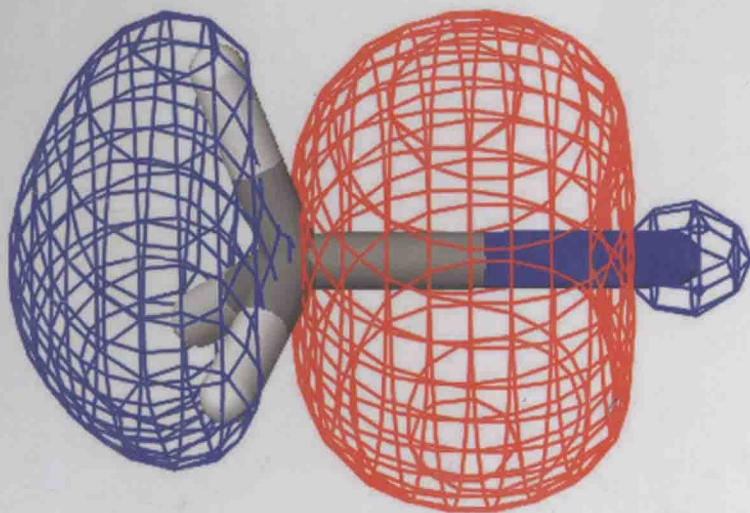


Ian Fleming

Molecular Orbitals  
*and* Organic  
Chemical Reactions

*Reference Edition*



 WILEY

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# Molecular Orbitals and Organic Chemical Reactions

## Reference Edition

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**Ian Fleming**

Department of Chemistry,  
University of Cambridge, UK



 **WILEY**

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# **Molecular Orbitals and Organic Chemical Reactions**

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# Preface

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Molecular orbital theory is used by chemists to describe the arrangement of electrons in chemical structures. It provides a basis for explaining the ground-state shapes of molecules and their many other properties. As a theory of bonding it has largely replaced valence bond theory,<sup>1</sup> but organic chemists still implicitly use valence bond theory whenever they draw resonance structures. Unfortunately, misuse of valence bond theory is not uncommon as this approach remains in the hands largely of the less sophisticated. Organic chemists with a serious interest in understanding and explaining their work usually express their ideas in molecular orbital terms, so much so that it is now an essential component of every organic chemist's skills to have some acquaintance with molecular orbital theory. The problem is to find a level to suit everyone. At one extreme, a few organic chemists with high levels of mathematical skill are happy to use molecular orbital theory, and its computationally more amenable offshoot density functional theory, much as theoreticians do. At the other extreme are the many organic chemists with lower mathematical inclinations, who nevertheless want to understand their reactions at some kind of physical level. It is for these people that I have written this book. In between there are more and more experimental organic chemists carrying out calculations to support their observations, and these people need to know some of the physical basis for what their calculations are doing.<sup>2</sup>

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

Molecular orbital theory is not only a theory of bonding, it is also a theory capable of giving some insight into the forces involved in the making and breaking of chemical bonds—the chemical reactions that are often the focus of an organic chemist's interest. Calculations on transition structures can be carried out with a bewildering array of techniques requiring more or less skill, more or fewer assumptions, and greater or smaller contributions from empirical input, but many of these fail to provide the organic chemist with insight. He or she wants to know what the physical forces are that give the various kinds of selectivity that are so precious in learning how to control organic reactions. The most accessible theory to give this kind of insight is frontier orbital theory, which is based on the perturbation treatment of molecular orbital theory, introduced by Coulson and Longuet-Higgins,<sup>3</sup> and developed and named as frontier orbital theory by Fukui.<sup>4</sup> Earlier theories of reactivity concentrated on the product-like character of transition structures—the concept of localisation energy in aromatic electrophilic substitution is a well-known example. The perturbation theory concentrates instead on the other side of the reaction coordinate. It looks at how the interaction of the molecular orbitals of the starting materials influences the transition structure. Both influences are obviously important, and it is therefore helpful to know about both if we want a better understanding of what factors affect a transition structure, and hence affect chemical reactivity.

Frontier orbital theory is now widely used, with more or less appropriateness, especially by organic chemists, not least because of the success of the predecessor to this book, *Frontier Orbitals and Organic Chemical Reactions*, which survived for more than thirty years as an introduction to the subject for a high proportion of the organic chemists trained in this period. However, there is a problem—computations show

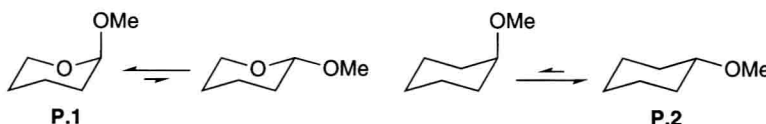
that the frontier orbitals do not make a significantly larger contribution than the sum of all the orbitals. One theoretician put it to me as: 'It has no right to work as well as it does.' The difficulty is that it works as an explanation in many situations where nothing else is immediately compelling.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

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

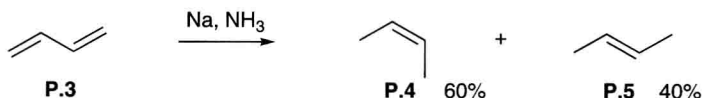
In this book, there is much detailed and not always convincing material, making it less suitable as a textbook for a lecture course; in consequence I have also written a second and shorter book on molecular orbital theory designed specifically for students of organic chemistry, *Molecular Orbitals and Organic Chemistry—The Student Edition*,<sup>5</sup> which serves in a sense as a long awaited second edition to my earlier book. The shorter book uses a selection of the same material as in this volume, with appropriately revised text, but dispenses with most of the references, which can all be found here. The shorter book also has problem sets at the ends of the chapters, whereas this book has the answers to most of them in appropriate places in the text. I hope that everyone can use whichever volume suits them, and that even theoreticians might find unresolved problems in one or another of them.

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

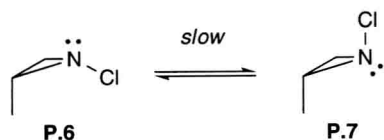
- (i) Why does methyl tetrahydropyranyl ether largely adopt the conformation **P.1**, with the methoxy group axial, whereas methoxycyclohexane adopts largely the conformation **P.2** with the methoxy group equatorial?



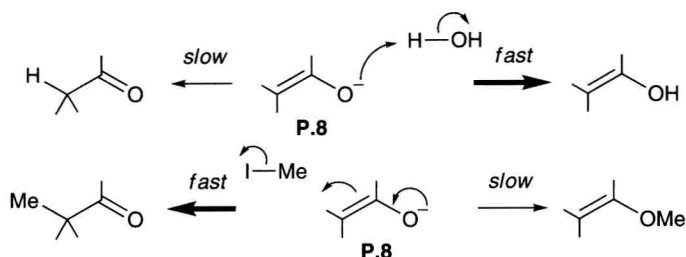
- (ii) Reduction of butadiene **P.3** with sodium in liquid ammonia gives more *cis*-2-butene **P.4** than *trans*-2-butene **P.5**, even though the *trans* isomer is the more stable product.



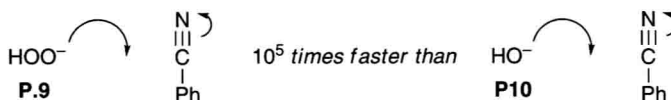
- (iii) Why is the inversion of configuration at nitrogen made slower if the nitrogen is in a small ring, and slower still if it has an electronegative substituent attached to it, so that, with the benefit of both features, an *N*-chloroaziridine can be separated into a pair of diastereoisomers **P.6** and **P.7**?



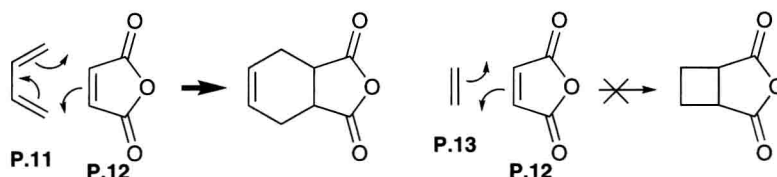
(iv) Why do enolate ions **P.8** react more rapidly with protons on oxygen, but with primary alkyl halides on carbon?



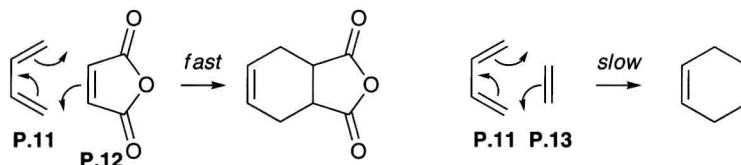
(v) Hydroperoxide ion **P.9** is much less basic than hydroxide ion **P.10**. Why, then, is it so much more nucleophilic?



(vi) Why does butadiene **P.11** react with maleic anhydride **P.12**, but ethylene **P.13** does not?



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



(viii) Why does diazomethane **P.15** add to methyl acrylate **P.16** to give the isomer **P.17** in which the nitrogen end of the dipole is bonded to the carbon atom bearing the methoxycarbonyl group, and not the other way round **P.14**?





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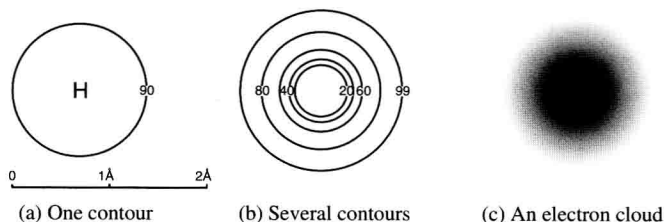
# 1 Molecular Orbital Theory

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## 1.1 The Atomic Orbitals of a Hydrogen Atom

To understand the nature of the simplest chemical bond, that between two hydrogen atoms, we look at the effect on the electron distribution when two atoms are held within bonding distance, but first we need a picture of the hydrogen atoms themselves. Since a hydrogen atom consists of a proton and a single electron, we only need a description of the spatial distribution of that electron. This is usually expressed as a *wave function*  $\phi$ , where  $\phi^2 d\tau$  is the probability of finding the electron in the volume  $d\tau$ , and the integral of  $\phi^2 d\tau$  over the whole of space is 1. The wave function is the underlying mathematical description, and it may be positive or negative; it can even be complex with a real and an imaginary part, but this will not be needed in any of the discussion in this book. Only when squared does it correspond to anything with physical reality—the probability of finding an electron in any given space. Quantum theory<sup>12</sup> gives us a number of permitted wave equations, but the only one that matters here is the lowest in energy, in which the distribution of the electron is described as being in a 1s orbital. This is spherically symmetrical about the nucleus, with a maximum at the centre, and falling off rapidly, so that the probability of finding the electron within a sphere of radius 1.4 Å is 90 % and within 2 Å better than 99%. This orbital is calculated to be 13.60 eV lower in energy than a completely separated electron and proton.

We need pictures to illustrate the electron distribution, and the most common is simply to draw a circle, Fig. 1.1a, which can be thought of as a section through a spherical contour, within which the electron would be found, say, 90 % of the time. This picture will suffice for most of what we need in this book, but it might be worth looking at some others, because the circle alone disguises some features that are worth appreciating. Thus a section showing more contours, Fig. 1.1b, has more detail. Another picture, even less amenable to a quick drawing, is to plot the electron distribution as a section through a cloud, Fig. 1.1c, where one imagines blinking one's eyes a very large number of times, and plotting the points at which the electron was at each blink. This picture contributes to the language often used, in which the electron population in a given volume of space is referred to as the electron density.



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

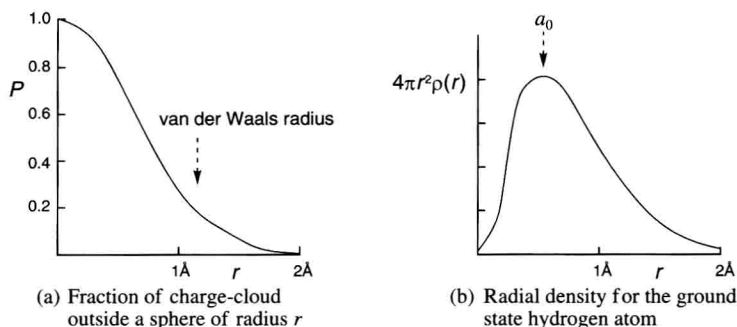


Fig. 1.2 Radial probability plots for the 1s orbital of a hydrogen atom

Taking advantage of the spherical symmetry, we can also plot the fraction of the electron population outside a radius  $r$  against  $r$ , as in Fig. 1.2a, showing the rapid fall off of electron population with distance. The van der Waals radius at  $1.2 \text{ \AA}$  has no theoretical significance—it is an empirical measurement from solid-state structures, being one-half of the distance apart of the hydrogen atom in a C—H bond and the hydrogen atom in the C—H bond of an adjacent molecule.<sup>13</sup> It does not even have a fixed value, but is an average of several measurements. Yet another way to appreciate the electron distribution is to look at the radial density, where we plot the probability of finding the electron between one sphere of radius  $r$  and another of radius  $r + dr$ . This has a revealing form, Fig. 1.2b, with a maximum  $0.529 \text{ \AA}$  from the nucleus, showing that, in spite of the wave function being at a maximum at the nucleus, the chance of finding an electron precisely there is very small. The distance  $0.529 \text{ \AA}$  proves to be the same as the radius calculated for the orbit of an electron in the early but untenable planetary model of a hydrogen atom. It is called the Bohr radius  $a_0$ , and is often used as a unit of length in molecular orbital calculations.

## 1.2 Molecules Made from Hydrogen Atoms

### 1.2.1 The $H_2$ Molecule

To understand the bonding in a hydrogen molecule, we have to see what happens when two hydrogen atoms are close enough for their atomic orbitals to interact. We now have two protons and two nuclei, and even with this small a molecule we cannot expect theory to give us complete solutions. We need a description of the electron distribution over the whole molecule—a molecular orbital. The way the problem is handled is to accept that a first approximation has the two atoms remaining more or less unchanged, so that the description of the molecule will resemble the sum of the two isolated atoms. Thus we combine the two atomic orbitals in a linear combination expressed in Equation 1.1, where the function which describes the new electron distribution, the *molecular orbital*, is called  $\sigma$  and  $\phi_1$  and  $\phi_2$  are the atomic 1s wave functions on atoms 1 and 2.

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

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.

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

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

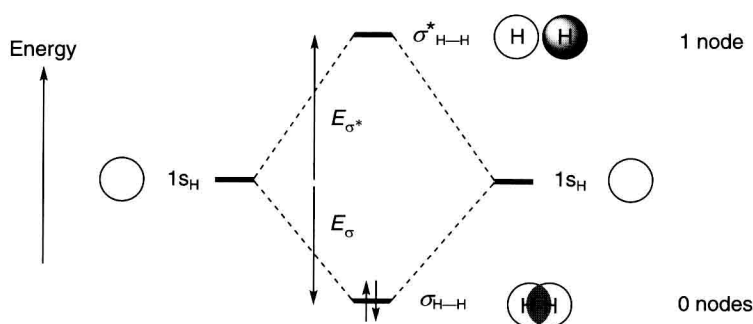
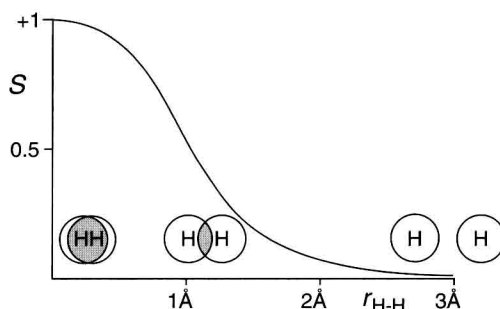


Fig. 1.3 The molecular orbitals of hydrogen

The force holding the two atoms together is obviously dependent upon the extent of the overlap in the bonding orbital. If we bring the two 1s orbitals from a position where there is essentially no overlap at 3 Å through the bonding arrangement to superimposition, the extent of overlap steadily increases. The mathematical description of the overlap is an integral  $S_{12}$  (Equation 1.3) called the *overlap integral*, which, for a pair of 1s orbitals, rises from 0 at infinite separation to 1 at superimposition (Fig. 1.4).

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

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



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

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:

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

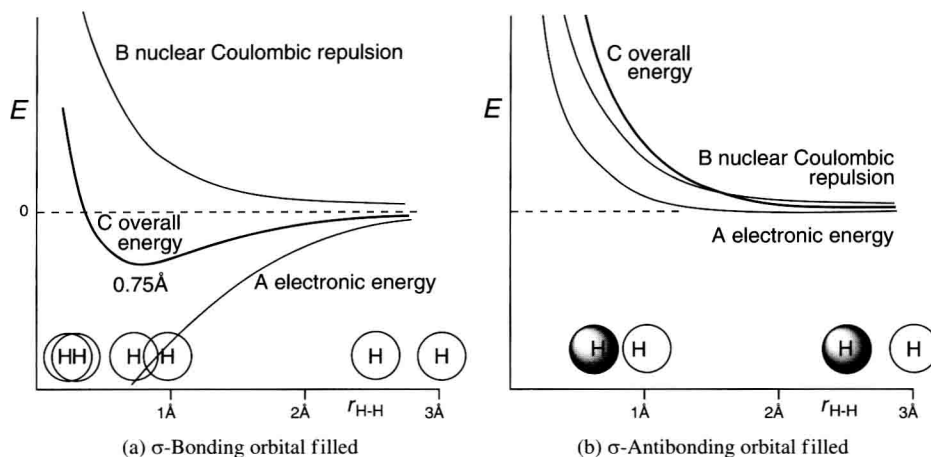
$$E = \frac{\alpha - \beta}{1 - S} \quad 1.5$$

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

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

The overall effect on the energy of the hydrogen molecule relative to that of two separate hydrogen atoms as a function of the internuclear distance is given in Fig. 1.5. If the bonding orbital is filled (Fig. 1.5a), the energy derived from the electronic contribution (Equation 1.4) steadily falls as the two hydrogen atoms are moved from infinity towards one another (curve A). At the same time the nuclei repel each other ever more strongly, and the nuclear contribution to the energy goes steadily up (curve B). The sum of these two is the familiar Morse plot (curve C) for the relationship between internuclear distance and energy, with a minimum at the bond length. If we had filled the antibonding orbital instead (Fig. 1.5b), there would have been no change to curve B. The electronic energy would be given by Equation 1.5 which provides only a little shielding between the separated nuclei giving at first a small curve down for curve A, and even that would change to a repulsion earlier than in the Morse curve. The resultant curve, C, is a steady increase in energy as the nuclei are pushed together. The characteristic of a bonding orbital is that the nuclei are held together, whereas the characteristic of an antibonding orbital, if it were to be filled, is that the nuclei would fly apart unless there are enough compensating filled bonding orbitals. In hydrogen, having both orbitals occupied is overall antibonding, and there is no possibility of compensating for a filled antibonding orbital.





**Fig. 1.5** Electronic attraction, nuclear repulsion and the overall effect as a function of internuclear distance for two  $1s_{\text{H}}$  atoms

We can see from the form of Equations 1.4 and 1.5 that the term  $\alpha$  relates to the energy levels of the isolated atoms labelled  $1s_{\text{H}}$  in Fig. 1.3, and the term  $\beta$  to the drop in energy labelled  $E_{\sigma}$  (and the rise labelled  $E_{\sigma^*}$ ). Equations 1.4 and 1.5 show that, since the denominator in the bonding combination is  $1 + S$  and the denominator in the antibonding combination is  $1 - S$ , the bonding orbital is not as much lowered in energy as the antibonding is raised. In addition, putting *two* electrons into a bonding orbital does not achieve exactly twice the energy-lowering of putting *one* electron into it. We are *allowed* to put two electrons into the one orbital if they have opposite spins, but they still repel each other, because they have to share the same space; consequently, in forcing a second electron into the  $\sigma$  orbital, we lose some of the bonding we might otherwise have gained. For this reason too, the value of  $E_{\sigma}$  in Fig. 1.3 is smaller than that of  $E_{\sigma^*}$ . This is why two helium atoms do not combine to form an  $\text{He}_2$  molecule. There are four electrons in two helium atoms, two of which would go into the  $\sigma$ -bonding orbital in an  $\text{He}_2$  molecule and two into the  $\sigma^*$ -antibonding orbital. Since  $2E_{\sigma^*}$  is greater than  $2E_{\sigma}$ , we would need extra energy to keep the two helium atoms together.

Two electrons in the same orbital can keep out of each other's way, with one electron on one side of the orbital, while the other is on the other side most of the time, and so the energetic penalty for having a second electron in the orbital is not large. This synchronisation of the electrons' movements is referred to as *electron correlation*. The energy-raising effect of the repulsion of one electron by the other is automatically included in calculations based on Equations 1.4 and 1.5, but each electron is treated as having an average distribution with respect to the other. The effect of electron correlation is often not included, without much penalty in accuracy, but when it is included the calculation is described as being with *configuration interaction*, a bit of fine tuning sometimes added to a careful calculation.

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

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

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