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* ϕ, 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

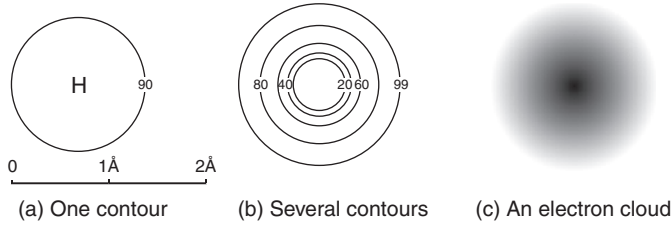


Fig. 1.1 The 1s atomic orbital of a hydrogen atom

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.

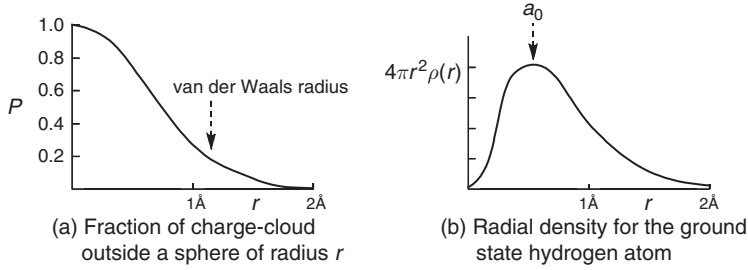


Fig. 1.2 Radial probability plots for the 1s orbital of a hydrogen atom

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 σ and ϕ_1 and ϕ_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 σ^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, σ and σ*, 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 σ. There is, therefore, when we make a bond, a lowering of energy equal to twice the value of E_σ in Fig. 1.3 (*twice* the value, because there are two electrons in the bonding orbital).

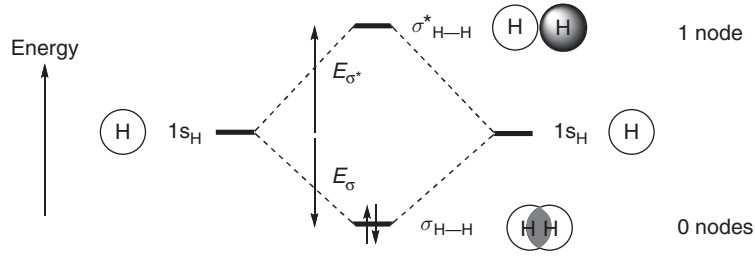


Fig. 1.3 The molecular orbitals of the hydrogen molecule

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).

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

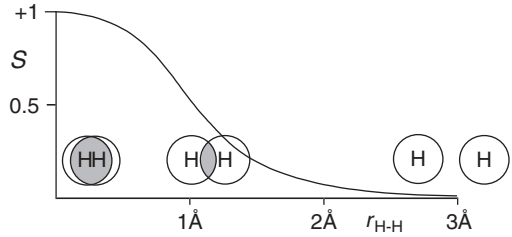


Fig. 1.4 The overlap integral S for two $1s_H$ orbitals as a function of internuclear distance

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:

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

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

in which the symbol α represents the energy of an electron in an isolated atomic orbital, and is called a *Coulomb integral*. The function represented by the symbol β 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 β function—unlike the words resonating and resonance, these are not misleading, and are the better words to use.

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

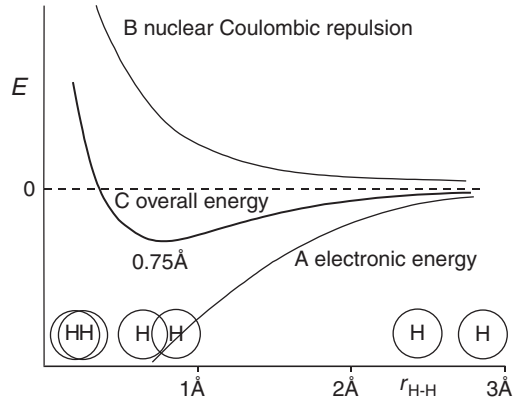


Fig. 1.5 Electronic attraction, nuclear repulsion and the overall effect as a function of internuclear distance for two $1s_H$ atoms

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 α relates to the energy levels of the isolated atoms labelled $1s_H$ in Fig. 1.3, and the term β to the drop in energy labelled E_σ (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 σ orbital, we lose some of the bonding we might otherwise have gained. For this reason too, the value of E_σ 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 σ-bonding orbital and two into the σ*-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 added to a careful calculation.

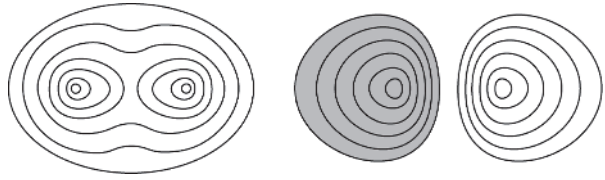
The detailed form that α and β take is where the mathematical complexity appears. They come from the Schrödinger equation, and they are integrals over all coordinates, represented here simply by $d\tau$, in the form of Equations 1.6 and 1.7:

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

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

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

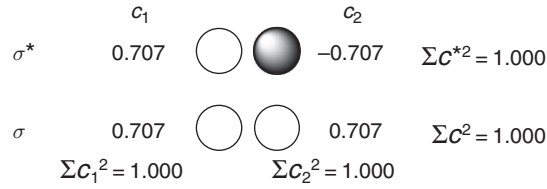
As with atomic orbitals, we need pictures to illustrate the electron distribution in the molecular orbitals. For most purposes, the conventional drawings of the bonding and antibonding orbitals in Fig. 1.3 are clear enough—we simply make mental reservations about what they represent. In order to be sure 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 σ-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 σ*-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 σ and σ* orbitals, on the right of Fig. 1.7, with the 1s orbital of the third hydrogen atom on the left.

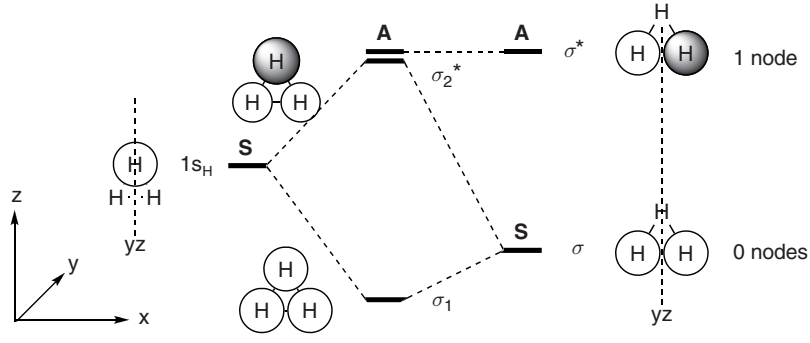


Fig. 1.7 Interacting orbitals for H_3

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 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 σ_1 and σ_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 σ^* orbital, but we cannot justify that now. In any case, the other orbital σ^* 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 σ_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 σ_1 and only *one* in σ_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.

1.2.3 The H_4 'Molecule'

There are several 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 to create the orbitals for two hydrogen molecules, and then ask ourselves what happens to the energy when the two molecules are held within bonding distance.

With one hydrogen molecule aligned along the x axis, on the right in Fig. 1.8, and the other along the y axis, on the left of Fig. 1.8, the symmetry elements present are then the xz and yz planes. The bonding orbital σ_x on the right is symmetric with respect to both planes, and is labelled SS. The antibonding orbital σ_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 σ_y on the left is symmetric with respect to both planes, and is also labelled SS. The antibonding orbital σ_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 σ_1 and an antibonding combination σ_2*. As it happens, the latter has the same energy as the unchanged orbitals σ_x* and σ_y*.

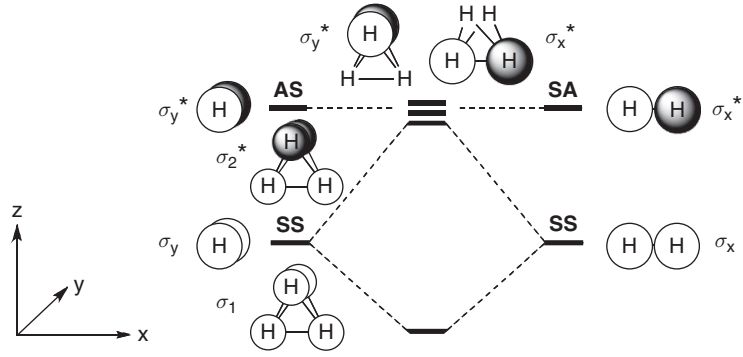


Fig. 1.8 The orbitals of tetrahedral H_4

We now have four molecular orbitals, σ_1, σ_2*, σ_x* and σ_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. Thus two H_2 molecules do not combine to form an H_4 molecule. This is true whatever geometry we use in the combination. It shows us why molecules exist—when two molecules approach each other, the interaction of their molecular orbitals usually leads to repulsion.

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

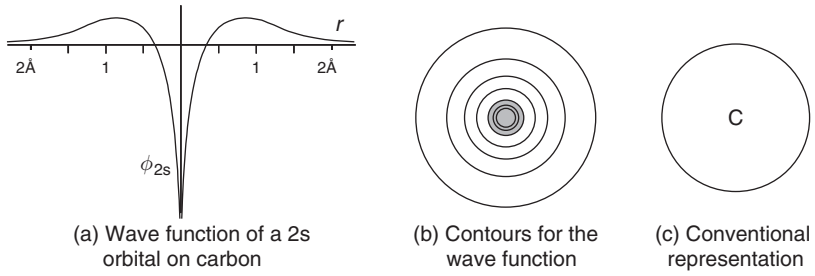


Fig. 1.9 The 2s atomic orbital on carbon

spherical node, with a wave function like that shown in Fig. 1.9a, and a contour plot like that in Fig. 1.9b. 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. 1.9c. 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 (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 3×0.35 atomic charges, giving the nucleus an effective charge of 3.25.

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 $2p_x$ orbital along the x axis is shown in Fig. 1.10a, and a contour plot of a slice through the orbital is shown in Fig. 1.10b. 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. 1.10c, and we make a mental

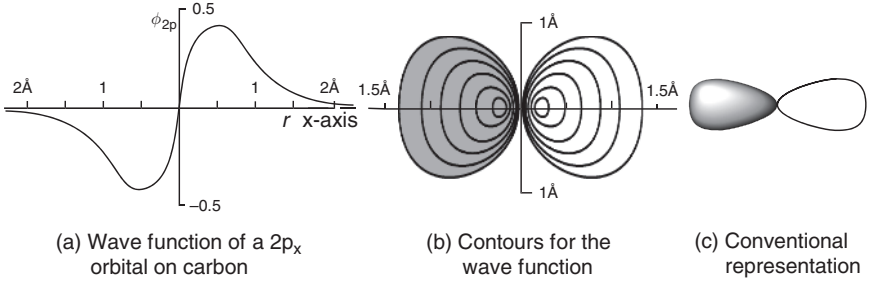
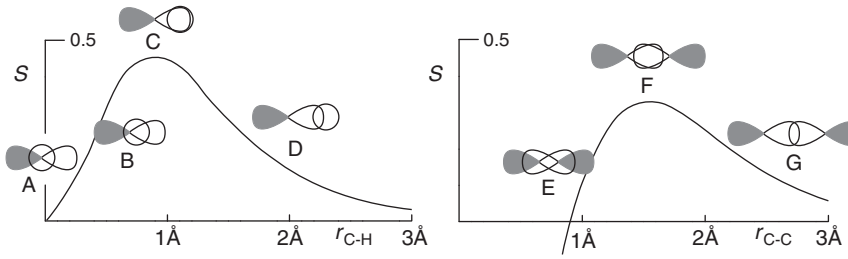


Fig. 1.10 The $2p_x$ orbital on carbon

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_x, p_y and p_z, 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, of s orbitals with p orbitals, and, for carbon-carbon bonds, of p orbitals with each other. The overlap integral *S* for a head on approach of an s orbital on hydrogen along the axis of a p orbital on carbon (Fig. 1.11a) 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 is exactly cancelled by overlap with the lobe (shaded) of opposite sign in the wave function. Of course this configuration is never reached, since the nuclei cannot coincide. The overlap integral for two p orbitals approaching head-on in the bonding mode (Fig. 1.11b), 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.



(a) Overlap integral for σ overlap of a p orbital on C with an s orbital on H

(b) Overlap integral for σ overlap of two p orbitals on C

Fig. 1.11 Overlap integrals for σ overlap with a p orbital on carbon

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. The overlap integral for a 1s orbital on hydrogen and a 2p orbital on carbon is proportional to the cosine of the angle of approach θ, where θ is 0° for head-on approach and 90° 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 H_4 unit, and then combine the orbitals of that species (Fig. 1.8) 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, 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 H_4 'molecule' taken from Fig. 1.8 are placed on the left in Fig. 1.12, 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. 1.8. 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 σ_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. 1.12) and four antibonding (not shown). One is lower in energy than the other three, 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.

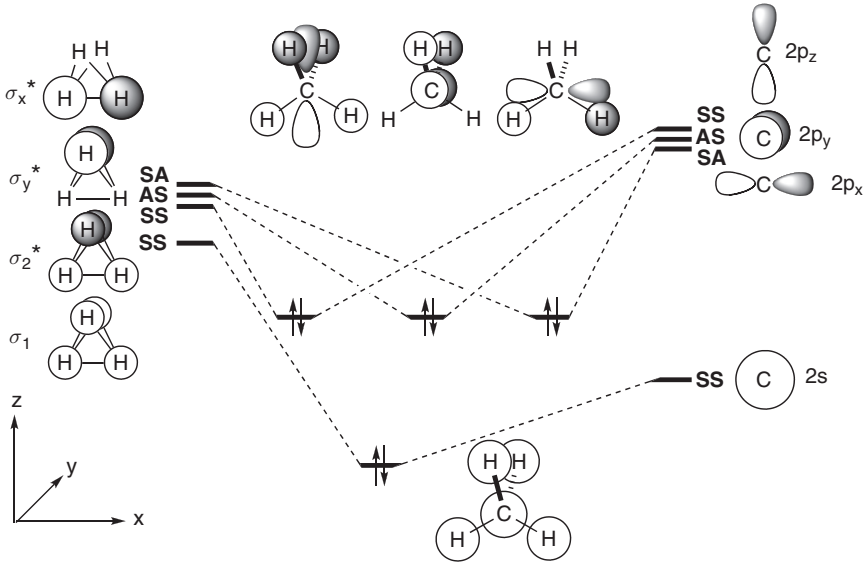


Fig. 1.12 The molecular orbitals of methane from the interaction of the orbitals of tetrahedral H_4 and a C atom

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. 1.12 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 $2p_x$ 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. 1.12 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. 1.13 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 lighter 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. 1.12.

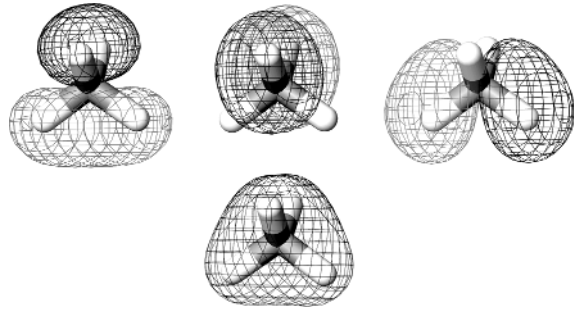


Fig. 1.13 One contour of the wave functions for the four filled molecular orbitals of methane

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. 1.14, 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, σ_{HH} and σ^*_{HH} in Fig. 1.14, are SSS and SAA with respect to these 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 σ_{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.

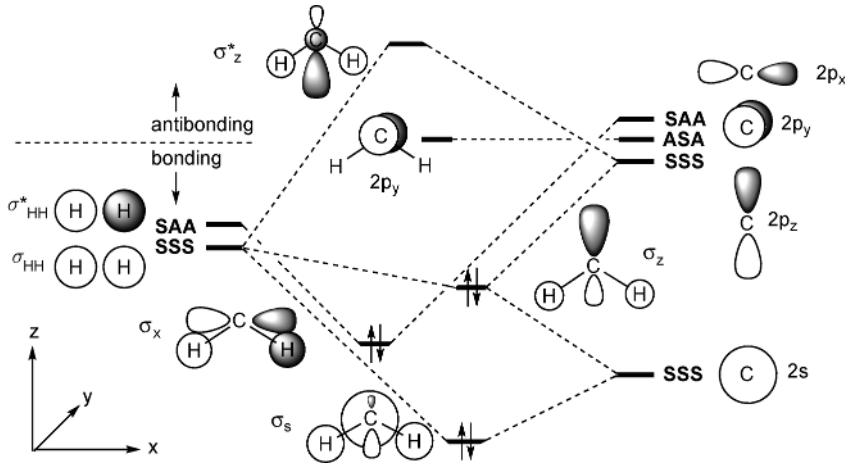


Fig. 1.14 The molecular orbitals of methylene from the interaction of the orbitals of H_2 and a carbon atom

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:

$$\sigma = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 \qquad 1.8$$

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 in Fig. 1.14, where there is a small p_z lobe, in phase, buried inside the s orbital σ_s. The second molecular orbital up in energy, the σ_z orbital, is a mix of the σ_{HH} orbital, the 2s orbital on carbon, out of phase, and the $2p_z$ orbital, out of phase, which has the effect of boosting the upper lobe, and reducing the lower lobe.

There is then a third orbital higher in energy, antibonding overall, with both the 2s and $2p_z$ orbitals out of phase with the σ_{HH} orbital. Thus, we have created three molecular orbitals from three atomic orbitals. The other interaction, between the σ^*_{HH} orbital and its SAA counterpart, the $2p_x$ orbital, gives a bonding combination σ_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.

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. 1.14 will account for the bent configuration which has the lowest energy. Methylene is a bent molecule, with a filled orbital of p character, labelled σ_z, in the same plane as the three atoms. The orbital σ_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_y orbital 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 by the orbital interactions.

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 equate with the C—H bond. To get round this difficulty, 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.

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 $2p_y$ and $2p_z$ orbitals unused (Fig. 1.15, 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 trigonal set is called sp^2 (Fig. 1.15, centre); it leaves the $2p_y$ orbital unused at right angles to the plane of the page. For the sp^3 hybrids of 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 (Fig. 1.15, bottom).

The conventional representations of hybrid orbitals used in Fig. 1.15 are just as misleading as the conventional representations of the p orbitals from which they are derived. A more accurate picture of the sp^3 hybrid is given by the contours of the wave function in Fig. 1.16. Because of the presence of the

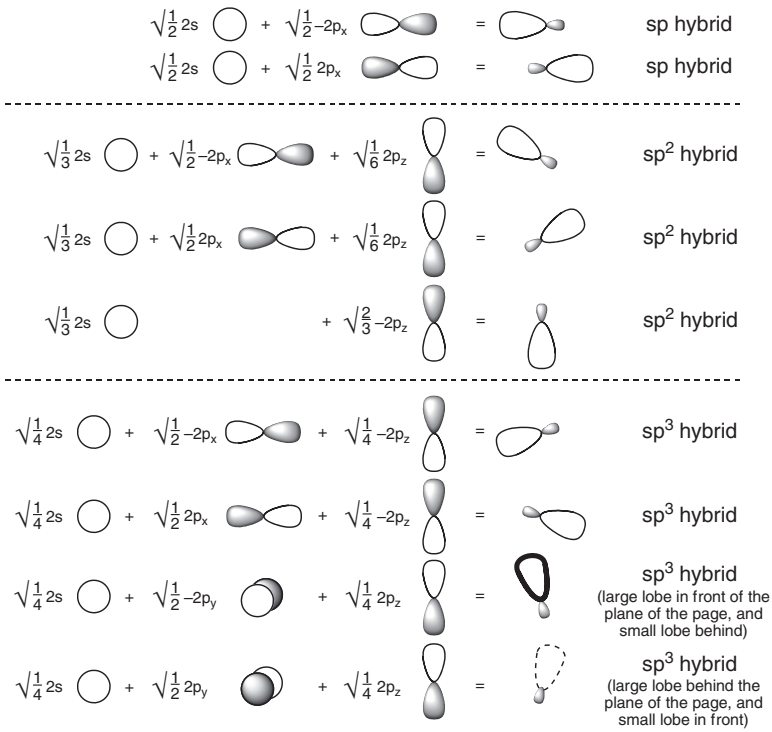


Fig. 1.15 Hybrid orbitals

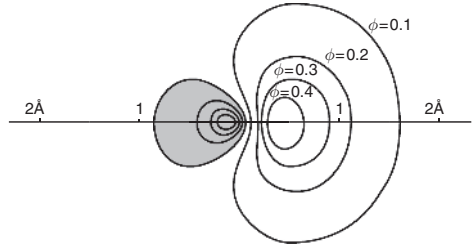


Fig. 1.16 A section through an sp^3 hybrid on carbon

inner sphere in the 2s orbital (Fig. 1.9a), 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. 1.9a) and three-quarters in total of the wave functions of the p orbitals (Fig. 1.10a). We draw the conventional hybrids relatively thin, and make the mental reservation that they are fatter than they are usually drawn.

The interaction of the 1s orbital of a hydrogen atom with an sp^3 hybrid on carbon leads to a σ_{CH}-bonding orbital or a σ^*_{CH}-antibonding orbital (Fig. 1.17). Four of the bonding orbitals, with two electrons in each, point towards the corners of a regular tetrahedron, and give rise to the familiar picture for the bonds in methane shown in Fig. 1.18a.

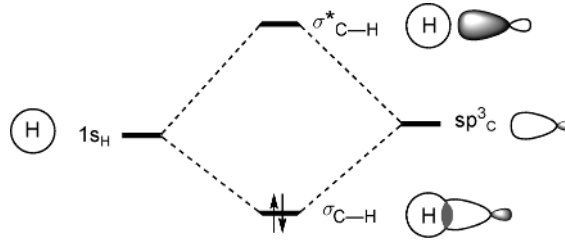
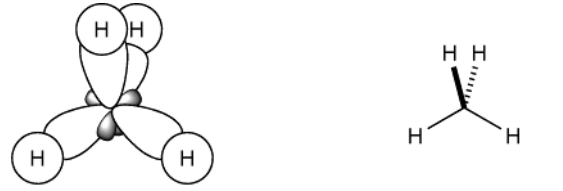


Fig. 1.17 Bonding and antibonding orbitals of a C—H bond



(a) The sp^3 hybrids on carbon overlapping with the s orbitals of hydrogen (b) Conventional bonds

Fig. 1.18 Methane built up with sp^3-hybridised orbitals

This picture has the advantage over that in Fig. 1.12 that the C—H bonds do have a direct relationship with the lines drawn on the conventional structure (Fig. 1.18b). The two descriptions of the overall wave function for methane lead to identical electron distributions; hybridisation involves the same approximations, and the taking of s and p orbitals in various proportions and various combinations, as those used to arrive at Fig. 1.12.

In some ways Fig. 1.12 is a more realistic model. Measurements of ionisation potentials, for example, show that there are two different energy levels from which electrons may be removed; this is immediately easy to understand because it has filled orbitals of different energy, whereas the picture of four identical bonds from Fig. 1.17 hides this information. For other purposes, however, it is undoubtedly helpful to take advantage of the simple picture provided by the hybridisation model. It immediately reveals, for example, that all four bonds are equal. It can be used whenever it offers a similar simplification, but it is good practice to avoid it wherever possible. The common practice of referring to a molecule or an atom as 'rehybridising' is not good usage—the rehybridisation in question is in *our* picture,

not in the molecule. It is likewise poor (but unfortunately common) practice to refer to atoms as being sp^3, sp^2 or sp hybridised. Again the atoms themselves are not hybridised, it is *we* who have chosen to picture them that way. It is better in such circumstances to refer to the atoms as being tetrahedral, trigonal, or digonal.

1.3.5 C—C σ Bonds and π Bonds: Ethane

With a total of fourteen valence electrons to accommodate in molecular orbitals, ethane presents a more complicated picture, and we now meet a C—C bond. We will not go into the full picture—finding the symmetry elements and identifying which atomic orbitals mix to set up the molecular orbitals. It is easy enough to see the various combinations of the 1s orbitals on the hydrogen atoms and the 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on the two carbon atoms giving the set of seven bonding molecular orbitals in Fig. 1.19.

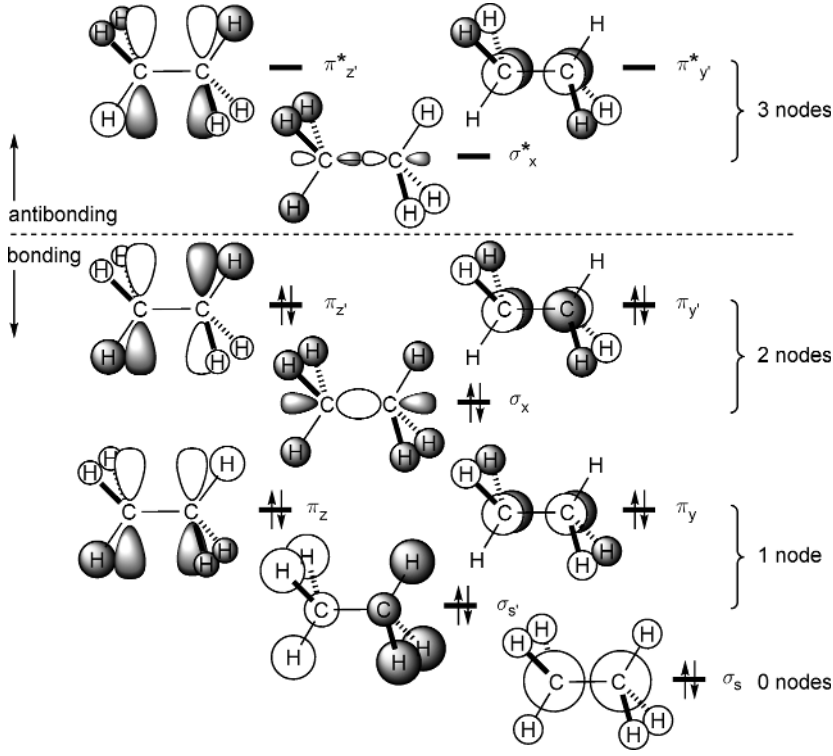


Fig. 1.19 The bonding orbitals and three antibonding orbitals of ethane

There is of course a corresponding picture using sp^3 hybrids, but the following account shows how easy it is to avoid them. We shall concentrate for the moment on those orbitals which give rise to the force holding the two carbon atoms together; between them they make up the C—C bond. The molecular orbitals (σ_s and σ_s'),

made up largely from 2s orbitals on carbon, are like the orbitals in hydrogen, in that the region of overlap is directly on a line between the carbon nuclei; as before, they are called σ orbitals. The bonding in the lower one is very strong, but it is somewhat offset by the antibonding (as far as the C—C bond is concerned) in the upper one. They are both strongly bonding with respect to the C—H bonds. There is actually a little of the $2p_x$ orbital mixed in with this orbital, just as we saw in Fig. 1.14 with a $2p_z$ orbital, but most of the $2p_x$ orbital contributes to the molecular orbital σ_x, which is also σ in character, and very strong as far as the C—C bond is concerned. This orbital has a little of the 2s orbital mixed in, resulting in the asymmetric extension of the lobes between the two carbon nuclei and a reduction in size of the outer lobes. This time, its antibonding counterpart (σ^*_x) is not involved in the total bonding of ethane, nor is it bonding overall. It is in fact the lowest-energy antibonding orbital.

In the molecular orbitals using the $2p_y$ and $2p_z$ orbitals of carbon, the lobes of the atomic orbitals overlap sideways on. This is the distinctive feature of what is called π bonding, although it may be unfamiliar to meet this type of bonding in ethane. Nevertheless, let us see where it takes us. The conventional way of drawing a p orbital (Fig. 1.10c) is designed to give uncluttered drawings, like those in Fig. 1.19. A better picture as we have already seen, and which we keep as a mental reservation when confronted with the conventional drawings, is the contour diagram (Fig. 1.10b). With these pictures in mind, the overlap sideways-on can be seen to lead to an enhanced electron population between the nuclei. However, since it is no longer directly on a line between the nuclei, it does not hold the carbon nuclei together as strongly as a σ-bonding orbital. The overlap integral S for two p orbitals with a dihedral angle of zero has the form shown in Fig. 1.20, where it can be compared with the corresponding σ overlap integral taken from Fig. 1.11b. Whereas the σ overlap integral goes through a maximum at about 1.5 Å and then falls rapidly to a value of –1, the π overlap integral rises more slowly but reaches unity at superimposition. Since C—C single bonds are typically about 1.54 Å long, the overlap integral at this distance for π bonding is a little less than half that for σ bonding. π Bonds are therefore much weaker.

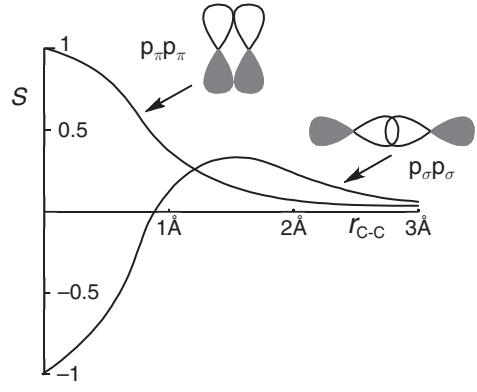


Fig. 1.20 Comparison of overlap integrals for π and σ bonding of p orbitals on C

Returning to the molecular orbitals in ethane made from the $2p_y$ and $2p_z$ orbitals, we see that they again fall in pairs, a bonding pair (π_y and π_z) and (as far as C—C bonding is concerned, but not overall) an antibonding pair (π_y' and π_z'). These orbitals have the wrong symmetry to have any of the 2s orbital mixed in with them. The electron population in the four orbitals (π_y, π_z, π_y' and π_z') is higher in the vicinity of the hydrogen atoms than in the vicinity of the carbon atoms, and these orbitals mainly contribute to C—H bonding. The amount both of bonding and antibonding that they contribute to the C—C bond is small, with the bonding and antibonding combinations more or less cancelling each other out. Thus the orbital (σ_x) is the most important single orbital making up the C—C bond. The other contribution to C—C bonding, which we cannot go into now, comes from the fact that σ_s is more C—C bonding than σ_s' is C—C antibonding.

Had we used the concept of hybridisation, the C—C bond would, of course, simply have been seen as coming from the bonding overlap of sp^3-hybridised orbitals on carbon with each other, and the overall picture for the C—C bond would have looked similar to σ_x in Fig. 1.19, except that it would have had no contribution to bonding to the hydrogen atoms, and would have been labelled σ. For simplicity, we shall often discuss the orbitals of σ bonds as though they could be localised into bonding and antibonding orbitals like σ_x and σ_x*. We shall not often need to refer to the full set of orbitals, except when they become important for one reason or another. Any property we may in future attribute to the bonding and antibonding orbitals of a σ bond, as though there were just one such pair, can always be found in the full set of all the bonding orbitals, or they can be found in the interaction of appropriately hybridised orbitals.

1.3.6 C=C π Bonds: Ethylene

The orbitals of ethylene are made up from the 1s orbitals of the four hydrogen atoms and the 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of the two carbon atoms (Fig. 1.21). One group,

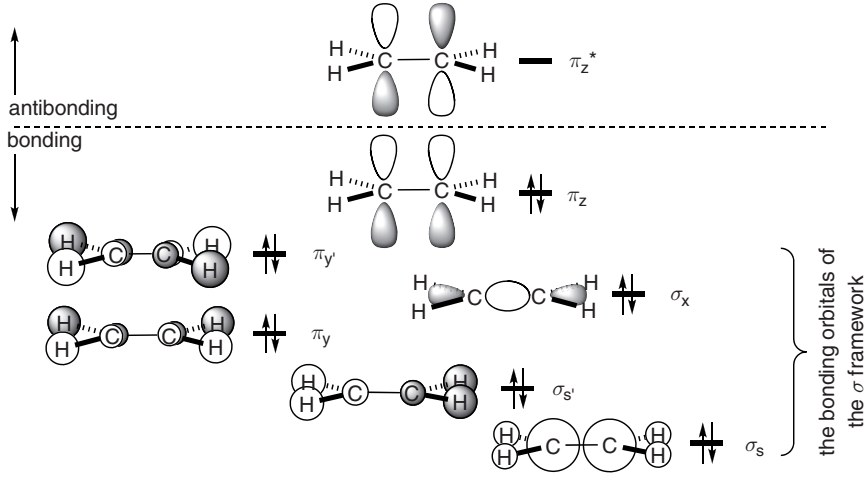


Fig. 1.21 The bonding orbitals and one antibonding orbital of ethylene

made up from the 1s orbitals on hydrogen and the 2s, $2p_x$ and $2p_y$ orbitals on carbon, is substantially σ bonding, which causes the orbitals to be relatively low in energy. These orbitals make up what we call the σ-framework. Standing out, higher in energy than the σ-framework orbitals, is an orbital made up entirely from the $2p_z$ orbitals of the carbon atom overlapping in a π bond. This time, the π orbital is localised on the carbon atoms, free of any complications from involvement with bonding to the hydrogen atoms, and we can draw the interaction diagram in Fig. 1.22. The C—C bonding is greater in the σ framework than the π bonding, because of the larger overlap integral for σ approach than for π (Fig. 1.20).

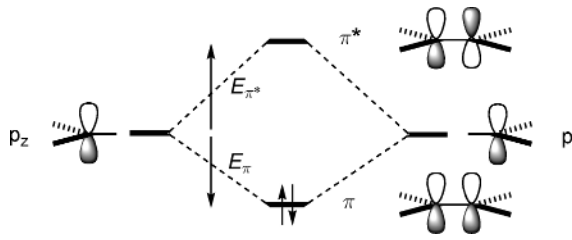


Fig. 1.22 A C=C π bond

Another consequence of having an orbital localised on two atoms is that the equation for the linear combination of atomic orbitals contains only two terms (Equation 1.1), and the c-values are again 0.707 in the bonding orbital and 0.707 and –0.707 in the antibonding orbital. The energy of the p orbital on carbon is given the value α, which is used as a reference point from which to measure rises and drops in energy, and will be especially useful when we come to deal with other elements. The value of E_π in Fig. 1.22 is given the symbol β, and is also used as a reference with which to compare the degree of bonding in other π-bonding systems. To give a sense of scale, the value of β for ethylene is approximately 140 kJ mol^{-1} (= 1.45 eV = 33 kcal mol^{-1}). In other words, the total π bonding in ethylene is 280 kJ mol^{-1}, since there are two electrons in the bonding orbital.

This separation of the σ framework and the π bond is the essence of *Hückel theory*. Because the π bond in ethylene in this treatment is self-contained, we may treat the electrons in it in the same way as we do for the fundamental quantum mechanical picture of an electron in a box. We look at each molecular wave function as one of a series of sine waves, with the limits of the box *one bond length* out from the atoms at the end of the conjugated system, and then inscribe sine waves so that a node always comes at the edge of the box. With two orbitals to consider for the π bond of ethylene, we only need the 180° sine curve for π and the 360° sine curve for π^*. These curves can be inscribed over the orbitals as they are on the left of Fig. 1.23, and we can see on the right how the vertical lines above and below the atoms duplicate the pattern of the coefficients, with both c_1 and c_2 positive in the π orbital, and c_1 positive and c_2 negative in π^*.

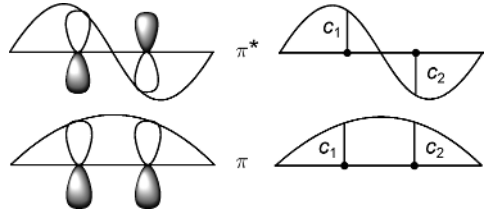


Fig. 1.23 The π orbitals of ethylene and the electron in the box

A better picture, which we keep as a mental reservation when confronted with the conventional drawings, is the contour diagram. A better sense of the π overlap from two p orbitals is given in Fig. 1.24, where we see more clearly from the contours on the left that in the bonding combination there is an enhanced electron population between the nuclei, but that it is no longer directly on a line between the nuclei. The wire-mesh diagrams illustrate the shapes of the π and π^* orbitals with some sense of their 3D character.

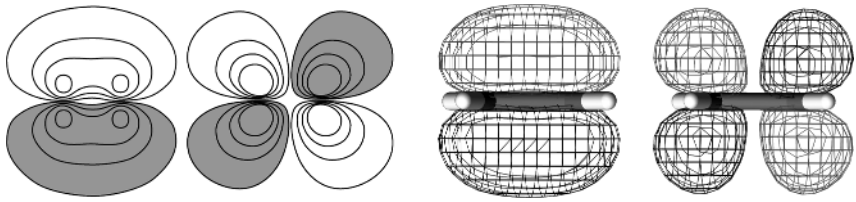


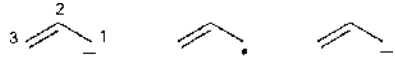
Fig. 1.24 A section through the contours of the π and π^* wave functions of ethylene, and wire-mesh outlines of one contour of each

1.4 Conjugation—Hückel Theory

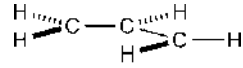
The two p orbitals of ethylene are described as being conjugated with each other in making the π bond. To make longer conjugated systems we add one p orbital at a time to the π bond to make successively the allyl system, butadiene, the pentadienyl system and so on. We continue to separate completely the σ framework (using the 2s, $2p_x$ and $2p_y$ orbitals on carbon with the 1s orbitals on hydrogen) from the π system made up from the $2p_z$ orbitals.

1.4.1 The Allyl System

The members of the allyl system are reactive intermediates, and there are three of them: the allyl cation **1.1**, the allyl radical **1.2** and the allyl anion **1.3**. They have the same orbitals, but different numbers of electrons.



The cation, radical and anion have the same σ framework **1.4**, with fourteen bonding molecular orbitals filled with 28 electrons made by mixing the 1s orbitals of the five hydrogen atoms either with the 2s, $2p_x$ and $2p_y$ orbitals of the three carbon atoms or with the sp^2 hybrids. The allyl systems are bent not linear, but we shall treat the π system as linear to simplify the discussion.



1.4

The π system is made up from the three p_z orbitals on the carbon atoms. The linear combination of these orbitals takes the form of Equation 1.9, with three terms, creating a pattern of three molecular orbitals, ψ_1, ψ_2 and ψ_3*. In the allyl cation there are two electrons left to go into the π system after filling the σ framework (and in the radical, three, and in the anion, four).

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 \qquad 1.9$$

We can derive a picture of these orbitals using the electron in the box, and recognising that we now have three orbitals and therefore three energy levels. If the lowest energy orbital is, as usual, to have no nodes (except the inevitable one in the plane of the molecule), and the next one up one node, we now need an orbital with two nodes. We therefore construct a diagram, Fig. 1.25, with one more turn of the sine curve, to include that for 540°, the next one up in energy that fulfils the criterion that there are nodes at the edges of the box, one bond length out, as well as the two inside.

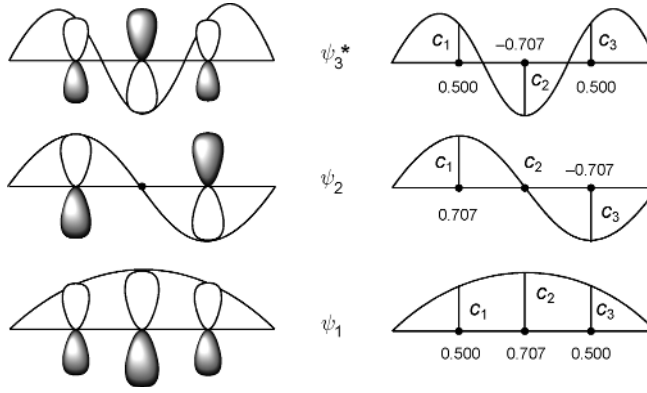


Fig. 1.25 The π orbitals of the allyl system

The lowest-energy orbital, ψ_1, has bonding across the whole conjugated system, with the electrons concentrated in the middle. The next orbital up in energy ψ_2 must have a node in the middle of the conjugated system occupied by an *atom* and not by a *bond*. Having a node in the middle means having a zero coefficient c_2 on C-2, and

hence the coefficients on C-l and C-3 in this orbital must be $\pm 1/\sqrt{2}$, if, squared and summed, they are to equal one. The atomic orbitals in ψ_2 are far apart in space and their repulsive interaction does not significantly raise the energy of this molecular orbital relative to that of an isolated p orbital—whether filled or not, it does not contribute significantly to the overall bonding. If the sum of the squares of the three orbitals on C-2 is also to equal one, then the coefficients on C-2 in ψ_1 and ψ_3* must also be $\pm 1/\sqrt{2}$. Finally, since symmetry requires that the coefficients on C-1 and C-3 in ψ_1 and ψ_3* have the same absolute magnitude, and the sum of their squares must equal $1–(1/\sqrt{2})^2$, we can deduce the set of *c*-values in Fig. 1.25.

In this picture of the bonding, we get no immediate appreciation of the energies of these orbitals relative to those of ethylene. The nonbonding orbital ψ_2 is clearly on the α level, that of a p orbital on carbon, and ψ_1 is lowered by the extra π bonding and ψ_3* is raised. To assess the energies, there is a simple geometrical device that works for linear conjugated systems. The conjugated system, *including the dummy atoms at the ends of the sine curves*, is inscribed vertically inside a circle of radius 2β, following the convention that one π bond in ethylene defines β. This is shown for ethylene and the allyl system in Fig. 1.26. The energies *E* of the π orbitals can then be calculated using Equation 1.10:

$$E = 2\beta\cos\frac{k\pi}{n+1} \qquad 1.10$$

where *k* is the number of the atom along the sequence of *n* atoms. This is simply an expression based on the trigonometry of Fig. 1.26. The π orbital of ethylene, the placing of which defines the value of β, is on the first level ($k = 1$) of the sequence of two ($n = 2$) reading anticlockwise from the bottom. Thus the energies of the π orbitals in the allyl system are 1.414β below the α level, and 1.414β above the α level.

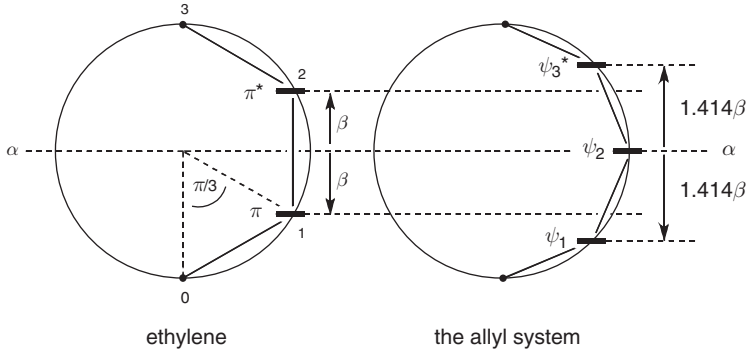


Fig. 1.26 Energies of π molecular orbitals in ethylene and the allyl system

We can gain further insight by building the picture of the π orbitals of the allyl system in another way. Instead of mixing together three p orbitals on carbon, we can combine two of them in a π bond first, and then work out the consequences of having a third p orbital held within bonding distance of the C=C π bond. We have

to consider the effect of the p orbital, on the right of Fig. 1.27, on both the π and π^* orbitals of ethylene on the left. If we look *only* at the interaction of the p orbital with the π orbital, we can expect to create two new orbitals in much the same way as we saw when the two $2p_z$ orbitals of carbon were allowed to interact in the formation of the π bond of Fig. 1.22. One orbital ψ_1 will be lowered in energy and the other ψ_x raised. Similarly if we look *only* at its interaction with the π^* orbital, we can expect to create two new orbitals, one lowered in energy ψ_y and one raised ψ_3^*. We cannot create four orbitals from three, because we cannot use the p orbital separately twice.

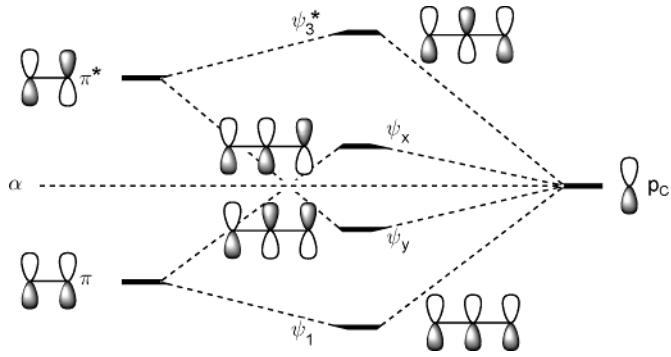


Fig. 1.27 A p orbital interacting independently with π and π^* orbitals. (No attempt is made to represent the relative sizes of the atomic orbitals)

We can see in Fig. 1.27 that the orbital ψ_1 has been created by mixing the p orbital with the π orbital in a *bonding* sense, with the signs of the wave function of the two adjacent atomic orbitals matching. We can also see that the orbital ψ_3^* has been created by mixing the p orbital with the π^* orbital in an *antibonding* sense, with the signs of the wave functions unmatched. The third orbital that we are seeking, ψ_2 in Fig. 1.28, is a combination created by mixing the p orbital with the π orbital in an *antibonding* sense *and* with the π^* orbital in a *bonding* sense. We do not get two

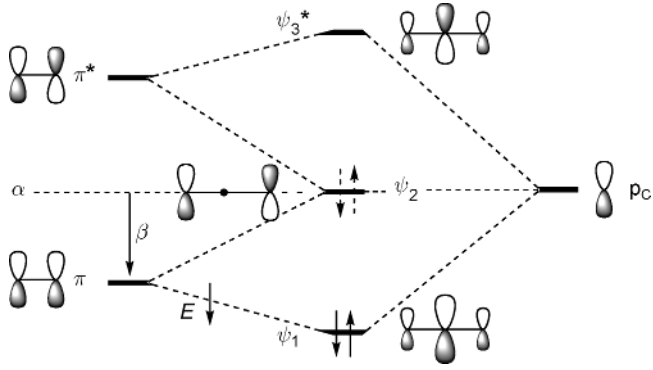
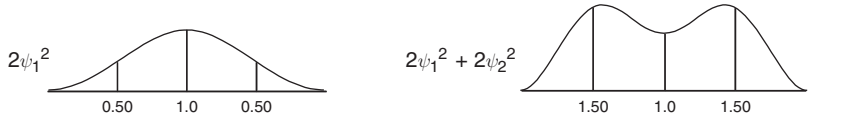


Fig. 1.28 The allyl system by interaction of a p orbital with π and π^* orbitals

orbitals, ψ_x and ψ_y in Fig. 1.27, but something in between, namely ψ_2 in Fig. 1.28. By adding ψ_x and ψ_y in this way, the atomic orbitals, drawn to the left of ψ_x and ψ_y in Fig. 1.27 cancel each other out on C-2 and reinforce each other on C-1 and C-3, thereby creating the molecular orbital ψ_2 in Fig. 1.28.

We have of course arrived at the same picture for the molecular orbitals as that created from mixing the three separate p orbitals in Fig. 1.25. The overall π energy of the allyl cation, radical and anion has dropped relative to the energy of an isolated p orbital and ethylene by $2E$, which we know from Fig. 1.26 is $2 \times 0.414\beta$ or something of the order of 116 kJ mol^{-1}. (It is not uncommon to express these drops in energy as a 'gain' in energy—in this sense, the gain is understood to be to us, or to the outside world, and hence means a loss of energy in the system and stronger bonding.)

The electron population in any molecular orbital is derived from the square of the atomic orbital functions, so that the sine waves in Fig. 1.25 describing the coefficients are squared to describe the electron distribution. The π electron population in the molecule as a whole is then obtained by adding up the electron populations, allowing for the number of electrons in each orbital, for all the *filled* π molecular orbitals. Looking only at the π system, we can see that the overall electron distribution for the cation is derived from the squares of the coefficients in ψ_1 alone. Roughly speaking, there is half an electron (2×0.5^2) on C-1 and C-3, and one electron (2×0.707^2) on C-2. This is illustrated graphically in Fig. 1.29a. Since the nucleus has a charge of $+1$, the excess charge on C-1 and C-3 is $+0.5$, in other words the electron deficiency in the cation is concentrated at the two ends.



(a) π electron population in the allyl cation (b) π electron population in the allyl anion

Fig. 1.29 Total π electron populations in the allyl cation and anion

For the anion, the electron population is derived by adding up the squares of the coefficients in both ψ_1 and ψ_2. Since there are two electrons in both orbitals, there are 1.5 electrons ($2 \times 0.5^2 + 2 \times 0.707^2$) roughly centred on each of C-1 and C-3, and one electron (2×0.707^2) centred on C-2. This is illustrated graphically in Fig. 1.29b. Subtracting the charge of the nucleus then gives the excess charge as –0.5 on C-1 and C-3, in other words the electron excess in the anion is concentrated at the two ends.

One final detail with respect to this, the most important orbital, is that it is not quite perfectly nonbonding. Although the two atoms are separated they do interact slightly, as can be seen in ψ_2 in the wire-mesh drawing of the nonlinear allyl system in Fig. 1.30, where the perspective allows one to see that the right-hand lobes, which are somewhat closer to the viewer, are just perceptibly repelled by the left-hand lobes. This orbital does not therefore have exactly the same energy as an isolated p orbital—it is slightly higher in energy.

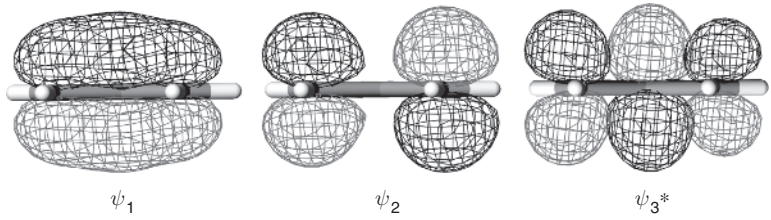
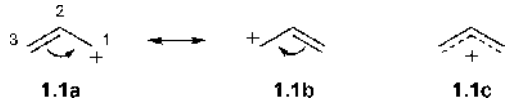


Fig. 1.30 The π molecular orbitals of the allyl system

There is a problem with the conventional representation **1.1** of an allyl cation, which seems to imply that C-1 has the positive charge (an empty p orbital), and that C-2 and C-3 are in a double bond. But we could have drawn the cation **1.1**, redrawn as **1.1a**, equally well the other way round as **1.1b**, and the curly arrow symbolism shows how the two *drawings* are interconvertible. This device is at the heart of valence bond theory. For now we need only to recognise that these two drawings are representations of the *same* species—there is no reaction connecting them, although many people sooner or later fall into the trap of thinking that 'resonance' like **1.1a** → **1.1b** is a step in a reaction sequence. The double-headed arrow interconnecting them is a useful signal; this symbol should only be used to show the equivalence of 'resonance structures' and never to represent an equilibrium. There are corresponding pairs of drawings for the radical and for the anion.



1.1a **1.1b** **1.1c**

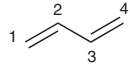
One way of avoiding these misleading structures is to draw the allyl cation as in **1.1c**, illustrating the delocalisation of the p orbitals with a dashed line, and placing the positive or negative charge in the middle. The trouble with these drawings is that they are hard to use clearly with curly arrows in mechanistic schemes, and they do not show that the positive charge is largely concentrated on C-1 and C-3. It is probably better in most situations to use one of the localised drawings for the cation, radical or anion, rather than the 'molecular orbital' version like **1.1c**, but always make the necessary mental reservation that each of the localised drawings implies the other, and that the molecular orbitals give a better picture.

As we shall see later, the most important orbitals with respect to reactivity are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These are the *frontier orbitals*. For the allyl cation, the LUMO is ψ_2, and the drawings of the allyl cation **1.1a** and **1.1b** emphasise the electron distribution in the LUMO. Similarly, the corresponding drawings of the allyl anion emphasise ψ_2, the HOMO for that species. It is significant that it is the LUMO of the cation and the HOMO of the anion that will prove to be the more important frontier orbital in each case. Similarly in the allyl radical, the localised

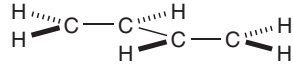
drawing illustrates the electron distribution in the singly occupied molecular orbital (SOMO), the most important orbital in that species.

1.4.2 Butadiene

The next step up in complexity comes with four p orbitals conjugated together, with butadiene **1.5** as the parent member. There is a σ framework **1.6** with 36 electrons and four p orbitals to house the remaining four. Using the electron in the box with four p orbitals, we can construct Fig. 1.31, which shows the four wave functions, inside which the p orbitals are placed at the appropriate regular intervals. We get a new set of orbitals, ψ_1, ψ_2, ψ_3*, and ψ_4*, each described by Equation 1.11 with four terms.



1.5



1.6

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 \qquad 1.11$$

The lowest-energy orbital ψ_1 has all the c-values positive, and hence bonding is at its best. The next-highest energy level has one node, between C-2 and C-3; in

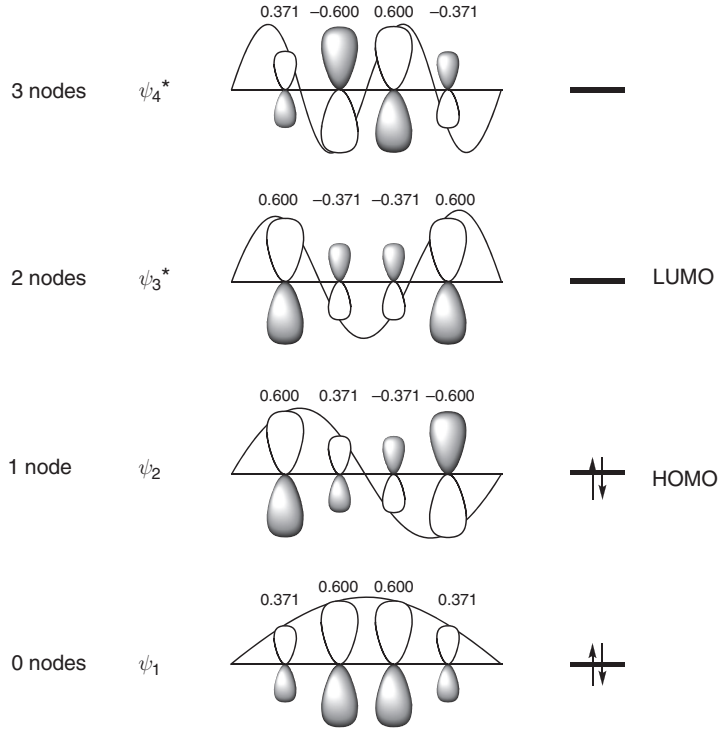


Fig. 1.31 π Molecular orbitals of butadiene

other words, c_1 and c_2 are positive and c_3 and c_4 are negative. There is therefore bonding between C-l and C-2 and between C-3 and C-4, but not between C-2 and C-3. With two bonding and one antibonding interaction this orbital is also overall bonding. Thus the lowest-energy orbital of butadiene, ψ_1, reasonably enough, has a high population of electrons in the middle, but in the next orbital up, ψ_2, because of the repulsion between the wave functions of opposite sign on C-2 and C-3, the electron population is concentrated at the ends of the conjugated system. Overall, summing the squares of the coefficients of the filled orbitals, ψ_1 and ψ_2, the π electrons are evenly spread over all four carbon atoms of the conjugated system.

We can easily give numerical values to these coefficients for the linear conjugated system. The coefficients are proportional to the sine of the angle, as defined by the position of the atom within the sine curve. Equation 1.12 is the algebraic expression for this idea, illustrated in Fig. 1.31 with the atomic orbitals inscribed within the sine curves:

$$c_{jr} = \sqrt{\frac{2}{n+1}} \sin \frac{rj\pi}{n+1} \qquad 1.12$$

giving the coefficient c_{jr} for atom j in molecular orbital r of a conjugated system of n atoms (so that j and $r = 1, 2, 3, \ldots, n$).

In butadiene, as in all alternant conjugated systems (those having no odd-membered rings), the $|c|$ values are reflected across a mirror plane placed horizontally, halfway between ψ_2 and ψ_3*, and also across a mirror plane placed vertically, halfway between C-2 and C-3. It is only necessary therefore to calculate four of the 16 numbers in Fig. 1.31, and deduce the rest from the symmetry.

We can set up the conjugated system of butadiene by looking at the consequences of allowing two isolated π bonds to interact, as they will if they are held within bonding distance. Let us first look at the consequence of allowing the orbitals close in energy to interact, which they will do strongly. (For a brief account of how the energy difference between interacting orbitals affects the extent of their interaction, see the discussion on page 47 of Equations 1.13 and 1.14.) We see that ψ_1 is derived by the interaction of π with π in a bonding sense, lowering the energy of ψ_1 below that of the π orbital, and ψ_2 is derived from the interaction of π with π in an antibonding sense, raising the energy above that of the π orbital. Similarly, the interaction of π* with π* in a bonding sense creates the orbital ψ_3* and in an antibonding sense the orbital ψ_4*. Now we look at the consequence of the weaker interactions of π with π*. The interaction of π with π* in a bonding sense lowers the energy of ψ_1 and ψ_2, and the interaction of π with π* in an antibonding sense raises the energy of ψ_3* and ψ_4*. Mixing these two sets together, and allowing for the greater contribution from the stronger interactions, we get the set of orbitals (Fig. 1.32), matching those we saw in Fig. 1.31. The net effect is to lower the energy of ψ_1 below the π level, and to raise the energy of ψ_2 above the π level, but without raising it up to the α level. Likewise ψ_3* is lowered in energy, but remains above the α level. Yet another way of looking at this

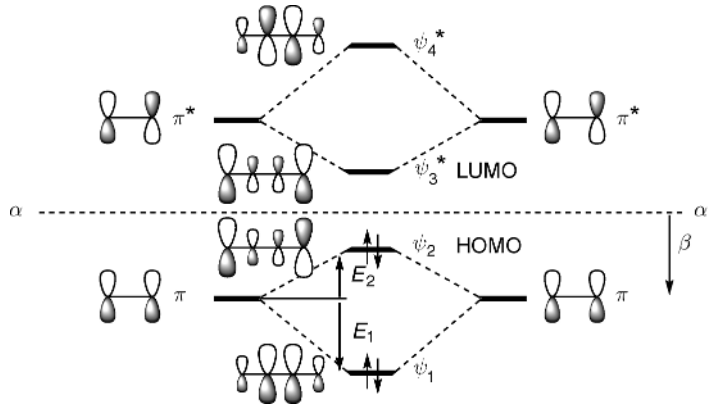


Fig. 1.32 Energies of the π molecular orbitals of ethylene and butadiene by orbital interaction

system, is to say that the orbitals ψ_1 and ψ_2 and the orbitals ψ_3* and ψ_4* mutually repel each other.

We are now in a position to explain the well-known property that conjugated systems are often, but not always, lower in energy than unconjugated systems. It comes about because ψ_1 is lowered in energy more than ψ_2 is raised (E_1 in Fig. 1.32 is larger than E_2). The energy (E_1) given out in forming ψ_1 comes from the overlap between the atomic orbitals on C-2 and C-3; this overlap did not exist in the isolated π bonds. It is particularly effective in lowering the energy of ψ_1, because the coefficients on C-2 and C-3 are large. By contrast, the increase in energy of ψ_2, caused by the repulsion between the orbitals on C-2 and C-3, is not as great, because the coefficients on these atoms are smaller in ψ_2. Thus the energy lost from the system in forming ψ_1 is greater than the energy needed to form ψ_2, and the overall π energy of the ground state of the system ($\psi_1^2\psi_2^2$) is lower. We can of course see the same pattern, and attach some approximate numbers, using the geometrical analogy.

This is illustrated in Fig. 1.33, which shows that ψ_2 is raised above π by 0.382β and ψ_1 is lowered below π by 0.618β. The overall lowering in energy for the extra

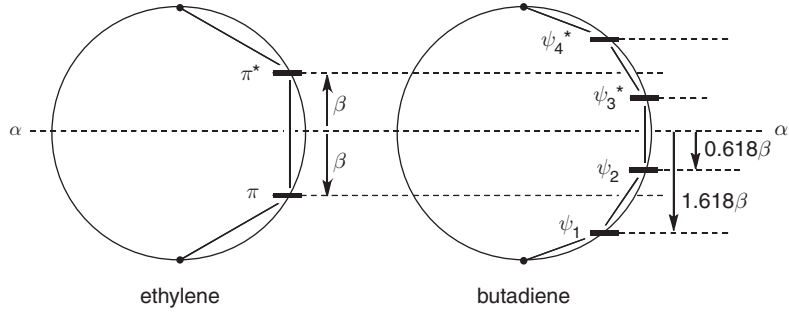


Fig. 1.33 Energies of the π molecular orbitals of ethylene and butadiene by geometry

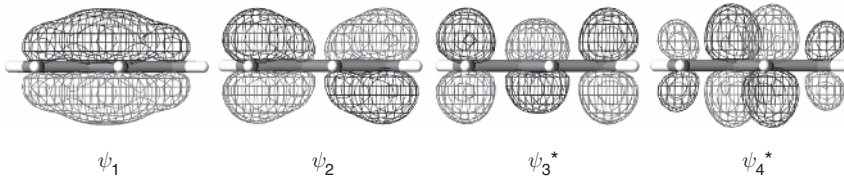


Fig. 1.34 The π molecular orbitals of butadiene

conjugation is therefore $(2 \times 0.618 + 2 \times 1.618) - 4 = 0.472\beta$ or about 66 kJ mol^{-1}. Finally, it is instructive to look at the same π orbitals in wire-mesh diagrams (Fig. 1.34) to reveal more accurately what the electron distribution in the π molecular orbitals looks like.

1.4.3 Longer Conjugated Systems

The π orbitals of longer linear conjugated systems are derived in essentially the same way. The energies and coefficients of the π molecular orbitals for all six systems from an isolated p orbital up to hexatriene are summarised in Fig. 1.35. The viewpoint in this drawing is directly above the p orbitals, which appear therefore to be circular. This is a common simplification, rarely likely to lead to confusion between a p orbital and an s orbital, and we shall use it through much of this book.

The longer the conjugated system, the lower the energy of ψ_1, but each successive drop in energy is less than that of the system with one fewer atoms, with a limit at infinite length of 2β. Among the even-atom species, the longer the conjugated system, the higher the energy of the HOMO, and the lower the energy

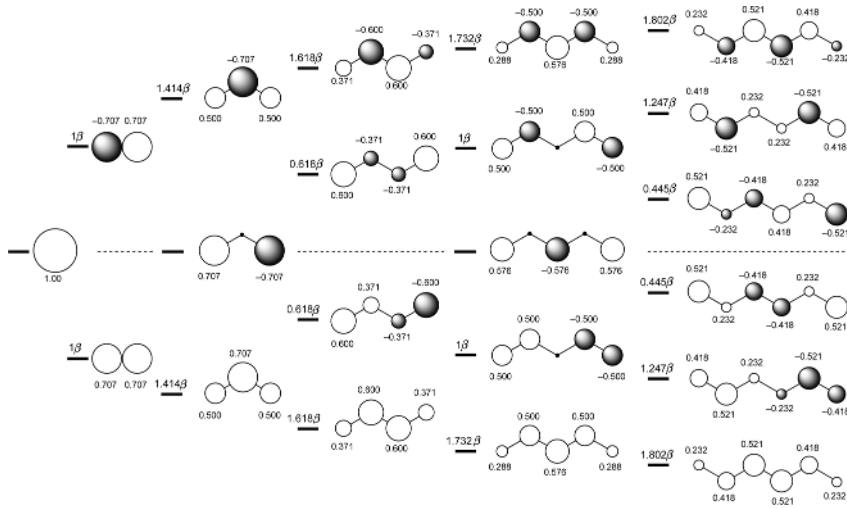


Fig. 1.35 The energies and coefficients of the π molecular orbitals of the smaller conjugated systems

of the LUMO, with the energy gap becoming ever smaller. With a narrow HOMO—LUMO gap, polyenes require less energy in order to promote an electron from the HOMO to the LUMO, leading the absorption of UV and visible light to take place at ever longer wavelength.

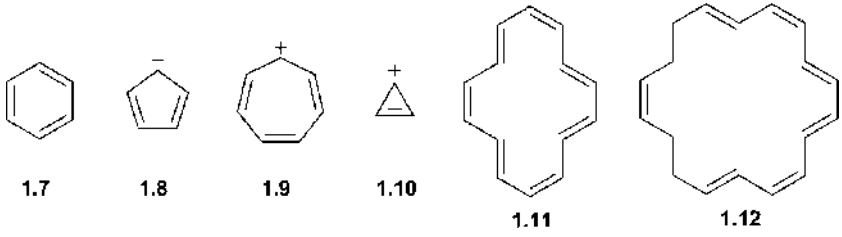
At the extreme of an infinite polyene, however, simple Hückel theory reduces the HOMO—LUMO gap to zero, since the secants in diagrams like Fig. 1.33, would become infinitely small. Such a polyene would have equal bond lengths between each pair of carbon atoms, the gap between the HOMO and the LUMO would be zero.

A zero gap between the HOMO and the LUMO is characteristic of a metallic conductor, but long polyenes have alternating double and single bonds, and their interconversion, which is the equivalent of the movement of current along the chain, requires energy. The theoretical description of this modification to simple Hückel theory is known by physicists as a Peierls distortion. It has its counterpart for chemists in the Jahn-Teller distortion seen, for example, in cyclobutadiene, which distorts to have alternating double and single bonds, avoiding the degenerate orbitals and equal bond lengths of square cyclobutadiene. The simple Hückel picture is seriously wrong at the extreme of long conjugated systems. One way of appreciating what is happening is to think of the HOMO and the LUMO repelling each other more strongly when they are close in energy, just as the filled and unfilled orbitals of butadiene repel each other (Fig. 1.32), but more so.

1.5 Aromaticity

1.5.1 Aromatic Systems

One of the most striking properties of conjugated organic molecules is the special stability found in the group of molecules called aromatic, with benzene **1.7** as the longest established example. Hückel predicted that benzene was by no means alone, and that cyclic conjugated polyenes would have exceptionally low energy if the total number of π electrons could be described as a number of the form $(4n + 2)$, where n is an integer. Other 6π-electron cyclic systems such as the cyclopentadienyl anion **1.8** and the cycloheptatrienyl cation **1.9** belong in this category, and the cyclopropenyl cation **1.10** ($n = 0$), [14]annulene **1.11** ($n = 3$), [18]annulene **1.12** ($n = 4$) and many other systems have been added over the years. Like conjugation in polyenes, however, aromaticity does not stretch to infinitely conjugated cyclic systems, even when they do have $(4n+2)$ electrons.



Where does this special stability come from? We can approach this question in much the same way as we approached the derivation of the molecular orbitals of conjugated systems. We begin with a σ framework containing the C—C and C—H σ bonds. We must then deduce the nodal properties of the molecular orbitals created from six p orbitals in the ring. They are all shown both in elevation and in plan in Fig. 1.36. The lowest-energy orbital ψ_1 has no node as usual, but because the conjugated system goes round the ring instead of spilling out at the ends of the molecule, as it did with the linear conjugated systems, the coefficients on all six atoms are equal. The other special feature is that there are two orbitals having the same energy with one node ψ_2 and ψ_3, because they can be created in two symmetrical ways, one with the node horizontal ψ_2 and one with it vertical ψ_3. Similarly, there are two antibonding orbitals, ψ_4* and ψ_5*, with the same energy having two nodes. Finally there is another antibonding orbital, ψ_6*, with three nodes.

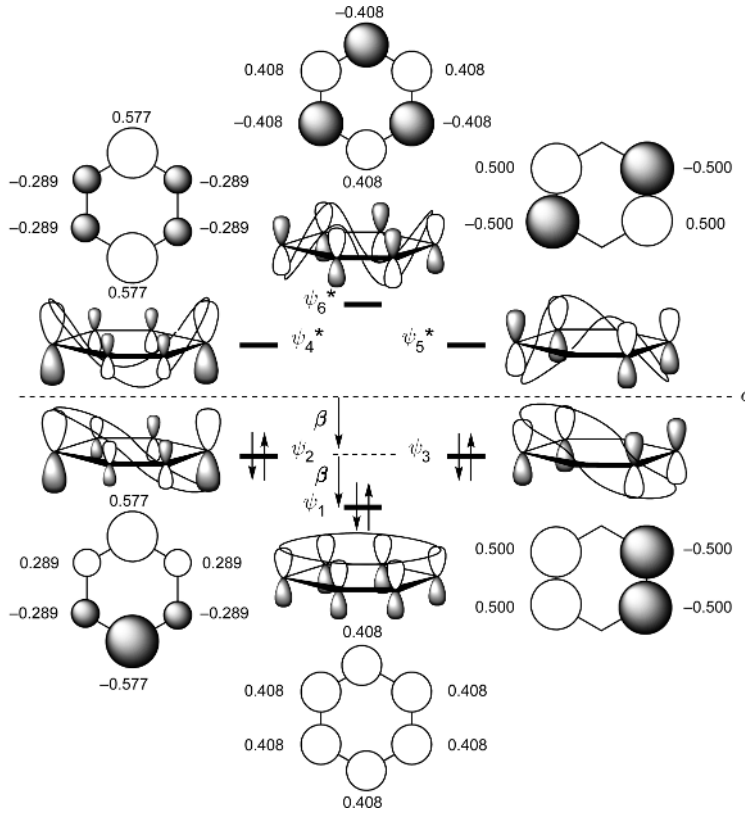


Fig. 1.36 The π molecular orbitals of benzene

The energies of the molecular orbitals can be deduced by inscribing the conjugated system inside a circle of radius 2β. There is no need for dummy atoms, since the sine curves go right round the ring, and the picture is therefore

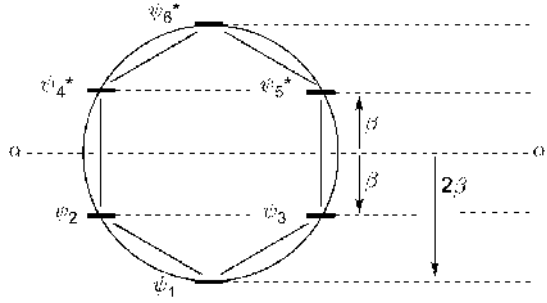


Fig. 1.37 The energies of the π molecular orbitals of benzene

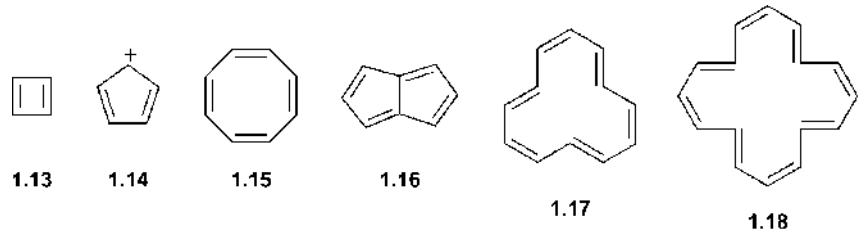
that shown in Fig. 1.37. The lowering of energy for ψ_2 and for ψ_3 is equal to that of the π bond in ethylene (β), and the fully bonding overlap of the six orbitals in ψ_1 gives rise to two π bond's worth of bonding. The total of π bonding is thus $2 \times 4\beta$, which is two more β units than three *isolated* π bonds. Benzene is also lowered in π energy by one β unit more than the π energy for three *linearly conjugated* π bonds: taking the numbers for hexatriene from Fig. 1.35, the total of π bonding is $2 \times (1.802 + 1.247 + 0.445)\beta = 7\beta$.

One of the most striking artifacts of aromaticity, in addition to the lowering in π energy, is the diamagnetic anisotropy, which is characteristic of these rings. Its most obvious manifestation is in the downfield shift experienced by protons on aromatic rings, and perhaps even more vividly by the upfield shift of protons on the inside of the large aromatic annulenes. The theory is beyond the scope of this book, but it is associated with the system of π molecular orbitals, and can perhaps be most simply appreciated from the idea that the movement of electrons round aromatic rings is free, like that in a conducting wire, as epitomised by the equal C—C bond lengths.

We saw earlier that long polyenes do not approach a state with equal bond lengths as the number of conjugated double bonds increases. In the same way, the simple $(4n+2)$ rule of aromaticity has been predicted to break down, with bond alternation setting in when n reaches a large number. It is not yet clear what that number is as neither theory nor experiment has proved decisive. Early predictions that the largest possible aromatic system would be [22] or [26]annulene were too pessimistic, and aromaticity, using the ring-current criterion, probably peters out between [34] and [38]annulene.

1.5.2 Antiaromatic Systems

A molecule with $4n$ π electrons in the ring, with the molecular orbitals made up from $4n$ p orbitals, does not show this extra stabilisation. Molecules in this class that have been made include cyclobutadiene **1.13** ($n = 1$), the cyclopentadienyl cation **1.14**, cyclooctatetraene **1.15** and pentalene **1.16** ($n = 2$), [12]annulene **1.17** ($n = 3$) and [16]annulene **1.18** ($n = 4$).



We can see this most easily by looking at the molecular orbitals of square cyclobutadiene in Fig. 1.38. As usual, the lowest-energy orbital ψ_1 has no nodes, and, as with benzene, and because of the symmetry, there are two exactly equivalent orbitals with one node, ψ_2 and ψ_3. The bonding in ψ_1 gives an energy lowering of 2β (this makes an assumption that the p orbitals are held at the same distance by the σ framework). In contrast, the bonding interactions both in ψ_2 and ψ_3 are exactly matched by the antibonding interactions, and there is no lowering of the energy below the line (α) representing the energy of a p atomic orbital on carbon. The molecular orbitals ψ_2 and ψ_3 are therefore nonbonding orbitals, and the net lowering in energy for the π bonding in cyclobutadiene is only $2 \times 2\beta$. The energies of the four π orbitals are similarly deduced from the model inscribing the conjugated system in a circle, with the point of the square at the bottom. The total π stabilisation of $2 \times 2\beta$ is no better than having two isolated π bonds. There is however less stabilisation than that found in a pair of *conjugated* double bonds—the overall π bonding in butadiene, taking values from Fig. 1.33, is 4.5β and the overall π bonding in cyclobutadiene is only 4β.

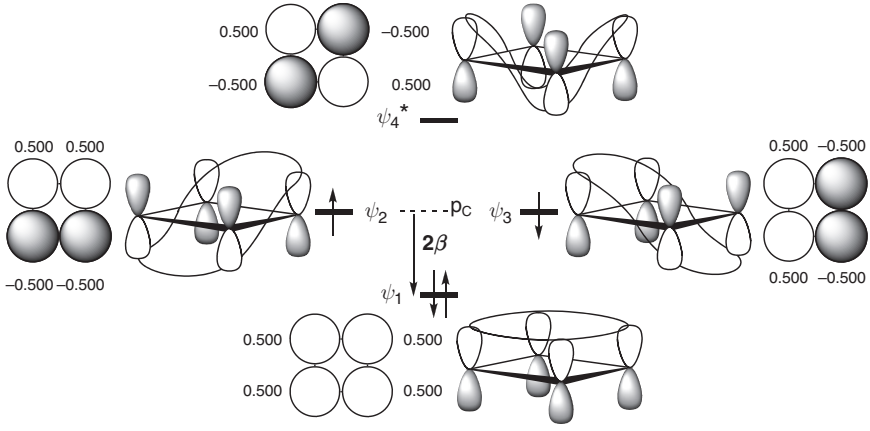


Fig. 1.38 The π molecular orbitals of cyclobutadiene

There is much evidence that cyclic conjugated systems of $4n$ electrons are significantly more reactive than the corresponding open-chain polyenes. There has been much speculation that they not only lack stabilisation but are actually destabilised. They have been called 'anti-aromatic' as distinct from nonaromatic.

Cyclobutadiene dimerises at extraordinarily low temperatures (>35 K). Cyclooctatetraene is not planar, and behaves like an alkene. When it is forced to be planar, as in pentalene, it becomes unstable to dimerisation at 0 °C. [12]Annulene and [16]annulene undergo electrocyclic reactions below 0 °C. We have seen that linear conjugation is more energy lowering than the cyclic conjugation of 4*n* electrons, which goes some way to setting the concept of anti-aromaticity on a physical basis. That 4*n* systems are unusually reactive is also explicable with an argument based on the frontier orbitals—the HOMO (at the nonbonding α level for cyclobutadiene) is unusually high in energy for a neutral molecule, significantly above the level of the HOMO of the linear conjugated hydrocarbon, and the LUMO is correspondingly low in energy.

The prediction from the argument in Fig. 1.38 is that square cyclobutadiene ought to be a diradical with one electron in each of ψ_2 and ψ_3, on the grounds that putting a second electron into an occupied orbital is not as energy lowering as putting the first electron into that orbital. This is not borne out by experiment, which has shown that cyclobutadiene is rectangular, with alternating double and single bonds, and shows no electron spin resonance (ESR) signal.

We can easily explain why the rectangular structure is lower in energy than the square. So far, we have made all π bonds contribute equally one β-value to every π bond. The difference in β-values, and hence in the strengths of π bonds, is a function of how closely the p orbitals are held. In the rectangular structure of cyclobutadiene, in which we have moved the upper pair of carbon atoms away from the lower pair but moved the left-hand pair closer to the right-hand pair, the symmetry is lowered, and the molecular orbitals corresponding to ψ_2 and ψ_3 are no longer equal in energy (Fig. 1.39). The overall bonding in ψ_1 is more or less the same as in the square structure—C-1 and C-2 (and C-3 and C-4) move closer together in ψ_1, and the level of bonding is actually increased by about as much as the level of bonding is decreased in moving the other pairs apart. In the other filled orbital, ψ_2, the same distortion, separating the pair (C-1 from C-4 and C-2 from C-3) will reduce the amount of π antibonding between them, and hence lower the energy. The corresponding argument on ψ_3 will lead to its being raised in energy and becoming an antibonding orbital. With one π orbital raised in energy and the other lowered, the overall π energy will be much the same, and the four electrons then go into the two bonding orbitals. This is known as a Jahn-Teller distortion, and can be expected to be a factor whenever a HOMO and a LUMO are close in energy, and can push each other apart.

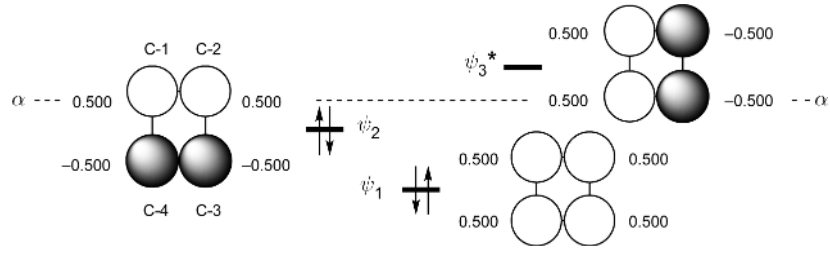


Fig. 1.39 The three lowest-energy π molecular orbitals of rectangular cyclobutadiene

1.5.3 The Cyclopentadienyl Anion and Cation

The device of inscribing the pentagon in a circle sets up the molecular orbitals of the cyclopentadienyl anion and cation in Fig. 1.40. The total of π-bonding energy is $2 \times 3.236\beta$ for the anion, in which there are two electrons in ψ_1, two electrons in ψ_2, and two electrons in ψ_3. The anion is clearly aromatic, since the open-chain analogue, the pentadienyl anion has only $2 \times 2.732\beta$ worth of π bonding (Fig. 1.35). The cyclopentadienyl anion **1.8**, a $4n+2$ system, is exceptionally stabilised, with the pK_a of cyclopentadiene at 16 being strikingly low for a hydrocarbon. The cation **1.14**, however, has π-bonding energy of $2 \times 2.618\beta$, whereas its open-chain analogue, the pentadienyl cation, has $2 \times 2.732\beta$ worth of π bonding. The cyclopentadienyl cation is not formed from its iodide by solvolysis under conditions where even the unconjugated cyclopentyl iodide ionises easily.

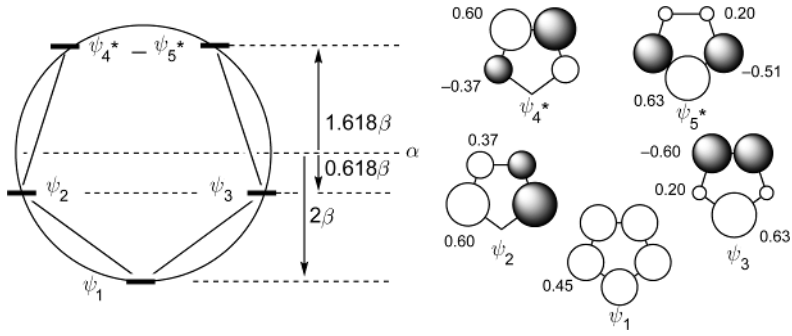


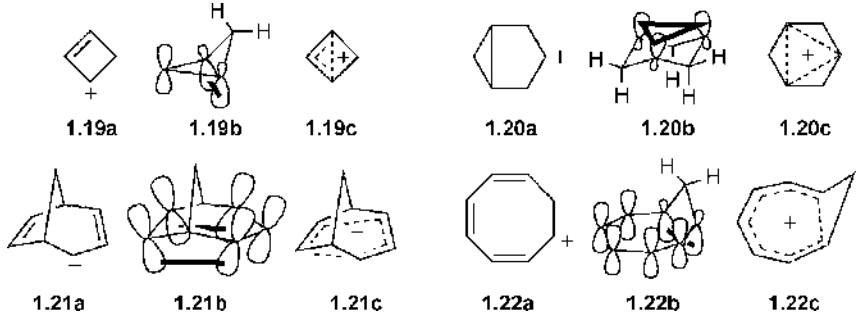
Fig. 1.40 The energies and coefficients of the π molecular orbitals of the cyclopentadienyl system

A striking difference between all the aromatic and all the anti-aromatic systems is the energy *difference* between the HOMO and the LUMO. The aromatic systems have a substantial gap between the frontier orbitals, and the anti-aromatic systems have, after the Jahn-Teller distortion, a small gap. The near degeneracy of the HOMO and the LUMO in the $4n$ annulenes allows a low-energy, one-electron transition between them with a magnetic moment perpendicular to the ring, whereas the aromatic systems do not. As a result, anti-aromatic rings with $4n$ electrons have a paramagnetic ring current—the protons at the perimeter of a $4n$ annulene come into resonance at high field, and protons on the inside of the ring at low field.

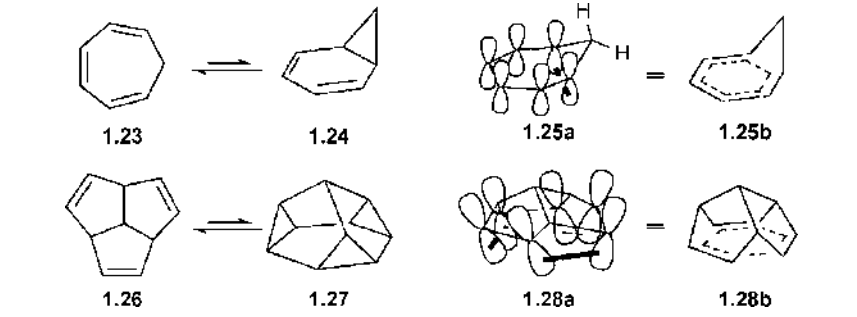
1.5.4 Homoaromaticity

The concept of aromaticity can also be extended to systems in which the conjugated system is interrupted, by a methylene group, or other insulating structural feature, provided that the overlap between the p orbitals of the conjugated systems can still take place through space. When such overlap has energy-lowering consequences, evident in the properties of the molecule, the phenomenon is called

homoaromaticity. Examples are the homocyclopropenyl cation **1.19**, the trishomocyclopropenyl cation **1.20**, the bishomocyclopentadienyl anion **1.21** and the homocycloheptatrienyl cation **1.22**, each of which shows evidence of transannular overlap, illustrated, and emphasised with a bold line on the orbitals in the drawings **1.19b**, **1.20b**, **1.21b** and **1.22b**.



However, homoaromatic stabilisation appears to be absent in neutral systems. Homobenzene (cycloheptatriene) **1.23** and trishomobenzene (triquinacene) **1.26**, even though transannular overlap looks feasible, show no aromatic properties. In both cases, the conventional structures **1.23** and **1.24**, and **1.26** and **1.27** are lower in energy than the homoaromatic structures **1.25** and **1.28**, which appear to be close to the transition structures for the interconversion.



1.5.5 Spiro Conjugation

In addition to σ and π overlap, p orbitals can overlap in another way, even less effective in lowering the energy, but still detectable. If one conjugated system is held at right angles to another in a spiro structure **1.29**, the p orbitals of one can overlap with the p orbitals of the other, as symbolised by the bold lines on the front lobes. The overlap integral will be small, but overlap of molecular orbitals with the right symmetry can raise or lower the orbital energy in the usual way. The hydrocarbons **1.30** and **1.31** are representative examples.

1.29 1.30 1.31

Take spiroheptatriene **1.30**, with the unperturbed orbitals of each component shown on the left and right in Fig. 1.41. The only orbitals that can interact are ψ_2 on the left and π^* on right, all the others having the wrong symmetry. For example, the interaction of the top lobes of ψ_1 on the left and the upper p orbital of the π orbital on the right, one in front and one behind, have one in phase and one out of phase, exactly cancelling each other out; similarly with the front π lobes on the right and the upper and lower lobes of the front-right p orbital of ψ_1 on the left. The two orbitals that do interact create the usual pair of new orbitals, one raised and one lowered. Since there are only two electrons to go into the new orbitals, the overall energy of the conjugated system is lowered. The effect, ΔE_s, is small, both because of the poor overlap, and because the two orbitals interacting are far apart in energy. Nevertheless, it is a general conclusion that if the total number of π electrons is a $(4n+2)$ number, the spiro system is stabilised, leading to the concept of spiro-aromaticity.

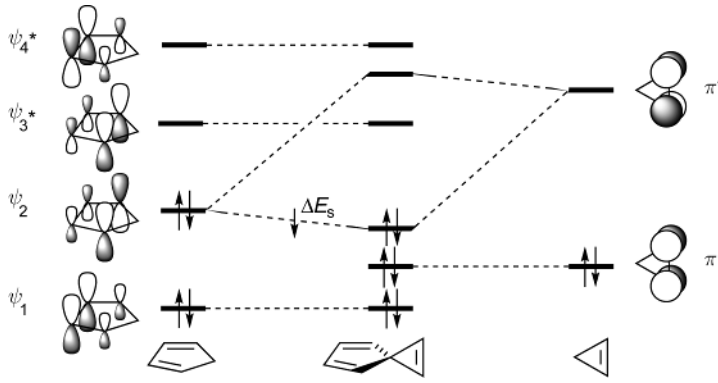


Fig. 1.41 π Molecular orbitals of the 'aromatic' spiroheptatriene **1.30**

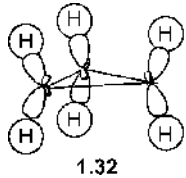
1.6 Strained σ Bonds—Cyclopropanes and Cyclobutanes

Another kind of imperfect sideways-on overlap, this time in σ bonds, is found in strained molecules like cyclopropane and cyclobutane.

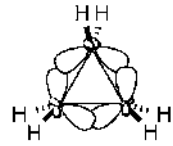
1.6.1 Cyclopropanes

There are several ways to describe the σ bonds in cyclopropane. The most simple is to identify the C—H bonds as coming from the straightforward sp^3 hybrids on the carbon atoms and the 1s orbitals on the hydrogen atoms **1.32** in

the usual way, and the C—C bonds as coming from the remaining sp^3 hybrids imperfectly aligned **1.33**.



1.32



1.33

In more detail, these orbitals ought to be mixed in bonding and antibonding combinations to create the full set of molecular orbitals, but even without doing so we can see that C—C bonding is somewhere between σ bonding (head-on overlap) and π bonding (sideways-on overlap). We can expect these bonds to have some of the character of each, which fits in with the general perception that cyclopropanes can be helpfully compared with alkenes in their reactivity and in their power to enter into conjugation. Thus cyclopropane is much less reactive than ethylene towards electrophiles, like bromine, but it does react, whereas ethane does not. Conjugation of a double bond or an aromatic ring with a cyclopropyl substituent is similar to conjugation with an alkene, but less effective.

Another way of understanding the C—C bonding, known as the Walsh description, emphasises the capacity of a cyclopropyl substituent to enter into π bonding. In this picture, which is like the picture of the bonding in ethane without using hybridisation (Fig. 1.19), the six C—H bonds are largely made up from the s orbitals on hydrogen and the s, p_x and p_z orbitals on carbon, with the x, y and z axes redefined at each corner to be local x, y and z coordinates. The picture of C—H bonding can be simplified by choosing sp hybridisation from the combination of the 2s and $2p_x$ orbitals, and using the three sp hybrids with the large lobes pointing outside the ring and the three p_z orbitals to make up the CH-bonding orbitals (Fig. 1.42). Some of these orbitals contribute to C—C bonding, notably the σ_{CH}, π_{CC} orbital, but the major contributors are the overlap of the three sp hybrids with the large lobes pointing into the ring, which produce one bonding combination σ_{CC}, and the three p_y orbitals, which combine to produce a pair of bonding orbitals π_{CC}, each with one node, and with coefficients to make the overall bonding between each of the C—C bonds equal.

The advantage of this picture is that it shows directly the high degree of π bonding in the C—C bonds, and gives directly a high-energy filled p orbital, the π_{CC} orbital at the top right, largely concentrated on C-1, and with the right symmetry for overlap with other conjugated systems [see (Section 2.2.1) page 72].

A remarkable property of cyclopropanes is that they are magnetically anisotropic, with the protons coming into resonance in their NMR spectra at unusually *high* field, typically 1 ppm *upfield* of the protons of an open-chain methylene group. For ^1H NMR spectroscopy, this is quite a large effect, and it is also strikingly in the opposite direction from that expected by the usual analogy

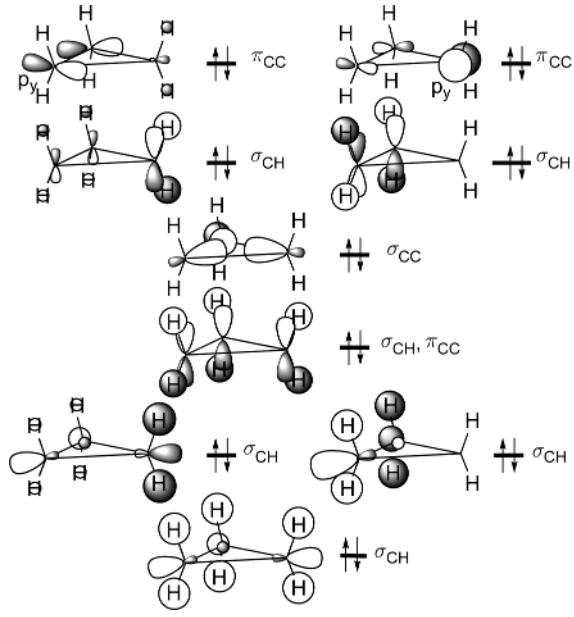
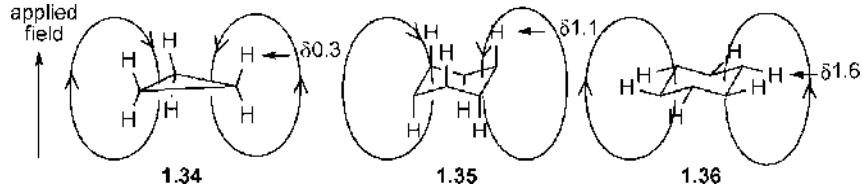


Fig. 1.42 A simplified version of the occupied Walsh orbitals of cyclopropane

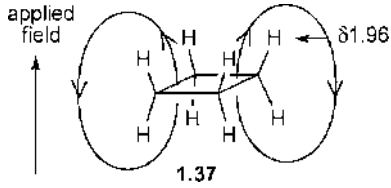
drawn between a cyclopropane and an alkene. The anisotropy is explained with the orbitals shown in Fig. 1.42: the pair of σ_{CH} orbitals just below the highest occupied orbitals, together with the σ_{CH},π_{CC} orbital, clearly have the same nodal pattern as the filled π orbitals of benzene, and the pattern is repeated in the three filled orbitals of lowest energy. This pattern of orbitals is associated with the capacity to support a ring current, but, in contrast to benzene, the derived field places the protons in cyclopropanes in the region experiencing a reduced magnetic field **1.34**.



The same explanation, although we shall not show the molecular orbitals, has been advanced to account for the small difference in chemical shift between the axial and equatorial protons in cyclohexanes, detectable in the ^{1}H NMR spectrum of cyclohexane by freezing out at –100 °C the otherwise rapid interconversion of the two chair conformations. The axial protons **1.35** come into resonance upfield at δ1.1 and the equatorial protons **1.36** downfield at δ1.6.

1.6.2 Cyclobutanes

The molecular orbitals of cyclobutanes, show many of the same features as cyclopropanes, only less so. Cyclobutanes also show enhanced reactivity over simple alkanes, but they are less reactive towards electrophiles, and cyclobutyl groups are less effective as stabilising substituents on electron-deficient centres than cyclopropyl groups. The most striking difference, however, is that the protons in cyclobutanes come into resonance in their ^{1}H NMR spectra *downfield* of the protons from comparable methylene groups in open chains. The effect is not large, typically only about 0.5 ppm, with cyclobutane itself, for example, at δ1.96 in contrast to cyclohexane at δ1.44. The pattern of orbitals will be similar to those of cyclobutadiene (Figs 1.38 and 1.39), with the highest-energy orbitals degenerate and suffering Jahn-Teller distortion.



1.37

The ring current is therefore in the opposite direction, adding to the applied field at the centre of the ring, and the protons experience therefore an enhanced field **1.37**. The effect may be rather less in cyclobutanes than in cyclopropanes, because the cyclobutane ring is flexible, allowing the ring to buckle from the planar structure, and the C—H bonds thereby avoid the full eclipsing interactions inevitable in cyclopropanes, and compensated there by the aromaticity they create.

1.7 Heteronuclear Bonds, C—M, C—X and C=O

So far, we have been concentrating on symmetrical bonds between identical atoms (homonuclear bonds) and on bonds between carbon and hydrogen. The important interaction diagrams were constructed by combining atomic orbitals of more or less *equal* energy, and the coefficients, c_1 and c_2, in the molecular orbitals were therefore more or less equal in magnitude. It is true that C—H bonds, with and without hybridisation, involve the overlap of atomic orbitals of different elements, but the difference in the energy of the atomic orbitals of these two elements, did not make a significant difference in the earlier part of this chapter. The interaction of orbitals of different energy is inescapable when we come to consider molecules, like methyl chloride and methyllithium. As we have mentioned in passing, *orbitals of different energy interact to lower (and raise) the energy of the resultant molecular orbitals less than orbitals of comparable energy*.

1.7.1 Atomic orbital energies and electronegativity

One way of assessing the relative energies of the orbitals of different elements is to use one of the empirical scales of *electronegativity*. Pauling's is empirically derived from the differences in dissociation energy for the molecules XX, YY and XY. Several refinements of Pauling's scale have been made since it first appeared in 1932. A good recent one is Allen's, reproduced to scale in Fig. 1.43, along with values assigned by Mullay to the carbon atoms in methyl, vinyl and ethynyl groups. In spite of the widespread use of electronegativity as a unifying concept in organic chemistry, the electronegativity of an element is almost never included in the periodic table. Redressing this deficiency, Allen strikingly showed his electronegativity scale as the third dimension of the periodic table, and his vivid picture is reproduced here as Fig. 1.44. The other way of assessing the relative energies of the orbitals of different elements is to accept the calculated values in Table 1.1, which are themselves supported by measurements of ionisation potentials (IPs).

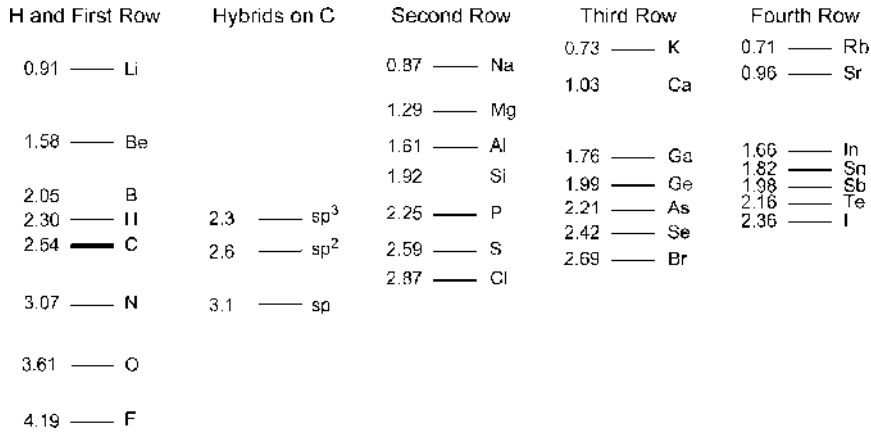


Fig. 1.43 Allen electronegativity values and Pauling-based values for carbon hybrids

1.7.2 C—X σ Bonds

We are now ready to construct an interaction diagram for a bond made by the overlap of atomic orbitals with different energies. Let us take a C—Cl σ bond, in which the chlorine atom is the more electronegative element. Other things being equal, the energy of an electron in an atomic orbital on an electronegative element is lower than that of an electron on a less electronegative element.

As usual, we can tackle the problem with or without using the concept of hybridisation. The C—X bond in a molecule such as methyl chloride, like the C—C bond in ethane, has several orbitals contributing to the force which keeps the two atoms bonded to each other; but, just as we could abstract one pair of atomic orbitals of ethane and make a typical interaction diagram for it, so can we now take the corresponding pair of orbitals from the set making up a C—Cl σ bond.

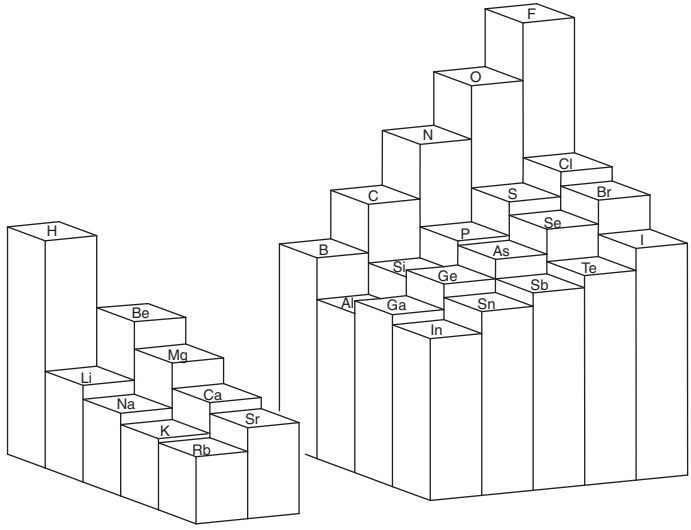


Fig. 1.44 Electronegativity as the third dimension of the periodic table (adapted with permission from L. C. Allen, *J. Am. Chem. Soc.*, 1989, **111**, 9003. Copyright 1989 American Chemical Society)

Table 1.1 Valence atomic orbital energies for s, p and selected hybrid orbitals in eV(1 eV = 96.5 kJ mol^{-1} = 23 kcal mol^{-1})

	H						
1s	−13.6						
	Li	**Be**	**B**	**C**	**N**	**O**	**F**
2s	−5.4	−9.4	−14.7	−19.4	−25.6	−32.4	−40.1
sp				−19.3	−19.3	−24.2	−29.4
sp^2				−17.1	−17.1	−21.4	−25.8
sp^3				−16.1	−16.1	−20.0	−24.4
2p	−3.5	−6.0	−5.7	−10.7	−12.9	−15.9	−18.6
	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
3s	−5.2	−7.6	−11.3	−15.0	−18.4	−20.9	−25.3
3p			−6.0	−7.8	−9.8	−11.7	−13.7

In making a covalent bond between carbon and chlorine from the $2p_x$ orbital on carbon and the $3p_x$ orbital on chlorine, we have an interaction (Fig. 1.45) between orbitals of *unequal* energy (–10.7 eV for C and –13.7 eV for Cl, from Table 1.1). The interaction diagram could equally have been drawn using sp^3 hybrids on

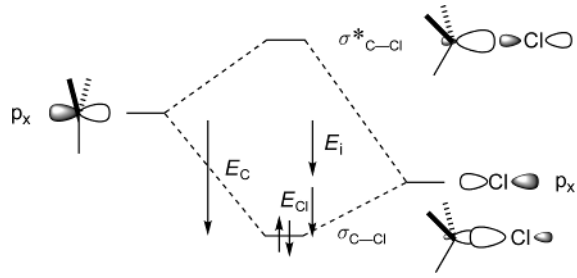


Fig. 1.45 A major part of the C—Cl σ bond

carbon and chlorine in place of the p orbitals. Because of the loss of symmetry, the chlorine atom has a larger share of the electron population. In other words, the coefficient on chlorine for the bonding orbital, σ_{CCl} is larger than that on carbon. It follows from the requirement that the sum of the squares of all the c-values on any one atom in all the molecular orbitals must equal one, that the coefficients in the corresponding antibonding orbital, σ^*_{CCl} must reverse this situation: the one on carbon will be larger than the one on chlorine.

What we have done in Fig. 1.45 is to take the lower-energy atomic orbital on the right and mix in with it, in a bonding sense, some of the character of the higher-energy orbital on the left. This creates the new bonding molecular orbital, which resembles the atomic orbital nearer to it in energy more than the one further away. We have also taken the higher-energy orbital and mixed in with it, in an anti-bonding way, some of the character of the lower-energy orbital. This produces the antibonding molecular orbital, which more resembles the atomic orbital nearer it in energy. When the coefficients are unequal, the overlap of a small lobe with a larger lobe does not lower the energy of the bonding molecular orbital as much as the overlap of two atomic orbitals of more equal size. The overlap integrals S for forming bonds to the first-row elements N, O and F are essentially parallel to the overlap integral for the formation of a C—C bond (Figs 1.11b and 1.20), but displaced successively by about 0.2 Å to shorter internuclear distances for each element. This is because the orbitals of the first-row elements have similar shapes, but the electrons are held closer to the nucleus of the more electronegative elements.

Thus we can set up the filled orbitals for methyl chloride schematically in Fig. 1.46a, along with the lowest of the unoccupied orbitals. The major orbital contributing to C—Cl bonding is the one labelled σ_{CCl}. There is more bonding than antibonding from the overlap of the s orbitals, but probably nearly equal bonding and antibonding from the orbitals having π bonding between the carbon and the chlorine. The same degree of bonding can be arrived at by using the hybrid orbitals shown in Fig. 1.46b, where all of the C—Cl bonding comes from the sp^3 hybrids.

We might be tempted at this stage to say that we have a weaker bond than we had for a C—C bond, but we must be careful in defining what we mean by a weaker bond. Tables of bond strengths give the C—Cl bond a strength of

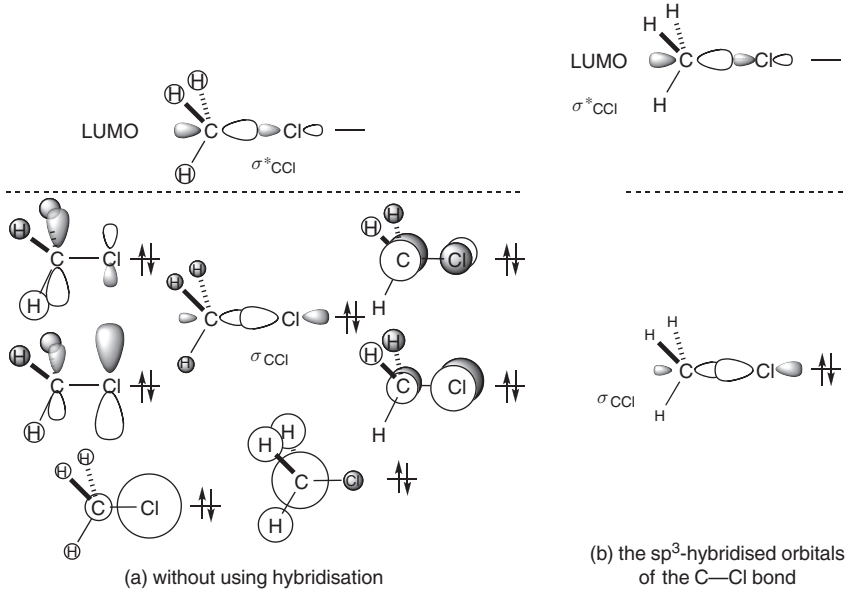


Fig. 1.46 The filled molecular orbitals and the lowest unfilled molecular orbital of methyl chloride

352 kJ mol^{-1} (84 kcal mol^{-1}), whereas a typical C—C bond strength is a little lower at 347 kJ mol^{-1} (83 kcal mol^{-1}). The C—Cl bond *is* strong, if we try to break it homolytically to get a pair of radicals, and the C—C bond *is* easier to break this way. This is what the numbers 352 and 347 kJ mol^{-1} refer to.

Only part of the C—Cl bond strength represented by these numbers comes from the purely covalent bonding given by $2E_{Cl}$ in Fig. 1.45. The other contribution to C—Cl bonding comes from the electrostatic attraction between the high electron population on the chlorine atom and the relatively exposed carbon nucleus. We say that the bond is polarised, or that it has ionic character. Thus it is much easier to break a C—Cl bond heterolytically to the cation (on carbon) and the anion (on chlorine) than to cleave a C—C bond this way. The energy of an ionic bond is related to the value E_i in Fig. 1.45, as we can see by taking it to an extreme: a 2s orbital on Li and a 2p orbital on F, with energies of –5.4 and –18.6 eV, respectively, will have negligible covalent overlap, and the molecule will consist almost entirely of isolated orbitals in which the higher-energy orbital has given up its electron to the lower-energy orbital. In other words, we shall have a pair of ions Li^+ and F^-. There will be no covalent bonding to speak of, and the drop in energy in going from the pair of radicals to the cation plus anion is now the difference in energy between the two orbitals, equivalent to E_i in Fig. 1.45.

The important thing to remember is that *when two orbitals of unequal energy interact, the lowering in energy is less than when two orbitals of very similar energy interact*. Conversely, when it comes to transferring an electron, the ideal situation has the electron in a high-energy orbital and the 'hole' in a low-energy

orbital. In a little more detail, the degree of energy lowering E_{Cl} is a function of the overlap integral S [see (Section 1.2.1) page 3]. When orbitals of significantly different energy interact, the energy lowering is roughly proportional to S^2 instead of S. The energy lowering is also inversely proportional to the difference in energy E_i. The equations for the energies of the lowered and raised orbitals in Fig. 1.45, take the form shown in Equations 1.13 and 1.14, where we see that the energy difference is in the denominator.

$$E_{\sigma_{CCl}} = E_{p_{Cl}} + \frac{(\beta_{CCl} - E_{p_{Cl}} S_{CCl})^2}{E_{p_{Cl}} - E_{p_C}} \qquad 1.13$$

$$E_{\sigma^*_{CCl}} = E_{p_C} + \frac{(\beta_{CCl} - E_{p_C} S_{CCl})^2}{E_{p_C} - E_{p_{Cl}}} \qquad 1.14$$

A picture of the electron distribution in the σ orbitals between carbon and chlorine is revealed in the wire-mesh diagrams for methyl chloride in Fig. 1.47, which shows one contour of the major orbital σ_{CCl} contributing to C—Cl bonding together with the LUMO, σ^*_{CCl}, which incidentally provides the cover illustration for this book. Comparing these with the schematic version in Fig. 1.46, we can see how the back lobe on carbon in σ_{CCl} includes overlap with the s orbitals on the hydrogen atoms, and that the front lobe in σ^*_{CCl} wraps back a little behind the carbon atom to include some overlap to the s orbitals of the hydrogen atoms.

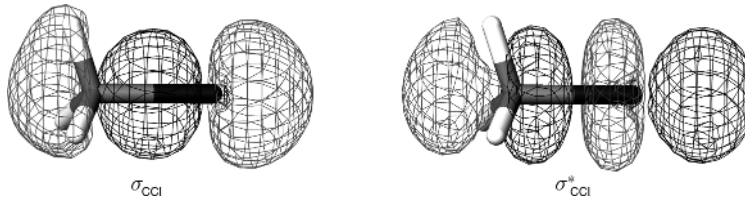


Fig. 1.47 The major C—Cl bonding orbital and the LUMO for methyl chloride

1.7.3 C—M σ Bonds

When the bond from carbon is to an electropositive element like lithium, carbon is the electronegative atom. The most strongly interacting orbitals are the 2s orbital on lithium and the $2p_x$ orbital on carbon, which has the form shown in Fig. 1.48, in which the lithium 2s orbital is at –5.4 eV and the carbon 2p orbital at –10.7 eV. The bonding orbital σ_{LiC} is polarised towards carbon, and the anti-bonding σ^*_{LiC} towards lithium. Organic chemists often refer to organolithium compounds as anions, but it is as well to bear in mind that they are usually highly polarised covalent molecules. Furthermore, they are rarely monomeric, almost always existing as oligomers, in which the lithium is coordinated to more than one carbon atom, making the molecular orbital description below greatly oversimplified.

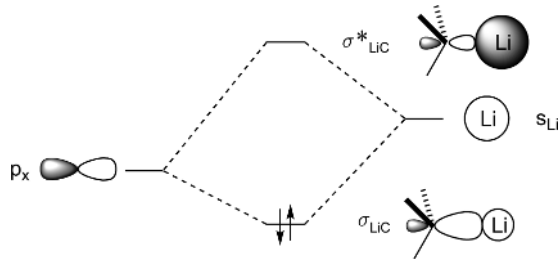


Fig. 1.48 A major contributory part of the Li—C σ bond

The filled and one of the unfilled orbitals for monomeric methyllithium are shown in Fig. 1.49. The lowest energy orbital is made up largely from the 2s orbital on carbon and the 1s orbitals on hydrogen, with only a little mixing in of the 2s orbital of lithium and even less of the 2p. The next two up in energy are largely π mixes of the $2p_z$ and $2p_y$ orbitals on carbon with a little of the $2p_z$ and $2p_y$ on lithium, and, as usual, the 1s orbitals on hydrogen. The $2p_z$ and $2p_y$ orbitals on lithium have the wrong symmetry to overlap with the 2s orbital on carbon. Then come the two orbitals we have seen in Fig. 1.48: the $2p_x$ orbital on carbon interacting productively with the 2s orbital on lithium, giving rise to the highest of the occupied orbitals σ_{CLi}, which has mixed in with it the usual 1s orbitals on hydrogen and a contribution from the $2p_x$ orbital on lithium, symbolised here by the displacement of the orbital on lithium towards the carbon. The next orbital up in energy, the lowest of the unfilled orbitals, is its counterpart σ^*_{LiC}, largely a mix of the 2s and the $2p_x$ orbital of lithium, symbolised again by the displacement of the orbital on lithium away from the carbon, with a little of the $2p_x$ orbital of carbon out of phase.

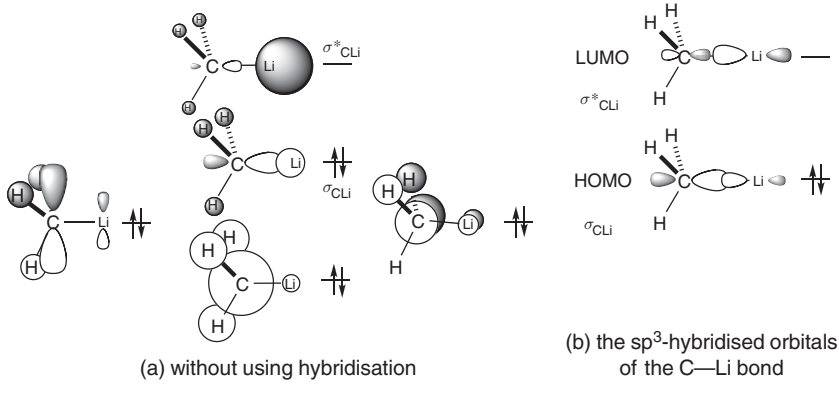


Fig. 1.49 The filled and one of the unfilled molecular orbitals of methyllithium

The electron distribution in the σ orbitals between carbon and lithium is revealed in Fig. 1.50, which shows one contour of the σ_{CLi} and σ^*_{CLi} orbitals of methyllithium, unrealistically monomeric and in the gas phase. Comparing Fig. 1.50 with Fig. 1.49, we can see better how the s and p_x orbitals on lithium mix to boost the electron population between the nuclei in σ_{CLi}, and to minimise it in σ^*_{CLi}.

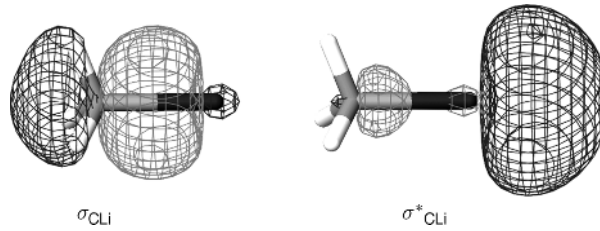


Fig. 1.50 The HOMO and LUMO for methyllithium in the vapour phase

1.7.4 C=O π Bonds

The C=O π bond is relatively straightforward, because the p orbitals in the π system in Hückel theory are free from the complicating effect of having to mix in contributions from s orbitals. The p_x orbital on oxygen is placed in Fig. 1.51 at a level somewhat more than 1β below that of the p_x orbital on carbon. The energy of a p orbital on oxygen is –15.9 eV and that on carbon –10.7 eV (Table 1.1). As with π bonds in general, the raising of the π^* and lowering of the π orbitals above and below the atomic p orbitals is less than for a C—O σ bond, and less than for a π bond between two carbon atoms. Both the $\pi_{C=O}$ and the $\pi^*_{C=O}$ orbitals are now lower in energy than the $\pi_{C=C}$ and $\pi^*_{C=C}$ orbitals of ethylene, which by definition are 1β above and 1β below the α level.

The contour plots in Fig. 1.52 show the electron distribution in more detail. To derive contours like these, we need values for α and β for electronegative atoms in

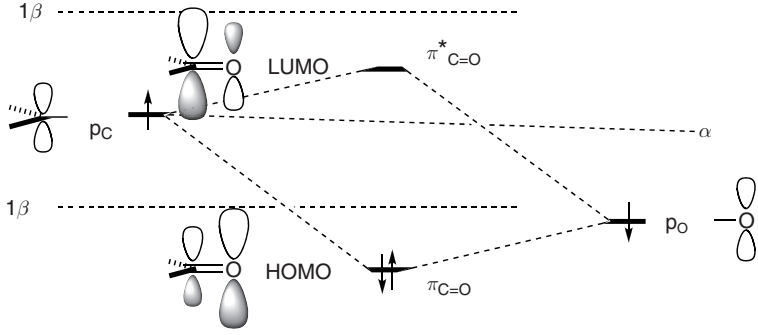


Fig. 1.51 The interaction of p orbitals in the formation of the π bond of a carbonyl group

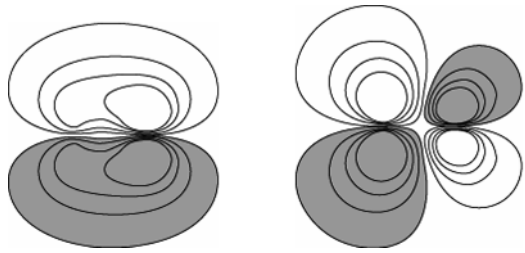


Fig. 1.52 Electron population contours for the π and π^* orbitals of formaldehyde

order to carry out Hückel calculations on the isolated π system. There are no fundamentally sound values for α and β, which we need for systems with heteroatoms. Everything is approximate, and any values for energies and coefficients that come from simple calculations must be taken only as a guide. In simple Hückel theory, the value of α is adjusted for the element in question X from the reference value for carbon α_0 by Equation 1.15. Likewise, the β value for the C=C bond in ethylene β_0 is adjusted for C=X by Equation 1.16.

$$\alpha_X = \alpha_0 + h_X\beta_0 \qquad 1.15$$

$$\beta_{CX} = k_{CX}\beta_0 \qquad 1.16$$

The adjustment parameters h and k take into account the trends in electronegativity, but are not quantitatively related to the numbers in Fig. 1.43 and Table 1.1. The values of h for some common elements and of k for the corresponding C=X π bonds in Table 1.2 have been recommended for use in Equations 1.15 and 1.16.

The polarisation of the carbonyl group is away from carbon towards oxygen in the bonding orbital, and the opposite in the antibonding orbital, as usual. The wire-mesh pictures in Fig. 1.53 show more realistically an outer contour of these two orbitals in formaldehyde itself. Note that in Figs 1.52 and 1.53, it *appears* from the shape of the outer contour that the electron population in the bonding orbital is very similar on oxygen to that on carbon.

Table 1.2 Parameters for simple Hückel calculations for bonds with heteroatoms

Element		h	k	Element		h	k
B	Trigonal	−0.45	0.73				
C	Trigonal	0	1	**Si**	Trigonal	0	0.75
N	Trigonal	0.51	1.02	**P**	Trigonal	0.19	0.77
N	Tetrahedral	1.37	0.89	**P**	Tetrahedral	0.75	0.76
O	Trigonal	0.97	1.06	**S**	Trigonal	0.46	0.81
O	Tetrahedral	2.09	0.66	**S**	Tetrahedral	1.11	0.69
F	Tetrahedral	2.71	0.52	**Cl**	Tetrahedral	1.48	0.62

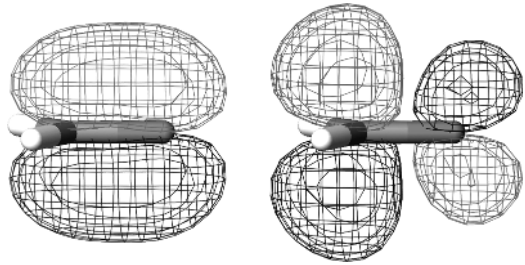
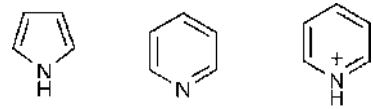


Fig. 1.53 Wire-mesh plot of the π and π^* orbitals of formaldehyde

This is not the case, as shown by the extra contour around the oxygen atom in the plot in Fig. 1.52. The electron distribution around the oxygen atom is simply more compact, as a consequence of the higher nuclear charge on that atom.

1.7.5 Heterocyclic Aromatic Systems

The concept of aromaticity is not restricted to hydrocarbons. Heterocyclic systems, whether of the pyrrole type **1.38** with trigonal nitrogen in place of one of the C=C double bonds, or of the pyridine type **1.39** with a trigonal nitrogen in place of a carbon atom, are well known. The π orbitals of pyrrole are like those of the cyclopentadienyl anion, and those of pyridine like benzene, but skewed by the presence of the electronegative heteroatom. The energies and coefficients of heteroatom-containing systems like these cannot be worked out with the simple



1.38 **1.39** **1.40**

devices that work for linear and monocyclic conjugated hydrocarbons. The numbers in Fig. 1.54 are the results of simple Hückel calculations using parameters like those in Table 1.2 for equations like Equations 1.15 and 1.16. The overall π energy is lowered by the cyclic conjugation. The lowest-energy orbital ψ_1 is polarised towards the electronegative atom, and the next orbital up in energy ψ_2 (and the highest unoccupied orbital) are polarised the other way. This polarisation is more pronounced in the pyridinium cation **1.40**, where the protonated nitrogen is effectively a more electronegative atom. In pyridine, the HOMO is actually localised as the nonbonding lone pair of electrons on nitrogen. The degeneracy of ψ_2 and ψ_3 is removed, but not by much. The orbitals with nodes through the heteroatoms are identical in energy and coefficients with those of the corresponding hydrocarbon, as in ψ_3 and ψ_5*, both in pyrrole and in pyridine and its cation.

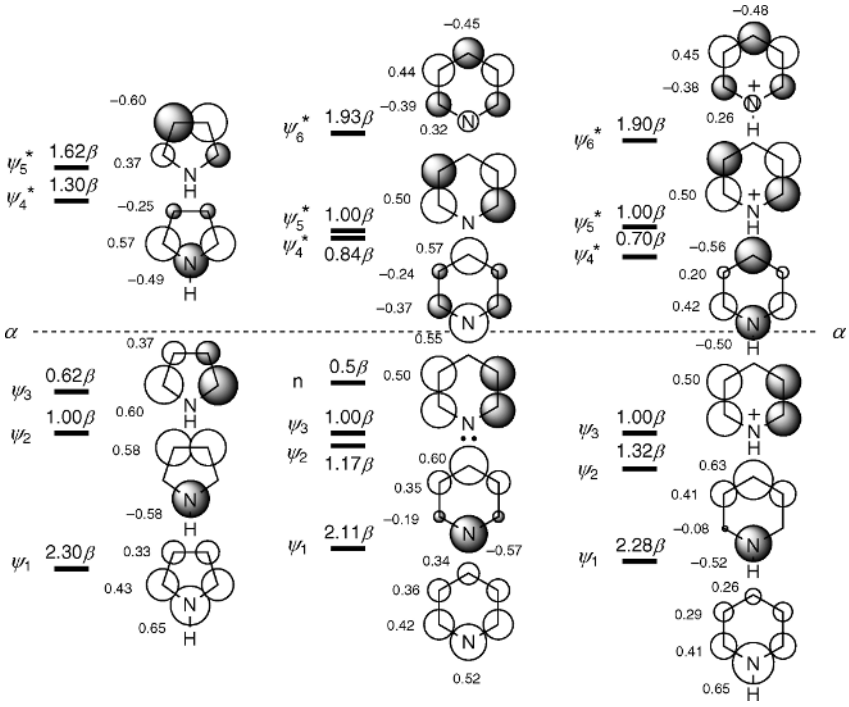
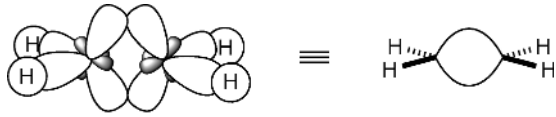


Fig. 1.54 π Molecular orbitals of pyrrole, pyridine and the pyridinium ion. (Calculated using $h = 1$ and $k = 1$ for pyrrole, $h = 0.5$ and $k = 1$ for pyridine, and $h = 1$ and $k = 1$ for the pyridinium cation)

1.8 The Tau Bond Model

The Hückel version of molecular orbital theory, separating the σ and π systems, is not the only way of accounting for the bonding in alkenes. Pauling showed that it is possible to explain the electron distribution in alkenes and conjugated polyenes using only sp^3-hybridised carbon atoms. For ethylene, instead of having sp^2-hybridised carbons involved in full σ bonding, and p orbitals involved in a pure π bond, two sp^3 hybrids can overlap in something between σ and π bonding **1.41**. The overall distribution of electrons in this model is exactly the same as the combination of σ and π bonding in the conventional Hückel picture. In practice, this model, usually drawn with curved lines called τ bonds **1.42**, has found few adherents, and the insights it gives have not proved as useful as the Hückel model. It is useful, however, to recognise that it is perfectly legitimate, and that on occasion it might have some virtues in trying to explain aspects of stereochemistry.



1.41 **1.42**

1.9 Spectroscopic Methods

A number of physical methods have found support in molecular orbital theory, or have provided evidence that the deductions of molecular orbital theory have some experimental basis. Electron affinities correlate moderately well with the calculated energies of the LUMO, ionisation potentials correlate moderately well with the calculated energies of the HOMO, and spectroscopic methods reveal features that support molecular orbital theory.

1.9.1 Ultraviolet Spectroscopy

When light of an appropriate energy interacts with an organic compound, an electron can be promoted from a low-lying orbital to a higher-energy orbital, with the lowest-energy transition being from the HOMO to the LUMO. Selection rules govern which transitions are allowed and which are forbidden. One rule states that electron spin may not change, and another that the orbitals should not be orthogonal. The remaining selection rule is based on the symmetries of the pair of orbitals involved. In most cases, the rules are too complicated to be made simple here. Group theory is exceptionally powerful in identifying which transitions are allowed, and it is one of the first applications of group theory that a chemist pursuing a more thorough understanding comes across. One case, however, is easy—that for molecules which only have a centre of symmetry, like s-*trans* butadiene. The allowed transitions for centro-symmetric molecules are between orbitals that are symmetric and antisymmetric with respect to the centre of symmetry. Thus the HOMO, ψ_2, is symmetric with respect to the centre of symmetry halfway between C-2 and C-3, and the LUMO, ψ_3*, is antisymmetric (Fig. 1.35). Accordingly this transition is allowed and is strong, as is the corresponding transition for each of the longer linear polyenes.

Fig. 1.55 is a plot of the experimentally determined values of λ_{max} for the longest wavelength absorption for a range of polyenes R(CH=CH)$_n$R, converted

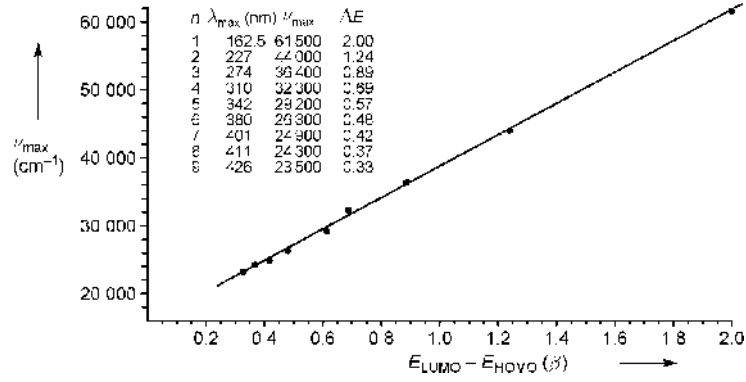


Fig. 1.55 Frequency of first $\pi \rightarrow \pi^*$ transitions of some representative polyenes R(CH=CH)$_n$R plotted against $E_{LUMO} - E_{HOMO}$

to frequency units, against calculated values of $E_{LUMO} - E_{HOMO}$ in β units. The correlation is astonishingly good—in view of the simplifications made in Hückel theory. Similarly impressive correlations can be made for aromatic and α,β-unsaturated carbonyl systems. It is not however a good measure of *absolute* energies, and the energy of the $\pi \rightarrow \pi^*$ transition measured by UV cannot be used directly as a measure of the energy difference between the HOMO and the LUMO. This can be seen from that fact that the line in Fig. 1.55 does not go through the origin, as Hückel theory would predict, but intersects the ordinate at 15 500 cm^{-1}, corresponding to an energy of 185 kJ mol^{-1} (44 kcal mol^{-1}).

1.9.2 Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) measures the energies (Table 1.3) of filled orbitals, and overcomes the problem that UV spectroscopy does not give good absolute values for the energies of molecular orbitals.

Table 1.3 Energies of HOMOs of some representative molecules as measured by PES (1 eV = 96.5 kJ mol^{-1} = 23 kcal mol^{-1})

Entry	Molecule	Type of orbital	Energy (eV)
1	$:PH_3$	n	−9.9
2	$:SH_2$	n	−10.48
3	$:NH_3$	n	−10.85
4	$:OH_2$	n	−12.6
5	:ClH	n	−12.8
6	$CH_2{=}CH_2$	π	−10.51
7	HC≡CH	π	−11.4
8	$:O{=}CH_2$	n	−10.88
9		π	−14.09
10	$CH_2{=}CH\text{-}CH{=}CH_2$	ψ_2	−9.1
11		ψ_1	−11.4 or −12.2
12	HC≡C-C≡CH	ψ_2	−10.17
13	$H_2NCH{=}O:$	n	−10.13
14		π	−10.5
15	$CH_2{=}CH\text{-}CH{=}O$	n	−10.1
16		π	−10.9
17	Furan	π	−8.9
18	Benzene	π	−9.25
19	Pyridine	π	−9.3
20		n	−10.5

Here we can see how the change from a simple double bond (entry 6) to a conjugated double bond (entry 10) *raises* the energy of the HOMO. Similarly, we can see how the change from a simple carbonyl group (entry 9) to an amide (entry 14) also raises the HOMO energy, just as it ought to, by analogy with the

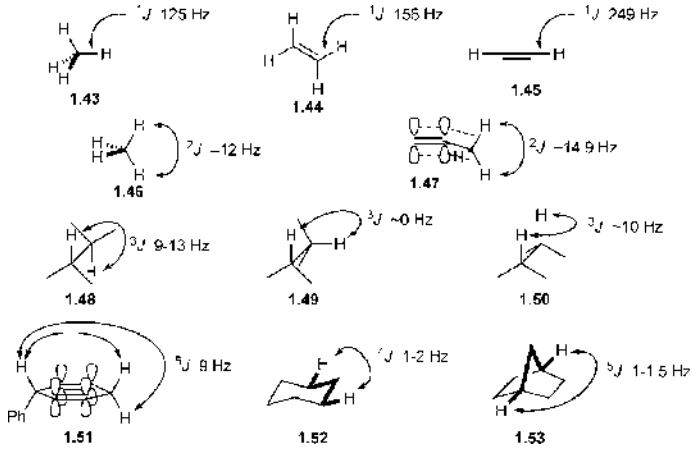
allyl anion, with which an amide is isoelectronic. The interaction between a C=C bond (π energy –10.5 eV) and a C=O bond (π energy –14.1 eV) gives rise to a HOMO of lower energy (–10.9 eV, entry 16) than when two C=C bonds are conjugated (–9.1 eV, entry 10). Finally, we can see that the more electronegative an atom, the lower is the energy of its HOMO (entries 1 to 5).

1.9.3 Nuclear Magnetic Resonance Spectroscopy

Chemical shift is substantially determined by the electron population surrounding the nucleus in question and shielding it from the applied field. Chemical shifts are therefore used to probe the *total* electron population. The chemical shift range with protons is so small that aromatic ring currents and other anisotropic influences make such measurements using proton spectra unreliable, but the agreement between calculated and observed ^{13}C chemical shifts is good.

Coupling constants J measure the efficiency with which spin information from one nucleus is transmitted to another. This is not usually mediated through space, but by interaction with the electrons in the intervening orbitals. The interaction between the nuclear magnetic moment and the electrons is only with s orbitals (only s orbitals have an electron population at the nucleus), but p and π orbitals can transmit spin information when the s orbital carrying that information is not orthogonal to a p orbital or π system. Transmission of information about the magnetic orientation of one nucleus to another is therefore dependent upon how well the intervening electrons interact with the nuclear spin and then with each other. In a crude approximation, the number of intervening orbital interactions affects both the sign and the magnitude of the coupling constant. Although the sign of the coupling constant does not affect the appearance of the ^{1}H-NMR spectrum, it does change the way in which structural variations affect the magnitude of the coupling constant. In general, although not always, one-bond couplings ^{1}J and three-bond couplings ^{3}J are positive in sign, and two- and four-bond couplings ^{2}J and ^{4}J are negative in sign. The full treatment of this topic is beyond this book, but manifestations of orbital interactions can be seen in several well known features of NMR spectra.

Thus, the ^{1}J values for ^{1}H—^{13}C coupling are positive, and correlated with the degree of s character at carbon **1.43–1.45**, whereas the ^{2}J coupling between geminal protons is negative. Although negative, it is larger in absolute magnitude when both C—H bonds are conjugated to the same π bond **1.47** than when they are not **1.46**. Vicinal hydrogen atoms, have positive ^{3}J coupling constants, large in absolute magnitude when the C—H bonds are antiperiplanar **1.48** or syncoplanar **1.50**, because they are conjugated with each other, but virtually zero when the C—H bonds are orthogonal **1.49** (the Karplus equation). Coupling constants are usually larger when the intervening bond is a π bond, with the *trans* and *cis* ^{3}J coupling in alkenes typically 15 and 10 Hz for the same 180° and 0° dihedral angles. Longer-range coupling is most noticeable when one or more of the intervening bonds is a π bond, most strikingly demonstrated by ^{5}J values as high as 8–10 Hz in 1,4-cyclohexadienes **1.51**. When there are no π bonds, the strongest long-range coupling is found when the intervening σ bonds are oriented and held rigidly for efficient conjugation with ^{4}J W-coupling **1.52** and **1.53**.



1.9.4 Electron Spin Resonance Spectroscopy

A final technique which both confirms some of our deductions and provides useful quantitative data for frontier orbital analysis is ESR spectroscopy. This technique detects the odd electron in radicals; the interaction of the spin of the electron with the magnetic nuclei (^{1}H, ^{13}C, etc.) gives rise to splitting of the resonance signal, and the degree of splitting is proportional to the electron population at the nucleus. Since we already know that the coefficients of the atomic orbitals, c, are directly related to the electron population, we can expect there to be a simple relationship between these coefficients and the observed coupling constants. The nucleus most often used is ^{1}H, and the atomic orbital whose coefficient is measured in this way is that on the carbon atom to which the hydrogen atom in question is bonded.

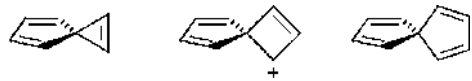
The McConnell equation (Equation 1.17) shows the relationship of the observed coupling constant (a_H) to the unpaired spin population on the adjacent carbon atom (ρ_C).

$$a_H = Q^H_{CH}\rho_C \qquad 1.17$$

The constant Q is different from one situation to another, but when an electron in a p_z orbital on a trigonal carbon atom couples to an adjacent hydrogen, it is about –24G. Applied to aromatic hydrocarbons, where it is particularly easy to generate radical anions and cations, there proves to be a good correlation between coupling constants and the calculated coefficients. The standard ways of generating radicals for ESR measurements involve adding an electron to a molecule or taking one away. In the former case the odd electron is fed into what was the LUMO, and in the latter case the odd electron is left in the HOMO. Since these are the orbitals which appear to be the most important in determining chemical reactivity, it is particularly fortunate that ESR spectroscopy should occasionally give us access to their coefficients.

1.10 Exercises

1. In the discussion about the H_3 molecule, we could have combined the three atoms in a straight line. Show that there would be less bonding both in σ_1 and σ_2* and less antibonding in the σ* orbital.
2. Using Equation 1.12, or by drawing the geometrical equivalent, calculate the coefficients for the frontier orbitals of the heptatrienyl cation.
3. Construct a diagram equivalent to that in Fig. 1.26 to calculate the energies of the frontier orbitals of the heptatrienyl cation.
4. Spiro-aromaticity (Section 1.5.5) is barely detectable. Explain why the spiro cation **1.54**, might have more π stabilisation by spiro conjugation than spiro-heptatriene **1.30**.



1.30 **1.54** **1.31**

5. Using a diagram adapted from that in Fig. 1.41, show that the spirononatetraene **1.31** is spiro-antiaromatic.