Molecular Orbitals and Organic Chemical Reactions

Reference Edition

Ian Fleming
Department of Chemistry,
University of Cambridge, UK
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Preface

Molecular orbital theory is used by chemists to describe the arrangement of electrons in chemical structures. It provides a basis for explaining the ground-state shapes of molecules and their many other properties. As a theory of bonding it has largely replaced valence bond theory, but organic chemists still implicitly use valence bond theory whenever they draw resonance structures. Unfortunately, misuse of valence bond theory is not uncommon as this approach remains in the hands largely of the less sophisticated. Organic chemists with a serious interest in understanding and explaining their work usually express their ideas in molecular orbital terms, so much so that it is now an essential component of every organic chemist’s skills to have some acquaintance with molecular orbital theory. The problem is to find a level to suit everyone. At one extreme, a few organic chemists with high levels of mathematical skill are happy to use molecular orbital theory, and its computationally more amenable offshoot density functional theory, much as theoreticians do. At the other extreme are the many organic chemists with lower mathematical inclinations, who nevertheless want to understand their reactions at some kind of physical level. It is for these people that I have written this book. In between there are more and more experimental organic chemists carrying out calculations to support their observations, and these people need to know some of the physical basis for what their calculations are doing.

I have presented molecular orbital theory in a much simplified and entirely nonmathematical language. I have simplified the treatment in order to make it accessible to every organic chemist, whether student or research worker, whether mathematically competent or not. In order to reach such a wide audience, I have frequently used oversimplified arguments. I trust that every student who has the aptitude will look beyond this book for a better understanding than can be found here. Accordingly, I have provided over 1800 references to the theoretical treatments and experimental evidence, to make it possible for every reader to go further into the subject.

Molecular orbital theory is not only a theory of bonding, it is also a theory capable of giving some insight into the forces involved in the making and breaking of chemical bonds—the chemical reactions that are often the focus of an organic chemist’s interest. Calculations on transition structures can be carried out with a bewildering array of techniques requiring more or less skill, more or fewer assumptions, and greater or smaller contributions from empirical input, but many of these fail to provide the organic chemist with insight. He or she wants to know what the physical forces are that give the various kinds of selectivity that are so precious in learning how to control organic reactions. The most accessible theory to give this kind of insight is frontier orbital theory, which is based on the perturbation treatment of molecular orbital theory, introduced by Coulson and Longuet-Higgins, and developed and named as frontier orbital theory by Fukui.

Earlier theories of reactivity concentrated on the product-like character of transition structures—the concept of localisation energy in aromatic electrophilic substitution is a well-known example. The perturbation theory concentrates instead on the other side of the reaction coordinate. It looks at how the interaction of the molecular orbitals of the starting materials influences the transition structure. Both influences are obviously important, and it is therefore helpful to know about both if we want a better understanding of what factors affect a transition structure, and hence affect chemical reactivity.

Frontier orbital theory is now widely used, with more or less appropriateness, especially by organic chemists, not least because of the success of the predecessor to this book, Frontier Orbitals and Organic Chemical Reactions, which survived for more than thirty years as an introduction to the subject for a high proportion of the organic chemists trained in this period. However, there is a problem—computations show
that the frontier orbitals do not make a significantly larger contribution than the sum of all the orbitals. One theorician put it to me as: ‘It has no right to work as well as it does.’ The difficulty is that it works as an explanation in many situations where nothing else is immediately compelling. In writing this book, I have therefore emphasised more the molecular orbital basis for understanding organic chemistry, about which there is less disquiet. Thus I have completely rewritten the earlier book, enlarging especially the chapters on molecular orbital theory itself. I have added a chapter on the effect of orbital interactions on the structures of organic molecules, a section on the theoretical basis for the principle of hard and soft acids and bases, and a chapter on the stereochemistry of the fundamental organic reactions. I have introduced correlation diagrams into the discussion of pericyclic chemistry, and a great deal more in that, the largest chapter. I have also added a number of topics, both omissions from the earlier book and new work that has taken place in the intervening years. I have used more words of caution in discussing frontier orbital theory itself, making it less polemical in furthering that subject, and hoping that it might lead people to be more cautious themselves before applying the ideas uncritically in their own work.

For all their faults and limitations, frontier orbital theory and the principle of hard and soft acids and bases remain the most accessible approaches to understanding many aspects of reactivity. Since they fill a gap between the chemist’s experimental results and a state of the art theoretical description of his or her observations, they will continue to be used, until something better comes along.

In this book, there is much detailed and not always convincing material, making it less suitable as a textbook for a lecture course; in consequence I have also written a second and shorter book on molecular orbital theory designed specifically for students of organic chemistry, Molecular Orbitals and Organic Chemistry—The Student Edition, which serves in a sense as a long awaited second edition to my earlier book. The shorter book uses a selection of the same material as in this volume, with appropriately revised text, but dispenses with most of the references, which can all be found here. The shorter book also has problem sets at the ends of the chapters, whereas this book has the answers to most of them in appropriate places in the text. I hope that everyone can use whichever volume suits them, and that even theoreticians might find unresolved problems in one or another of them.

As in the earlier book, I begin by presenting some experimental observations that chemists have wanted to explain. None of the questions raised by these observations has a simple answer without reference to the orbitals involved.

(i) Why does methyl tetrahydropyranyl ether largely adopt the conformation P.1, with the methoxy group axial, whereas methoxycyclohexane adopts largely the conformation P.2 with the methoxy group equatorial?

(ii) Reduction of butadiene P.3 with sodium in liquid ammonia gives more cis-2-butene P.4 than trans-2-butene P.5, even though the trans isomer is the more stable product.

(iii) Why is the inversion of configuration at nitrogen made slower if the nitrogen is in a small ring, and slower still if it has an electronegative substituent attached to it, so that, with the benefit of both features, an N-chloroaziridine can be separated into a pair of diastereoisomers P.6 and P.7?
(iv) Why do enolate ions $\text{P.8}$ react more rapidly with protons on oxygen, but with primary alkyl halides on carbon?

(v) Hydroperoxide ion $\text{P.9}$ is much less basic than hydroxide ion $\text{P.10}$. Why, then, is it so much more nucleophilic?

(vi) Why does butadiene $\text{P.11}$ react with maleic anhydride $\text{P.12}$, but ethylene $\text{P.13}$ does not?

(vii) Why do Diels-Alder reactions of butadiene $\text{P.11}$ go so much faster when there is an electron-withdrawing group on the dienophile, as with maleic anhydride $\text{P.12}$, than they do with ethylene $\text{P.13}$?

(viii) Why does diazomethane $\text{P.15}$ add to methyl acrylate $\text{P.16}$ to give the isomer $\text{P.17}$ in which the nitrogen end of the dipole is bonded to the carbon atom bearing the methoxycarbonyl group, and not the other way round $\text{P.14}$?
(ix) When methyl fumarate \( \textbf{P.18} \) and vinyl acetate \( \textbf{P.19} \) are copolymerised with a radical initiator, why does the polymer \( \textbf{P.20} \) consist largely of alternating units?

(x) Why does the Paterno-Büchi reaction between acetone and acrylonitrile give only the isomer \( \textbf{P.21} \) in which the two ‘electrophilic’ carbon atoms become bonded?

In the following chapters, each of these questions, and many others, receives a simple answer. Other books commend themselves to anyone able and willing to go further up the mathematical slopes towards a more acceptable level of explanation—a few introductory texts take the next step up, and several others take the story further.

I have been greatly helped by a number of chemists: first and foremost Professor Christopher Longuet-Higgins, whose inspiring lectures persuaded me to take the subject seriously at a time when most organic chemists who, like me, had little mathematics, had abandoned any hope of making sense of the subject; secondly, and more particularly those who gave me advice for the earlier book, and who therefore made their mark on this, namely Dr W. Carruthers, Professor R. F. Hudson, Professor A. R. Katritzky and Professor A. J. Stone. In addition, for this book, I am indebted to Dr Jonathan Goodman for help with computer programs, to Professor Wes Borden for some helpful discussions and collaboration on one topic, and to Professor A. D. Buckingham for several important corrections. More than usually, I must absolve all of them for any errors left in the book.
1 Molecular Orbital Theory

1.1 The Atomic Orbitals of a Hydrogen Atom

To understand the nature of the simplest chemical bond, that between two hydrogen atoms, we look at the effect on the electron distribution when two atoms are held within bonding distance, but first we need a picture of the hydrogen atoms themselves. Since a hydrogen atom consists of a proton and a single electron, we only need a description of the spatial distribution of that electron. This is usually expressed as a wave function $\psi$, where $\psi^2 \, dt$ is the probability of finding the electron in the volume $dt$, and the integral of $\psi^2 \, dt$ over the whole of space is 1. The wave function is the underlying mathematical description, and it may be positive or negative; it can even be complex with a real and an imaginary part, but this will not be needed in any of the discussion in this book. 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 only one that matters here is the lowest in energy, in which the distribution of the electron is described as being 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. This picture will suffice for most of what we need in this book, but it might be worth looking at some others, because the circle alone disguises some features that are worth appreciating. Thus a section showing more contours, Fig. 1.1b, has more detail. Another picture, even less amenable to a quick drawing, is to plot the electron distribution as a section through a cloud, Fig. 1.1c, 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.

![Fig. 1.1](image.png) The 1s atomic orbital of a hydrogen atom
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 atom in a C—H bond and the hydrogen atom in the C—H bond of an adjacent molecule.\(^\text{13}\) It does not even have a fixed value, but 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 a revealing 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 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.

### 1.2 Molecules Made from Hydrogen Atoms

#### 1.2.1 The \( \text{H}_2 \) Molecule

To understand the bonding in a hydrogen molecule, we have to see what happens when two hydrogen atoms are close enough for their atomic orbitals to interact. We now have two protons and two nuclei, and even with this small a molecule we cannot expect theory to give us complete solutions. We need a description of the electron distribution over the whole molecule—a molecular orbital. The way the problem is handled is to 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.

\[
\sigma = c_1 \phi_1 + c_2 \phi_2
\]  \hspace{1cm} 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.

\[
\sigma^2 = (c_1 \phi_1 + c_2 \phi_2)^2 = (c_1 \phi_1)^2 + (c_2 \phi_2)^2 + 2c_1 \phi_1 c_2 \phi_2
\]  \hspace{1cm} 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 $2c_1\phi_1 c_2\phi_2$. 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 horizontal line next to the drawing of this orbital is placed low on the diagram. In the second way in which the orbitals can combine, $c_1$ and $c_2$ are of opposite sign, and, if there were any electrons in this orbital, there would be a low electron population in the space between the nuclei, since the function is changing sign. We represent the sign change by shading one of the orbitals, and we call 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; thus, if we wanted to have electrons in this orbital and still keep the nuclei reasonably close, energy would have to be put into the system. 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 hydrogen](image)

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 3 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).

\[
S_{12} = \int \phi_1 \phi_2 d\tau
\]

The mathematical description of the effect of overlap on the electronic energy is complex, but some of the terminology is worth recognising, and will be used from time to time in the rest of this book. 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:

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

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

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 exactly 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 refer 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 (Fig. 1.5a), 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). 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 (Fig. 1.5b), there would have been no change to curve B. The electronic energy would be given by Equation 1.5 which provides only a little shielding between the separated nuclei giving at first a small curve down for curve A, and even that would change to a repulsion earlier than in the Morse curve. The resultant curve, C, is 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 \( 1/C_1 \) relates to the energy levels of the isolated atoms labelled 1s\(_H\) in Fig. 1.3, and the term \( 1/C_2 \) 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 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 \( \text{He}_2 \) molecule. There are four electrons in two helium atoms, two of which would go into the \( \sigma \)-bonding orbital in an \( \text{He}_2 \) molecule 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’ 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 sometimes added to a careful calculation.

The detailed form that \( 1/C_1 \) and \( 1/C_2 \) 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:

\[
\alpha = \int \phi_1 H \phi_1 d\tau 
\]

\[
\beta = \int \phi_1 H \phi_2 d\tau 
\]
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 half way 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, explaining the rise in energy of curve A in Fig. 1.5b.

![Molecular orbitals](image)

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

We can take away the sign changes in the wave function by plotting $\sigma^2$ along the internuclear axis, as in Fig. 1.7. The solid lines are the plots for the molecular orbitals, and the dashed lines are plots, for comparison, of the undisturbed atomic orbitals $\phi^2$. The electron population in the bonding orbital (Fig. 1.7a) can be seen to be slightly contracted relative to the sum of the squares of the atomic orbitals, and the electron population

![Molecular orbitals](image)

**Fig. 1.7** Plots of the square of the wave function for the molecular orbitals of $H_2$ (solid lines) and its component atomic orbitals (dashed lines). [The atomic orbital plot is scaled down by a factor of 2 to allow us to compare $\sigma^2$ with the sum of the atomic densities $(\phi_1^2 + \phi_2^2)/2$]
between the nuclei is increased relative to that sum, as we saw when we considered Equation 1.2. In the antibonding orbital (Fig. 1.7b) it is the other way round, if there were electrons in the molecular orbital, the electron population would be slightly expanded relative to a simple addition of the squares of the atomic orbitals, and the electron population between the nuclei is correspondingly decreased.

Let us return to the coefficients \( c_1 \) and \( c_2 \) of Equation 1.1, which are a measure of the contribution which each atomic orbital is making to the molecular orbital (equal in this case). 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 \( \text{H}_2 \), we have defined what the values of \( c_1 \) and \( c_2 \) in the bonding orbital must be, namely \( 1/\sqrt{2} = 0.707 \):

\[
\begin{array}{ccc}
\sigma^* & c_1 & c_2 \\
0.707 & \bigcirc & -0.707 \\
\sigma & 0.707 & 0.707 \\
\Sigma c^2 = 1.000 & & \\
\end{array}
\]

\[
\Sigma c^2 = 1.000 \hspace{1cm} \Sigma c^2 = 1.000
\]

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. Of course, we could have taken \( c_1 \) and \( c_2 \) in the antibonding orbital the other way round, giving \( c_1 \) the negative sign and \( c_2 \) the positive.

This derivation of the coefficients is not strictly accurate—a proper normalisation involves the overlap integral \( S \), which is present with opposite sign in the bonding and the antibonding orbitals (see Equations 1.4 and 1.5). As a result the coefficients in the antibonding orbitals are actually slightly larger than those in the bonding orbital. This subtlety need not exercise us at the level of molecular orbital theory used in this book, and it is not a problem at all in Hückel theory, which is what we shall be using for \( \pi \) systems. We can, however, recognise its importance when we see that it is another way of explaining that the degree of antibonding from the antibonding orbital (\( E_{\sigma^*} \) in Fig. 1.3) is greater than the degree of bonding from the bonding orbital (\( E_{\sigma} \)).

### 1.2.2 The \( \text{H}_3 \) 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. It presents us for the first time with the problem of how to account for three atoms forming bonds to each other. 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. In this case, we take two of the hydrogen atoms, and allow them to interact to form a hydrogen molecule, and then we combine the \( \sigma \) and \( \sigma^* \) orbitals, on the right of Fig. 1.8, with the 1s orbital of the third hydrogen atom on the left.

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 need to match, and to maintain, symmetry will become a constant refrain as the molecules get more complex. The first task is to identify the symmetry elements, and to 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 σ orbital and the 1s orbital are symmetric with respect to this plane, but the σ* orbital is antisymmetric, because the component atomic orbitals are out of phase. We therefore label the orbitals as S (symmetric) or A (antisymmetric).

The σ 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 σ₁ and σ₂*. 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 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 σ* orbital, but we cannot justify that fully now. In any case, the other orbital σ* remains unchanged in the H₃ 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 H₃⁺, in other words a protonated hydrogen molecule, they would both go into the σ₁ orbital, and the molecule would have a lower electronic energy than the separate proton and H₂ molecule. If we had three electrons H₃⁺ from combining three hydrogen atoms, we would also have a stable ‘molecule’, with two electrons in σ₁ and only one in σ₂*, making the combination overall more bonding than antibonding. Only if four electrons in H₃⁻ is the overall result of the interaction 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.

We could have combined the three atoms in a straight line, pulling the two lower hydrogen atoms in Fig. 1.8 out to lay one on each side of the upper atom. Since the symmetries do not change, the result would have been similar (Fig. 1.9). There would be less bonding in σ₁ and σ₂*, because the overlap between the two lower hydrogen atoms would be removed. There would also be less antibonding from the σ* orbital, since it would revert to having the same energy as the two more or less independent 1s orbitals.
1.2.3 The H$_4$ ‘Molecule’

There are even more possible ways of arranging four hydrogen atoms, but we shall limit ourselves to tetrahedral, since we shall be using these orbitals later. This time, we combine them in pairs, as in Fig. 1.3, to create two hydrogen molecules, and then we ask ourselves what happens to the energy when the two hydrogen molecules are held within bonding distance, one at right angles to the other.

We can keep one pair of hydrogen atoms aligned along the x axis, on the right in Fig. 1.10, and orient the other along the y axis, on the left of Fig. 1.10. The symmetry elements present are then the xz and yz planes. The bonding orbital $\sigma_x$ on the right is symmetric with respect to both planes, and is labelled SS. The antibonding orbital $\sigma_x^*$ is symmetric with respect to the xz plane but antisymmetric with respect to the yz plane, and is accordingly labelled SA. The bonding orbital $\sigma_y$ on the left is symmetric with respect to both planes, and is also labelled SS. The antibonding orbital $\sigma_y^*$ is antisymmetric with respect to the xz plane but symmetric with respect to the yz plane, and is labelled AS. The only orbitals with the same symmetry are therefore the two bonding orbitals, and they can interact to give a bonding combination $\sigma_1$ and an antibonding combination $\sigma_2^*$. As it happens, the latter has the same energy as the unchanged orbitals $\sigma_x^*$ and $\sigma_y^*$. This is not too difficult to understand: in the new orbitals $\sigma_1$ and $\sigma_2^*$, the coefficients $c$, will be (ignoring the full
treatment of normalisation) 0.5 instead of 0.707, in order that the sum of their squares shall be 1. In the antibonding combination $\sigma_2^*$, there are two bonding relationships between hydrogen atoms, and four antibonding relationships, giving a net value of two antibonding combinations, compared with the one in each of the orbitals $\sigma_x^*$ and $\sigma_y^*$. However the antibonding in the orbital $\sigma_2^*$ is between $s$ orbitals with coefficients of $1/\sqrt{4}$, and two such interactions is the same as one between orbitals with coefficients of $1/\sqrt{2}$ (see Equation 1.3, and remember that the change in electronic energy is roughly proportional to the overlap integral $S$).

We now have four molecular orbitals, $\sigma_1$, $\sigma_2^*$, $\sigma_x^*$ and $\sigma_y^*$, one lowered in energy and one raised relative to the energy of the orbitals of the pair of hydrogen molecules. If we have four electrons in the system, the net result is repulsion, as usual when two filled orbitals combine with each other. Thus two $\text{H}_2$ molecules do not combine to form an $\text{H}_4$ molecule. This is an important conclusion, and is true no matter what geometry we use in the combination. It is important, because it shows us in the simplest possible case why molecules exist, and why they largely retain their identity—when two molecules approach each other, the interaction of their molecular orbitals usually leads to this repulsion. Overcoming the repulsion is a prerequisite for chemical reaction and the energy needed is a major part of the activation energy.

1.3 C–H and C–C Bonds

1.3.1 The Atomic Orbitals of a Carbon Atom

Carbon has s and p orbitals, but we can immediately discount the 1s orbital as contributing to bonding, because the two electrons in it are held so tightly in to the nucleus that there is no possibility of significant overlap with this orbital—the electrons simply shield the nucleus, effectively giving it less of a positive charge. We are left with four electrons in 2s and 2p orbitals to use for bonding. The 2s orbital is like the 1s orbital in being spherically symmetrical, but it has a spherical node, with a wave function like that shown in Fig. 1.11a, and a contour plot like that in Fig. 1.11b. The node is close to the nucleus, and overlap with the inner sphere is never important, making the 2s orbital effectively similar to a 1s orbital. Accordingly, a 2s orbital is usually drawn simply as a circle, as in Fig. 1.11c. The overlap integral $S$ of a 1s orbital on hydrogen with the outer part of the 2s orbital on carbon has a similar form to the overlap integral for two 1s orbitals in Fig. 1.4 (except that it does not rise as high, is at a maximum at greater atomic separation, and would not reach unity at superimposition). The 2s orbital on carbon, at $-19.5$ eV, is $5.9$ eV lower in energy than the 1s orbital in hydrogen. The attractive force on the 2s electrons is high because the nucleus has six protons, even though this is offset by the greater average distance of the electrons from the nucleus and by the shielding from the other electrons. Slater’s rules suggest that the two 1s electrons reduce the nuclear charge by 0.85 atomic charges each, and the other 2s and the two 2p electrons reduce it by $3 \times 0.35$ atomic charges, giving the nucleus an effective charge of 3.25.

![Fig. 1.11](image) The 2s atomic orbital on carbon
The 2p orbitals on carbon also have one node each, but they have a completely different shape. They point mutually at right angles, one each along the three axes, x, y and z. A plot of the wave function for the 2p<sub>x</sub> orbital along the x axis is shown in Fig. 1.12a, and a contour plot of a slice through the orbital is shown in Fig. 1.12b. Scale drawings of p orbitals based on the shapes defined by these functions would clutter up any attempt to analyse their contribution to bonding, and so it is conventional to draw much narrower lobes, as in Fig. 1.12c, and we make a mental reservation about their true size and shape. The 2p orbitals, at –10.7 eV, are higher in energy than the 2s, because they are held on average further from the nucleus. When wave functions for all three p orbitals, p<sub>x</sub>, p<sub>y</sub> and p<sub>z</sub>, are squared and added together, the overall electron probability has spherical symmetry, just like that in the corresponding s orbital, but concentrated further from the nucleus.

Bonds to carbon will be made by overlap of s orbitals with each other, as they are in the hydrogen molecule, of s orbitals with p orbitals, and of p orbitals with each other. The overlap integrals <i>S</i> between a p orbital and an s or p orbital are dependent upon the angles at which they approach each other. The overlap integral for a head on approach of an s orbital on hydrogen along the axis of a p orbital on carbon with a lobe of the same sign in the wave function (Fig. 1.13a), leading to a σ bond, grows as the orbitals begin to overlap (D), goes through a maximum when the nuclei are a little over 0.9 Å apart (C), falls fast as some of the s orbital overlaps with the back lobe of the p orbital (B), and goes to zero when the s orbital is centred on the carbon atom (A). In the last configuration, whatever bonding there would be from the overlap with the lobe of the same sign (unshaded lobes are conventionally used to represent a positive sign in the wave function) is exactly cancelled by overlap with the lobe (shaded) of opposite sign in the wave function. Of course this
configuration is never reached, in chemistry at least, since the nuclei cannot coincide. The overlap integral for two p orbitals approaching head-on in the bonding mode with matching signs (Fig. 1.13b) begins to grow when the nuclei approach (G), rises to a maximum when they are about 1.5 Å apart (F), falls to zero as overlap of the front lobes with each other is cancelled by overlap of the front lobes with the back lobes (E), and would fall eventually to –1 at superimposition. The signs of the wave functions for the individual s and p atomic orbitals can get confusing, which is why we adopt the convention of shaded and unshaded. The signs will not be used in this book, except in Figs. 1.17 and 1.18, where they are effectively in equations.

In both cases, s overlapping with p and p overlapping with p, the overlap need not be perfectly head-on for some contribution to bonding to be still possible. For imperfectly aligned orbitals, the integral is inevitably less, because the build up of electron population between the nuclei, which is responsible for holding the nuclei together, is correspondingly less; furthermore, since the overlapping region will also be off centre, the nuclei are less shielded from each other. The overlap integral for a 1s orbital on hydrogen and a 2p orbital on carbon is actually proportional to the cosine of the angle of approach $\theta$, where $\theta$ is $0^\circ$ for head-on approach and $90^\circ$ if the hydrogen atom is in the nodal plane of the p orbital.

### 1.3.2 Methane

In methane, there are eight valence electrons, four from the carbon and one each from the hydrogen atoms, for which we need four molecular orbitals. We can begin by combining two hydrogen molecules into a composite H₄ unit, and then combine the orbitals of that species (Fig. 1.10) with the orbitals of the carbon atom. It is not perhaps obvious where in space to put the four hydrogen atoms. They will repel each other, and the furthest apart they can get is a tetrahedral arrangement. In this arrangement, it is still possible to retain bonding interactions between the hydrogen atoms and the carbon atoms in all four orbitals, as we shall see, and the maximum amount of total bonding is obtained with this arrangement.

We begin by classifying the orbitals with respect to the two symmetry elements, the xz plane and the yz plane. The symmetries of the molecular orbitals of the H₄ ‘molecule’ taken from Fig. 1.10 are placed on the left in Fig. 1.14, but the energies of each are now close to the energy of an isolated 1s orbital on hydrogen, because the four hydrogen atoms are now further apart than we imagined them to be in Fig. 1.10. The s and p
orbitals on the single carbon atom are shown on the right. There are two SS orbitals on each side, but the overlap integral for the interaction of the 2s orbital on carbon with the $\sigma^*_2$ orbital is zero—there is as much bonding with the lower lobes as there is antibonding with the upper lobes. This interaction leads nowhere. We therefore have four interactions, leading to four bonding molecular orbitals (shown in Fig. 1.14) and four antibonding (not shown). One is lower in energy than the others, because it uses overlap from the 2s orbital on carbon, which is lower in energy than the 2p orbitals. The other three orbitals are actually equal in energy, just like the component orbitals on each side, and the four orbitals are all we need to accommodate the eight valence electrons. There will be, higher in energy, a corresponding set of antibonding orbitals, which we shall not be concerned with for now.

In this picture, the force holding any one of the hydrogen atoms bonded to the carbon is derived from more than one molecular orbital. The two hydrogen atoms drawn below the carbon atom in Fig. 1.14 have bonding from the low energy orbital made up of the overlap of all the s orbitals, and further bonding from the orbitals, drawn on the upper left and upper right, made up from overlap of the 1s orbital on the hydrogen with the 2p$_z$ and 2p$_y$ orbitals on carbon. These two hydrogen atoms are in the node of the 2p$_y$ orbital, and there is no bonding to them from the molecular orbital in the centre of the top row. However, the hydrogens drawn above the carbon atom, one in front of the plane of the page and one behind, are bonded by contributions from the overlap of their 1s orbitals with the 2s, 2p$_y$ and 2p$_z$ orbitals of the carbon atom, but not with the 2p$_x$ orbital.

Fig. 1.14 uses the conventional representations of the atomic orbitals, revealing which atomic orbitals contribute to each of the molecular orbitals, but they do not give an accurate picture of the resulting electron distribution. A better picture can be found in Jorgensen’s and Salem’s pioneering book, *The Organic Chemist’s Book of Orbitals*, which is also available as a CD. There are also several computer programs which allow you easily to construct more realistic pictures. The pictures in Fig. 1.15 come from one of these, Jaguar, and show the four filled orbitals of methane. The wire mesh drawn to represent the outline of each molecular orbital shows one of the contours of the wave function, with the signs symbolised by light and heavier shading. It is easy to see what the component s and p orbitals must have been, and for comparison the four orbitals are laid out here in the same way as those in Fig. 1.14.

![Fig. 1.15](image)

**Fig. 1.15** One contour of the wave function for the four filled molecular orbitals of methane

### 1.3.3 Methylene

Methylene, CH$_2$, is not a molecule that we can isolate, but it is a well known reactive intermediate with a bent H—C—H structure, and in that sense is a ‘stable’ molecule. Although more simple than methane, it brings us for the first time to another feature of orbital interactions which we need to understand. We take the orbitals
of a hydrogen molecule from Fig. 1.3 and place them on the left of Fig. 1.16, except that again the atoms are further apart, so that the bonding and antibonding combination have relatively little difference in energy. On the right are the atomic orbitals of carbon. In this case we have three symmetry elements: (i) the xz plane, bisecting all three atoms; (ii) the yz plane, bisecting the carbon atom, and through which the hydrogen atoms reflect each other; and (iii) a two-fold rotation axis along the z coordinate, bisecting the H—C—H angle. The two orbitals, \( \sigma_{HH} \) and \( \sigma^*_{HH} \) in Fig. 1.16, are SSS and SAA with respect to these symmetry elements, and the atomic orbitals of carbon are SSS, SSS, ASA and SAA. Thus there are two orbitals on the right and one on the left with SSS symmetry, and the overlap integral is positive for the interactions of the \( \sigma_{HH} \) and both the 2s and 2p\(_z\) orbitals, so that we cannot have as simple a way of creating a picture as we did with methane, where one of the possible interactions had a zero overlap integral.

In more detail, we have three molecular orbitals to create from three atomic orbitals, and the linear combination is Equation 1.8, like Equation 1.1 but with three terms:

\[
\sigma = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3
\]

Because of symmetry, \( |c_1| \) must equal \( |c_3| \), but \( |c_2| \) can be different. On account of the energy difference, it only makes a small contribution to the lowest-energy orbital, as shown in Fig. 1.17, where there is a small p lobe, in phase, buried inside the s orbital \( \sigma_x \). It would show in a full contour diagram, but does not intrude in a simple picture like that in Fig. 1.16. The second molecular orbital up in energy created from this interaction, the \( \sigma_z \) orbital, is a mix of the \( \sigma_{HH} \) orbital, the 2s orbital on carbon, out of phase, and the 2p\(_z\) orbital, in phase, which has the effect of boosting the upper lobe, and reducing the lower lobe. There is then a third orbital higher in energy, shown in Fig. 1.17 but not in Fig. 1.16, antibonding overall, with both the 2s and 2p\(_x\) orbitals out of phase with the \( \sigma_{HH} \) orbital. Thus, we have created three molecular orbitals from three atomic orbitals.

Returning to Fig. 1.16, the other interaction, between the \( \sigma^*_{HH} \) orbital and its SAA counterpart, the 2p\(_x\) orbital, gives a bonding combination \( \sigma_x \) and an antibonding combination (not shown). Finally, the remaining p orbital, 2p\(_y\) with no orbital of matching symmetry to interact with, remains unchanged, and, as it happens, unoccupied.

If we had used the linear arrangement H—C—H, the \( \sigma_x \) orbital would have had a lower energy, because the overlap integral, with perfect head-on overlap (\( \theta = 0^\circ \)), would be larger, but the \( \sigma_z \) orbital would have made no contribution to bonding, since the H atoms would have been in the node of the p orbital. This orbital would

![Fig. 1.16](image-url)
simply have been a new orbital on carbon, half way between the s and p orbitals, making no contribution to bonding, and the overall lowering in energy would be less than for the bent structure.

We do not actually need to combine the orbitals of the two hydrogen atoms before we start. All we need to see is that the combinations of all the available s and p orbitals leading to the picture in Fig. 1.16 will account for the bent configuration which has the lowest energy. Needless to say, a full calculation, optimising the bonding, comes to the same conclusion. Methylene is a bent molecule, with a filled orbital of p character, labelled \( \sigma_z \), bulging out in the same plane as the three atoms. The orbital \( \sigma_s \) made up largely from the s orbitals is lowest in energy, both because the component atomic orbitals start off with lower energy, and because their combination is inherently head-on. An empty p orbitals is left unused, and this will be the lowest in energy of the unfilled orbitals—it is nonbonding and therefore lower in energy than the various antibonding orbitals created, but not illustrated, by the orbital interactions shown in Fig. 1.16.

1.3.4 Hybridisation

One difficulty with these pictures, explaining the bonding in methane and in methylene, is that there is no single orbital which we can associate with the C—H bond. To avoid this inconvenience, chemists often use Pauling’s idea of hybridisation; that is, they mix together the atomic orbitals of the carbon atom, adding the s and p orbitals together in various proportions, to produce a set of hybrids, before using them to make the molecular orbitals. We began to do this in the account of the orbitals of methylene, but the difference now is that we do all the mixing of the carbon-based orbitals first, before combining them with anything else.

Thus one-half of the 2s orbital on carbon can be mixed with one-half of the 2p\(_x\) orbital on carbon, with its wave function in each of the two possible orientations, to create a degenerate pair of hybrid orbitals, called sp hybrids, leaving the 2p\(_x\) and 2p\(_z\) orbitals unused (Fig. 1.18, top). The 2s orbital on carbon can also be mixed with the 2p\(_x\) and 2p\(_z\) orbitals, taking one-third of the 2s orbital in each case successively with one-half of the 2p\(_x\) and one-sixth of the 2p\(_z\) in two combinations to create two hybrids, and with the remaining two-thirds of the 2p\(_z\) orbital to make the third hybrid. This set is called sp\(^2\) (Fig. 1.18, centre); it leaves the 2p\(_y\) orbital unused at right angles to the plane of the page. The three hybrid orbitals lie in the plane of the page at angles of 120\(^\circ\) to each other, and are used to describe the bonding in trigonal carbon compounds. For tetrahedral carbon, the mixing is one-quarter of the 2s orbital with one-half of the 2p\(_x\) and one-quarter of the 2p\(_z\) orbital, in two combinations, to make one pair of hybrids, and one quarter of the 2s orbital with one-half of the 2p\(_y\) and one-quarter of the 2p\(_z\) orbital, also in two combinations, to make the other pair of hybrids, with the set of four called sp\(^3\) hybrids (Fig. 1.18, bottom).
The conventional representations of hybrid orbitals used in Fig. 1.18 are just as misleading as the conventional representations of the p orbitals from which they are derived. A more accurate picture of the sp\textsuperscript{3} hybrid is given by the contours of the wave function in Fig. 1.19. Because of the presence of the inner sphere in the 2s orbital (Fig. 1.11a), the nucleus is actually inside the back lobe, and a small proportion of the front lobe reaches behind the nucleus. This follows from the way a hybrid is constructed by adding one-quarter of the wave function of the s orbital (Fig. 1.11a) and three-quarters in total of the wave functions of the p orbitals (Fig. 1.12a). As usual, we draw the conventional hybrids relatively thin, and make the mental reservation that they are fatter than they are usually drawn.

Fig. 1.18  Hybrid orbitals

Fig. 1.19  A section through an sp\textsuperscript{3} hybrid on carbon