2 The $H_3$ Molecule

We might ask whether we can join more than two hydrogen atoms together. We shall consider first the possibility of joining three atoms together in a triangular arrangement. With three atomic orbitals to combine, we can no longer simply draw an interaction diagram as we did in Fig. 1.3, where there were only two atomic orbitals. One way of dealing with the problem is first to take two of them together to form a hydrogen molecule, and then we combine the $\sigma$ and $\sigma^*$ orbitals, on the right of Fig. 1.7, with the 1s orbital of the third hydrogen atom on the left.

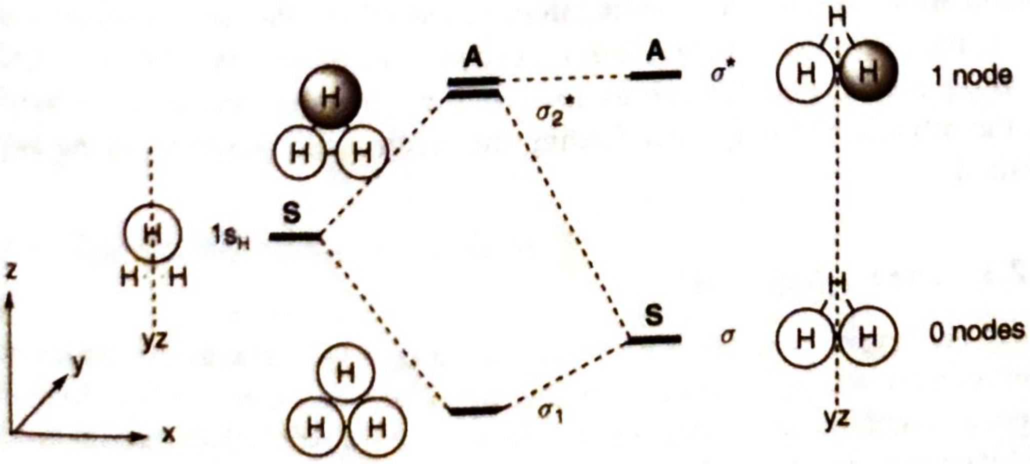


Fig. 1.7 Interacting orbitals for $H_3$

We now meet an important rule: we are only allowed to combine those orbitals that have the same symmetry with respect to all the symmetry elements present in the structure of the product and in the orbitals of the components we are combining. This problem did not arise in forming a bond between two identical hydrogen atoms, because they have inherently the same symmetry, but now we are combining different sets of orbitals with each other. The first task is to identify the symmetry elements, and classify the orbitals with respect to them. Because all the orbitals are s orbitals, there is a trivial symmetry plane in the plane of the page, which we shall label throughout this book as the xz plane. We can ignore it, and other similar symmetry elements, in this case. The only symmetry element that is not trivial is the plane in what we shall call the yz plane, running from top to bottom of the page and rising vertically from it. The $\sigma$ orbital and the 1s orbital are symmetric with respect to this plane, but the $\sigma^*$ orbital is antisymmetric, because the component atomic orbitals are out of phase. We therefore label the orbitals as S (symmetric) or A (antisymmetric).

The $\sigma$ orbital and the 1s orbital are both S and they can interact in the same way as we saw in Fig. 1.3, to create a new pair of molecular orbitals labelled $\sigma_1$ and $\sigma_2^*$. The former is lowered in energy, because all the s orbitals are of the same sign, and the latter is raised in energy, because there is a node between the top hydrogen atom and the two bottom ones. The latter orbital is antibonding overall, because, in the triangular arrangement we have chosen here, there are two antibonding interactions between hydrogen atoms and only one bonding interaction. As it happens, its energy is the same as that of the $\sigma^*$ orbital, but we cannot justify that now. In any case, the other orbital $\sigma^*$ remains unchanged in the $H_3$ molecule, because there is no orbital of the correct symmetry to interact with it.

Thus we have three molecular orbitals, just as we had three atomic orbitals to make them from. Whether we have a stable 'molecule' now depends upon how many electrons we have. If we have two in a protonated hydrogen molecule, $H_3^+$, they would both go into the $\sigma_1$ orbital, and the molecule would have a lower electronic energy than the separate proton and $H_2$ molecule. If we had three electrons $H_3\bullet$ from combining three hydrogen atoms, we would also have a stable 'molecule', with *two* electrons in $\sigma_1$ and only *one* in $\sigma_2^*$, making the combination overall more bonding than antibonding. Only with four electrons in $H_3^-$ is the overall result antibonding, because the energy-raising interaction is, as usual, greater than the energy-lowering interaction. This device of building up the orbitals and only then feeding the electrons in is known as the *aufbau* method.