THE MOLECULAR-ORBITAL AND EQUIVALENT-ORBITAL APPROACH TO MOLECULAR STRUCTURE

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Introduction

The electronic theory of chemical valency has to explain a set of facts and empirical rules some of which suggest an interpretation in terms of localised electrons and others require a picture of electrons spread throughout the whole molecule. In the pre-electronic era a chemical bond was regarded as a genuinely local link joining neighbouring atoms in a molecule, and this was associated with a pair of bonding electrons in the early electronic theory developed by Lewis and Langmuir. In accounting for all the electrons some were assigned to atomic inner shells and others were supposed to form inert pairs (or " lone pairs ") on a single atom. The rules of stereochemistry implied certain restrictions about the geometrical arrangement of neighbouring bonds, but, apart from this, there seemed to be considerable evidence that the pairs of electrons in different bonds behaved independently to a large extent. For a great many molecules it was found possible to interpret heats of formation on the assumption that there was a definite energy associated with each type of bond (the bond energy). The refractivity of a large molecule can usually be predicted by assuming that the total is a sum of standard contributions from the various atoms and bonds. Similar additive laws also hold for magnetic susceptibilities. All these facts, which imply the existence of a standard type of bond between two given atoms, are best interpreted in terms of a theory in which a pair of electrons is moving in localised orbits in each bond and is mainly independent of electron pairs in neighbouring bonds.

On the other hand, there are properties of molecules which do not seem to fit this picture. Consider the ionisation of (removal of an electron from) a simple molecule. According to the localised picture, we might expect this process to consist of the removal of an electron from one of the bonds, or possibly from one of the lone pairs. However, in the case of a molecule such as methane, where there are several bonds exactly equivalent to one another, there are various possibilities. There is no *a priori* reason why the electron should be removed from one bond rather than another and, in such circumstances, what actually happens is that the electron is removed partly from them all, or, an equivalent statement, the electron which is removed was moving in an orbit or path extending over the whole molecule. Similar situations arise when we consider the electronic excitation of a molecule. Methane being taken as an example again, instead of exciting the electrons in a single bond, an electron is taken out of one orbit spread over the whole molecule and placed in another excited orbit. It seems, therefore, that in order to interpret spectroscopic properties of molecules such as methane, we ought to treat the electrons as moving in orbits extending over the whole molecule, processes such as ionisation and excitation corresponding to the removal or reallocation of electrons among these paths. Such a procedure is, in fact, a logical extension of the ideas originally used by spectroscopists to interpret atomic spectral lines and it has since proved its value in the theory of the electronic spectra of molecules.

It appears, then, that there are two apparently divergent modes of description of molecular structure, localised electrons in bonds and lone-pair orbits on the one hand and electrons moving in orbits covering the whole molecular framework on the other. But the success of both descriptions in their respective fields of application is so considerable that the two must be more closely related than appears at first sight. When we consider the general quantum-mechanical problem of finding the distribution of electrons in a molecule we find that this is so and that the localised and delocalised pictures are just two different ways of breaking down the same total wave function describing the combined motion of all electrons. The purpose of this Review is to elaborate this transformation and show how it links together alternative descriptions of certain simple molecules.

To do this we begin by considering the general properties that the wave function for the electrons in a molecule must possess. If we consider only one electron moving in the electrostatic field of the nuclei, then it is quite clear that its path or orbital must extend over the whole nuclear framework. Thus the electron in the hydrogen molecule-ion, H_2^+, is equally distributed around both nuclei. When we come to systems of several electrons, however, we also have to take into account the indistinguishability of electrons and, further, the all-important antisymmetry property of the wave-function. The way in which this is incorporated into the molecular-orbital theory is discussed in the next section and its consequences are then illustrated in terms of a simple one-dimensional model. In the remaining sections the transformation between the localised and delocalised descriptions is carried out for certain simple molecules. In this way we can see the relation between the bonding- and antibonding-orbital picture of a diatomic molecule such as F_2 and the alternative description in terms of lone pairs. The relation between the σ–π and the two-bent-bond descriptions of the standard carbon double bond in ethylene also becomes apparent. Similarly a triple bond, as in nitrogen or acetylene, can be regarded as three equivalent bent bonds or as a σ bond and two π bonds.

Quantum-mechanical basis of orbital theories

The basic quantum-mechanical problem is to formulate the wave-like description of an electron moving in the electrostatic field of the nuclei and other electrons. If the potential energy of an electron at a point (x, y, z) is $V(x, y, z)$, this is accomplished by solving the well-known Schrödinger equation for a wave function $\psi(x, y, z)$

$$-\frac{\boldsymbol{h}^2}{8\pi^2\boldsymbol{m}}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V(x, y, z)\psi = E\psi \quad . \quad . \quad (1)$$

where E is the energy of the electron and $\boldsymbol{h}$ and $\boldsymbol{m}$ are Planck's constant and the electronic mass respectively. (For many-electron systems some care has to be taken in obtaining the potential energy V for which a knowledge of other electron distributions is required. The calculations have to be made self-consistent. The details are not relevant to the present topic, however, and we shall not go into them.) The function ψ which depends on the co-ordinates (x, y, z) of the electron in space will be referred to as a *space orbital* or often just as an *orbital.* Its physical interpretation is that $\psi^2 \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z$ represents the probability that the electron will be found in a small rectangular element of volume $\mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z$ near the point (x, y, z). Thus ψ^2 is a probability density and the electron is most likely to be found where this density has its largest value.

The other important property of an electron that must be specified besides its spatial distribution is its spin. According to quantum-mechanical arguments, into which we need not go in detail, each electron has a spin which can take one of two values. It is convenient to include this description in the wave function by defining α and β so that $\alpha = 1$ if the spin is in one direction and $\alpha = 0$ if it is in the other. β is defined in a complementary manner. Thus the electron moving in an orbital $\psi(x, y, z)$ may be associated with two functions $\psi(x, y, z)\alpha$ and $\psi(x, y, z)\beta$ according to the direction of its spin. A function such as $\psi(x, y, z)\alpha$ which gives the probability distribution of the spin co-ordinate as well as that of its spatial co-ordinates is sometimes referred to as a *spin orbital.*

All this is very straightforward if we are dealing with a system which contains only one electron such as the hydrogen atom or the hydrogen molecule-ion $H_2{}^+$. But when we consider a many-electron molecule we are faced with the problem of combining the orbitals for the individual electrons into a total wave function for the whole system. Suppose we are dealing with two electrons which occupy space orbitals ψ_1 and ψ_2. The simplest compound wave function for both electrons is the product

$$\Psi_{\text{product}} = \psi_1(x_1, y_1, z_1)\psi_2(x_2, y_2, z_2) \quad . \quad . \quad . \quad (2)$$

where (x_1, y_1, z_1) and (x_2, y_2, z_2) are the Cartesian co-ordinates of electrons 1 and 2 respectively. To be complete this should be multiplied by one of the four possible spin functions $\alpha(1)\alpha(2)$, $\alpha(1)\beta(2)$, $\alpha(2)\beta(1)$, or $\beta(1)\beta(2)$. The physical interpretation of this compound wave function is again in terms of probability. Ψ^2 is now proportional to the joint probability of electron 1 being at position (x_1, y_1, z_1) and electron 2 at position (x_2, y_2, z_2) *simultaneously.* If the product form is used this is just the product of the two separate probabilities. Thus the product wave function implies that the two electrons move independently of one another.

Product wave functions can clearly be constructed for any number of electrons. Early wave functions were constructed on this basis together with the empirical rule that not more than two electrons could be assigned to a single orbital, one of each spin. Further, electrons tend to occupy the orbitals with lowest possible energy in the absence of other factors.

The major disadvantage of the product function is that it fails to satisfy another important quantum-mechanical principle, namely that of antisymmetry. This is really a consequence of the indistinguishability of electrons. If we consider the operation of interchanging the positions of two electrons the probability of the new configuration must be just the same as previously. Thus the square of the total wave function must be unaltered, and consequently the wave function itself can only be multiplied by $+1$ or by -1. It is found that the second choice is demanded for electrons so that we formulate the antisymmetry principle by requiring that the wave function changes sign if we interchange the co-ordinates of any two electrons. Clearly the product function (2) does not satisfy this condition, for if we interchange the co-ordinates of electrons 1 and 2 we obtain $\psi_1(x_2, y_2, z_2)\psi_2(x_1, y_1, z_1)$ which is not a direct multiple of its previous form.

The next step is to construct a wave function from products of the type (2) which satisfies this further condition. This can be done in terms of what is called an *antisymmetrised product.* Let us consider, first of all, the case of two electrons in the same space orbital ψ_1 with two different spins. The simple product function is

$$\psi_1(x_1, y_1, z_1)\psi_1(x_2, y_2, z_2)\alpha(1)\beta(2) \quad . \quad . \quad . \quad (3)$$

The antisymmetrised product is obtained by subtracting from this the corresponding product with the suffixes 1 and 2 interchanged. This gives

$$(1/\sqrt{2})\psi_1(x_1, y_1, z_1)\psi_1(x_2, y_2, z_2)\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\} \quad . \quad . \quad (4)$$

The factor $(1/\sqrt{2})$ is inserted so that the total probability added over all configurations is unity. This function may be said to be symmetric in the space co-ordinates but antisymmetric in the spins. For an overall interchange it is antisymmetric.

Next, suppose we have two electrons in different space orbitals ψ_1 and ψ_2 but with the same spin α. Then the simple product function is

$$\psi_1(x_1, y_1, z_1)\psi_2(x_2, y_2, z_2)\alpha(1)\alpha(2) \quad . \quad . \quad . \quad (5)$$

and the antisymmetrised product constructed in the same way is

$$(1/\sqrt{2})\{\psi_1(x_1, y_1, z_1)\psi_2(x_2, y_2, z_2) - \psi_1(x_2, y_2, z_2)\psi_2(x_1, y_1, z_1)\}\alpha(1)\alpha(2) \quad (6)$$

Both the antisymmetric functions (4) and (6) can be written as 2×2 determinants. Thus (4) is

$$\frac{1}{\sqrt{2}}\begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(2)\alpha(2) \\ \psi_1(1)\beta(1) & \psi_1(2)\beta(2) \end{vmatrix} \quad . \quad . \quad . \quad . \quad (7)$$

and (6) is

$$\frac{1}{\sqrt{2}}\begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(2)\alpha(2) \\ \psi_2(1)\alpha(1) & \psi_2(2)\alpha(2) \end{vmatrix} \quad . \quad . \quad . \quad . \quad (8)$$

Here we have written $\psi_1(1)$ as a short form of $\psi_1(x_1, y_1, z_1)$.

These simple determinantal functions for two electrons suggest that we can construct antisymmetric wave functions for any number of electrons in a similar manner. Thus if we have a set of orbitals $\psi_1, \psi_2 \ . \ . \ . \ \psi_n$ each containing two electrons, one of each spin (this applies to most molecules), an antisymmetric wave function can be constructed as a determinant with a different spin orbital in each row.

$$\Psi = \sqrt{\frac{1}{(2n)!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(2)\alpha(2) & \ldots & \psi_1(2n)\alpha(2n) \\ \psi_1(1)\beta(1) & \psi_1(2)\beta(2) & \ldots & \\ \psi_2(1)\alpha(1) & \psi_2(2)\alpha(2) & \ldots & \\ \cdot & \cdot & \cdots & \cdot \\ \psi_n(1)\beta(1) & \psi_n(2)\beta(2) & \ldots & \psi_n(2n)\beta(2n) \end{vmatrix} \quad . \quad . \quad (9)$$

The interchange of the co-ordinates and spins of two electrons corresponds to interchanging two columns of this determinant. This leads to a change of sign, so that the antisymmetry property is satisfied. This type of total wave function is that used in molecular-orbital theory.

Another well-known property of determinants is that they vanish if they have two identical rows. This means that it is not possible to construct a non-vanishing antisymmetrised product in which two electrons in the same orbital have the same spin. Thus the rule that not more than two electrons must be assigned to any one space orbital follows as a direct consequence of the antisymmetry principle ; for product wave functions it had to be introduced as an extra postulate.

Another important physical interpretation of the molecular-orbital determinant follows from an application of a similar argument to the columns. The elements of two columns become identical if two electrons have the same spin (α or β) and are at the same point (x, y, z). The determinant then vanishes and consequently the probability of such a configuration is zero. Such an argument does not apply to electrons of different spin, however. The antisymmetry principle operates, therefore, in such a way that electrons of the same spin are kept apart. We shall see in later sections that this is an important factor in determining stereochemical valence properties.

The antisymmetry principle is also of great importance in understanding the dualism between localised and delocalised descriptions of electronic structure. We shall see that these are just different ways of building up the same total determinantal wave functions.[1] This can be developed mathematically from general properties of determinants, but a clearer picture can be formed if we make a detailed study of the antisymmetric wave function for some highly simplified model systems.

Simple models illustrating the effects of antisymmetry

The simplest system that can be used for illustrative purposes is one in which electrons are free to move in one dimension along a wire of length l. The potential energy will be constant and can be taken as zero. If the position of a point on the wire is measured by the distance x from one end, the Schrödinger equation is

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} = E\psi \quad . \quad . \quad . \quad . \quad (10)$$

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[1] Lennard-Jones, *Proc. Roy. Soc.*, 1949, *A*, **198,** 1, 14.

where E is the energy. This is just the simple harmonic equation which has the general solution

$$\psi = A \sin\left\{\sqrt{\left(\frac{8\pi^2 mE}{h^2}\right)}x\right\} + B \cos\left\{\sqrt{\left(\frac{8\pi^2 mE}{h^2}\right)}x\right\} . \quad . \quad (11)$$

where A and B are constants of integration. The wave function must also satisfy the boundary conditions of being zero at both ends (that is at $x = 0$ and $x = l$). The first condition requires that $B = 0$ and the second that $\sqrt{(8\pi^2 mE/h^2)}l$ is an integral multiple of π. The lowest orbitals that electrons can occupy (those with least nodes) are therefore

$$\psi_1 = \sqrt{(2/l)} \sin(\pi x/l)$$
$$\psi_2 = \sqrt{(2/l)} \sin(2\pi x/l) \quad . \quad . \quad . \quad . \quad (12)$$

ψ_1 is positive over the whole length of the segment while ψ_2 is zero at the centre of the wire (Fig. 1).

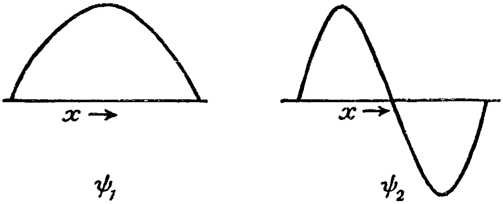

FIG. 1

Lowest occupied molecular orbitals in model system.

Now suppose two electrons are placed one in each of these orbitals. The distribution of these electrons in their individual orbitals will simply be given by ψ_1^2 and ψ_2^2. If we wish to examine the probability of various simultaneous positions of the two electrons, we have to consider the total wave function Ψ, which will be an antisymmetric product with a form depending on the spins of the electrons. If we wish to investigate the effect of the antisymmetry principle on the spatial arrangement of the electrons, it is convenient to examine the case in which they both have the same spin α. Then the wave function will be of the form given in equations (6) and (8). If the factor $\alpha(1)\alpha(2)$ is omitted,

$$\Psi = \begin{vmatrix} \psi_1(1) & \psi_1(2) \\ \psi_2(1) & \psi_2(2) \end{vmatrix} = (2/l)\{\sin(\pi x_1/l)\sin(2\pi x_2/l) - \sin(\pi x_2/l)\sin(2\pi x_1/l)\}$$
$$= (4/l)\sin(\pi x_1/l)\sin(\pi x_2/l)\{\cos(\pi x_1/l) - \cos(\pi x_2/l)\} \quad . \quad . \quad (13)$$

Ψ^2 is then proportional to the probability of electron 1 being found at position x_1 and electron 2 at x_2. The significant points to be noted are (1) that if $x_1 = x_2$ the wave function vanishes so that the configuration has zero probability and (2) that there are two equivalent most probable configurations in which the electrons are in different halves of the wire. These two configurations differ only in the numbering of the electrons and are otherwise indistinguishable.

The effect of using antisymmetrised wave function instead of an ordinary product, therefore, is to cause the electrons to move in two different regions in the two halves of the segment, the probability of configurations in which both are in the same segment at the same instant being relatively small. This suggests that the system could be alternatively described in terms of two localised orbitals, one in either segment with one electron in each.

This alternative description in terms of localised orbitals can indeed be set up by taking linear combinations of the orbitals ψ_1 and ψ_2 and using these in the determinant instead. If the linear combinations are suitably chosen, the value of the determinant is unaltered, although the individual rows change. Let us consider, therefore, how we can construct localised orbitals from our two starting orbitals ψ_1 and ψ_2. As we have already noted, ψ_1 is positive everywhere while ψ_2 is positive in the left-hand part of the segment and negative in the right. If we consider $\psi_1 + \psi_2$, the two components will add on the left, but partly cancel on the right. This, therefore, can be used as a localised orbital mainly concentrated in the left-hand part. Similarly $\psi_1 - \psi_2$ is mainly concentrated on the right. We therefore define two new localised orbitals χ_a and χ_b by

$$\begin{aligned} \chi_a &= (\psi_1 + \psi_2)/\sqrt{2} = \sqrt{(4/l)} \cos (\pi x/2l) \sin (3\pi x/2l) \\ \chi_b &= (\psi_1 - \psi_2)/\sqrt{2} = \sqrt{(4/l)} \sin (\pi x/2l) \cos (3\pi x/2l) \end{aligned} \quad . \quad . \quad (14)$$

The factor $(1/\sqrt{2})$ is included to keep the total probability equal to unity. These functions are illustrated in Fig. 2. They are mirror images in the mid-point of the line-segment. They are sometimes called *equivalent orbitals*.[1, 2]

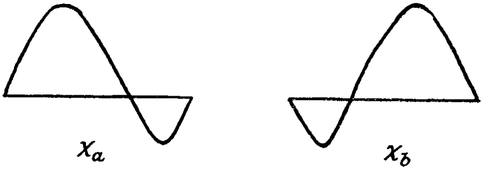

FIG. 2
Equivalent orbitals in model system.

The total wave function can now be written in terms of the equivalent orbitals

$$\Psi = - \begin{vmatrix} \chi_a(1) & \chi_a(2) \\ \chi_b(1) & \chi_b(2) \end{vmatrix} \quad . \quad . \quad . \quad . \quad (15)$$

If we substitute for χ_a and χ_b and expand the expression, it is easily confirmed that the value of this determinant is identical with the original total wave function (13). This is a particular example of what is known as an orthogonal transformation of the rows of the determinant.

It appears, therefore, that we have two possible descriptions of this system. We can describe it as two electrons, each of which occupies one of the delocalised (or molecular) orbitals which are solutions of the

[2] Lennard-Jones and Pople, *Proc. Roy. Soc.*, 1950, *A*, **202,** 166.

Schrödinger equation. Or alternatively, we may say, equally accurately, that the two electrons occupy two localised orbitals χ_a and χ_b, one at each end of the segment. These are just two different ways of interpreting the same total wave function.

The two descriptions are useful in rather different contexts. If we are interested in the relative positions of the two electrons, then the interpretation in terms of localised orbitals gives a clearer description of the qualitative features of the overall probability distribution. On the other hand, if we are interested in the removal of an electron, the first description is more appropriate, for the remaining electron must occupy an orbital which is a solution of the original Schrödinger equation. Thus the electron must be removed from ψ_1 or ψ_2.

This sort of model can easily be generalised to deal with more than two electrons and other assignments of the spins. The case of most interest in molecular studies is that in which a set of molecular orbitals are all occupied by two electrons. Thus if there were two electrons, one of either spin, in both orbitals ψ_1 and ψ_2, the total wave function would be a 4 × 4 determinant. But most of the features of the two-electron model are retained. The system could be alternatively described as consisting of two electrons in each of the equivalent orbitals. The effect of the antisymmetry principle is then to keep electrons of the same spin apart, the motion of the two opposite spin-types being uncorrelated.

Although the one-dimensional model bears little resemblance to any real molecular system, many of its features carry over to cases of practical interest. Suppose we consider three-dimensional motion in a central field as in atoms. The orbitals or single-electron functions now become atomic orbitals and can be classified in the usual manner as 1*s*, 2*s*, . . . 2*p*, 3*p*, . . . 3*d*, . . . Suppose we are dealing with an atom in which there are two electrons of the same spin (α, say) occupying the 2*s* and 2*p* orbitals (inner shells being ignored for the present). Then the antisymmetric product function is

$$\Psi = \begin{vmatrix} \psi_{2s}(1) & \psi_{2s}(2) \\ \psi_{2p}(1) & \psi_{2p}(2) \end{vmatrix} \alpha(1)\alpha(2) \qquad . \quad . \quad . \ (16)$$

This wave function has many features in common with that of the previous model. While ψ_{2s} is spherically symmetric, ψ_{2p} has a nodal plane through the centre of symmetry. A similar transformation can be applied and we can use two equivalent orbitals

$$\begin{aligned} \chi_1 &= \sqrt{(1/2)}(\psi_{2s} + \psi_{2p}) \\ \chi_2 &= \sqrt{(1/2)}(\psi_{2s} - \psi_{2p}) \end{aligned} \qquad . \quad . \quad . \ (17)$$

Atomic orbitals of this mixed type are usually referred to as hybrids (or more specifically digonal *s–p* hydrids). As with the one-dimensional model, they reinforce on one side of the nucleus and partly cancel on the other. Hence the transformation is from the delocalised *s* and *p* description to a description in terms of two equivalent orbitals, localised on opposite sides of the nucleus. Again a similar transformation may be applied to a 4 × 4 determinant describing a system with two electrons in each of these orbitals.

For the next example, consider a system of three electrons of the same spin occupying atomic orbitals $2s$, $2px$, and $2py$. Here the antisymmetric wave function is

$$\Psi = \begin{vmatrix} \psi_{2s}(1) & \psi_{2s}(2) & \psi_{2s}(3) \\ \psi_{2px}(1) & \psi_{2px}(2) & \psi_{2px}(3) \\ \psi_{2py}(1) & \psi_{2py}(2) & \psi_{2py}(3) \end{vmatrix} \alpha(1)\alpha(2)\alpha(3) \quad . \qquad (18)$$

In this case we can transform these into three equivalent orbitals which are s–p hybrids (called trigonal hybrids) pointing towards the vertices of an equilateral triangle, so that the angle between neighbouring directions is 120°. The actual transformation is

$$\begin{aligned} \chi_1 &= \sqrt{(1/3)}\psi_{2s} + \sqrt{(2/3)}\psi_{2px} \\ \chi_2 &= \sqrt{(1/3)}\psi_{2s} - \sqrt{(1/6)}\psi_{2px} + \sqrt{(1/2)}\psi_{2py} \\ \chi_3 &= \sqrt{(1/3)}\psi_{2s} - \sqrt{(1/6)}\psi_{2px} - \sqrt{(1/2)}\psi_{2py} \end{aligned} \quad . \quad . \quad (19)$$

It is not immediately clear from the form in which these are written that they are equivalent functions, that is, differ only in their orientation, but it is easily confirmed that they do transform into each other if the axes are rotated through 120°. Again it can be shown that the determinant of χ-functions has the same value as (18). One other point about this set of equivalent orbitals is that there appears to be no preferential direction in which any one of the vertices of this triangle may be chosen. The choice is, in fact, arbitrary and any set of three equivalent directions perpendicular to the z direction would suffice. This only applies for an atomic wave function, of course. In molecules (such as planar XY_3) there may be a preferred choice of axes on account of symmetry. This will be clear from some examples considered in the next section.

The case of four electrons in the atomic orbitals $2s$, $2px$, $2py$, and $2pz$ can be handled in a similar manner. Here we can transform the expression into four equivalent orbitals given by

$$\begin{aligned} \chi_1 &= \tfrac{1}{2}(\psi_{2s} + \psi_{2px} + \psi_{2py} + \psi_{2pz}) \\ \chi_2 &= \tfrac{1}{2}(\psi_{2s} + \psi_{2px} - \psi_{2py} - \psi_{2pz}) \\ \chi_3 &= \tfrac{1}{2}(\psi_{2s} - \psi_{2px} + \psi_{2py} - \psi_{2pz}) \\ \chi_4 &= \tfrac{1}{2}(\psi_{2s} - \psi_{2px} - \psi_{2py} + \psi_{2pz}) \end{aligned} \quad . \quad . \quad . \quad (20)$$

which are directed towards the vertices of a regular tetrahedron. These equivalent orbitals are usually called tetrahedral s–p hybrids. If we have eight electrons (two of each spin in each orbital) this description can be applied directly to the outermost shell of electrons in the neon atom. The neon atom is not usually described in terms of localised tetrahedral orbitals, but such a description is just as valid as the more conventional s^2p^6. We shall see in the next section that the localised picture is useful in discussing the structure of molecules isoelectronic with neon.

The orbital description of molecules

We now turn to the description of actual molecules in terms of molecular orbitals. The usual procedure is to find orbital functions ψ_1, ψ_2, . . . which are solutions of a suitable Schrödinger equation, assign the electrons in pairs to those orbitals of lowest energy, and then construct an antisymmetric determinantal wave function [as in eqn. (9)]. We can then consider possible alternative descriptions obtained by transformations of the rows of the determinant as with the models of the previous section.

In the complex electrostatic field of a molecule, it is usually impracticable to obtain accurate molecular orbitals, so it is customary to express them approximately as linear combinations of atomic orbitals belonging to the constituent atoms. This is called the " linear combination of atomic orbital " or LCAO form. Although they are only approximate, the LCAO functions do show most of the properties of the precise orbitals. Both molecular and localised equivalent orbitals can be expressed in this manner.

Diatomic Molecules.—We shall begin by discussing diatomic molecules, which bear some relation to the models discussed in the previous section. To begin with, the hydrogen molecule has two electrons which both occupy the lowest molecular orbital whose LCAO form is

$$\psi_1 = \lambda(1s_A + 1s_B) \quad . \quad . \quad . \quad . \quad (21)$$

$1s_A$ and $1s_B$ are the two hydrogen $1s$ atomic orbitals. The factor λ is introduced so that the total probability adds up to unity. If the overlap between the atomic orbitals is small, λ is approximately $1/\sqrt{2}$. Since there is only one space orbital in the determinantal wave function [eqn. (7)] no transformation of the orbitals is possible.

If we now go to a pair of interacting helium atoms, there will be four electrons of which the first pair will go into the corresponding orbital ψ_1 and the second pair into the next lowest orbital for the system whose LCAO form will be

$$\psi_2 = \mu(1s_A - 1s_B) \quad . \quad . \quad . \quad . \quad (22)$$

This function is zero for all points equidistant from the two nuclei (that is, it has a nodal plane). The orbital ψ_1 is large in the region between the nuclei (where $1s_A$ and $1s_B$ overlap and the electrostatic potential is low) and is generally referred to as a *bonding* orbital. Similarly, ψ_2, which keeps its electron away from the internuclear region, is *antibonding*. The two functions ψ_1 and ψ_2 are analogous to the symmetric and antisymmetric orbitals for the one-dimensional model. A similar transformation can be applied and two equivalent orbitals constructed. These are

$$\begin{aligned} \chi_A &= (1/\sqrt{2})(\psi_1 + \psi_2) = (1/\sqrt{2})(\lambda + \mu)1s_A + (1/\sqrt{2})(\lambda - \mu)1s_B \\ \chi_B &= (1/\sqrt{2})(\psi_1 - \psi_2) = -(1/\sqrt{2})(\lambda - \mu)1s_A + (1/\sqrt{2})(\lambda + \mu)1s_B \end{aligned} \quad . \quad (23)$$

If the overlap of the functions is not large, λ and μ are both nearly $1/\sqrt{2}$ and so the equivalent orbitals approximate to the atomic orbitals for the isolated atoms. The complete equivalence of the two configurations $\psi^2_{\text{bonding}}\psi^2_{\text{antibonding}}$ and $\chi_A{}^2\chi_B{}^2$ is the simplest example of the dual description of a molecular system.

Proceeding further along the series of homonuclear diatomic molecules, the $1s$ inner shells can still be described in either manner. Since the $1s$

electrons do not play any appreciable part in bonding, it is usually most convenient to treat them as localised. The lithium molecule Li_2 can be described in terms of a pair of inner shells and a bonding orbital which is similar to that in H_2. There is a difference, however, in that there is now a possibility of appreciable hybridisation between the $2s$ and $2p$ atomic orbitals which have comparable energies. The best LCAO representation of the bonding orbital will be a sum of two hybrid orbitals of the form

$$\alpha(2s) + \beta(2p\sigma)$$

where $2p\sigma$ represents an atomic $2p$ orbital with its axis along the internuclear line. Again, since this is the only occupied orbital formed from valence shell atomic orbitals, no transformation to localised orbitals is possible.

Proceeding further along the Periodic Table, let us next consider the nitrogen molecule N_2. Here we have to consider molecular orbitals constructed from all the $2p$ functions for each atom. (The $2p$ orbitals with axes perpendicular to the molecular axis are usually called $2p\pi$ functions.) To begin with, four electrons are assigned to the inner shells, represented by equivalent orbitals $1s_A$ and $1s_B$. Secondly, there will be two molecular orbitals, bonding and antibonding, formed from the next s orbitals, $2s_A$ and $2s_B$. These can be transformed into two equivalent orbitals in a similar manner and correspond to lone-pair or inert electrons. Then there will be a bonding orbital formed from $2p\sigma$ functions

$$\psi_{\sigma\text{-bonding}} = (1/\sqrt{2})(2p\sigma_A + 2p\sigma_B) \quad . \quad . \quad . \quad (24)$$

and two bonding orbitals whose LCAO forms are sums of the $2p\pi$ atomic orbitals

$$\left.\begin{aligned} \psi_{\pi x\text{-bonding}} &= (1\sqrt{2})(2p\pi x_A + 2p\pi x_B) \\ \psi_{\pi y\text{-bonding}} &= (1/\sqrt{2})(2p\pi y_A + 2p\pi y_B) \end{aligned}\right\} \quad . \quad . \quad . \quad (25)$$

If two electrons are assigned to each of these orbitals, all fourteen in the molecule are accounted for. This set of orbitals would be slightly modified if hybridisation between the $2s$ and $2p\sigma$ electrons is allowed.

This description of the triple bond represents it as an axially symmetric σ bond together with two perpendicular π bonds. This is appropriate for spectroscopy and must be used if we are discussing excited N_2 or $N_2{}^+$. But for N_2 in its ground state, another description in terms of three equivalent bonding orbitals can be obtained by applying the trigonal transformation to (24) and (25). Thus if we write

$$\begin{aligned} \chi_{1\text{-bonding}} &= \frac{1}{\sqrt{3}}\psi_{\sigma\text{-bonding}} + \frac{\sqrt{2}}{\sqrt{3}}\psi_{\pi x\text{-bonding}} \\ \chi_{2\text{-bonding}} &= \frac{1}{\sqrt{3}}\psi_{\sigma\text{-bonding}} + \frac{1}{\sqrt{6}}\psi_{\pi x\text{-bonding}} + \frac{1}{\sqrt{2}}\psi_{\pi y\text{-bonding}} \quad . \quad (26) \\ \chi_{3\text{-bonding}} &= \frac{1}{\sqrt{3}}\psi_{\sigma\text{-bonding}} + \frac{1}{\sqrt{6}}\psi_{\pi x\text{-bonding}} - \frac{1}{\sqrt{2}}\psi_{\pi y\text{-bonding}} \end{aligned}$$

the three new orbitals will be turned into one another by a rotation through 120° about the axis of the molecule. They represent three bent bonds concentrated in three different azimuthal planes. If we square the orbitals and add to get the total electron density

$$\rho = (\chi_{1\text{-bonding}})^2 + (\chi_{2\text{-bonding}})^2 + (\chi_{3\text{-bonding}})^2$$

this is found to be axially symmetric. Nevertheless, the existence of the three equivalent orbitals implies that the pairs of electrons dispose themselves relative to each other in such a way that their distributions are similar and interrelated by a 120° rotation.

Although the nitrogen molecule represents the standard type of triple bond, the bond in O_2 is in no way typical of a double bond. There are two extra electrons and the next orbitals to be filled are the antibonding π orbitals

$$\left.\begin{aligned}\psi_{\pi x\text{-antibonding}} &= (1/\sqrt{2})(2p\pi x_{\mathrm{A}} - 2p\pi x_{\mathrm{B}})\\ \psi_{\pi y\text{-antibonding}} &= (1/\sqrt{2})(2p\pi y_{\mathrm{A}} - 2p\pi y_{\mathrm{B}})\end{aligned}\right\} \quad . \quad . \quad . \quad (27)$$

These both have the same energy so that, in the absence of other determining factors, the electrons go one into each with the same spin (or an equivalent state). This means that they are kept apart by the antisymmetry principle and so the energy is lowered by the reduction of Coulomb repulsion. In this rather exceptional case, therefore, the orbitals are not all doubly occupied and we cannot carry out any simple transformation into localised orbitals.

If we now proceed further to the fluorine molecule, both the π-antibonding orbitals will be doubly occupied. As with the *s* functions, the configuration $(\psi_{\pi x\text{-bonding}})^2(\psi_{\pi x\text{-antibonding}})^2$ can be transformed into two π-lone-pair orbitals, one on each atom. Similarly with the πy orbitals. The localised description of F_2, therefore, has four localised π-lone-pairs, there being only one single bonding orbital.

Molecules Isoelectronic with Neon.—Another set of molecules whose structure is typical of many standard chemical environments is the set of ten-electron first row hydrides Ne, HF, H_2O, NH_3, and CH_4. On p. 281 we saw how the outer electrons of the neon atom could be described either as being in the configuration $(2s)^2(2p)^6$ or, alternatively, as occupying four tetrahedral orbitals χ_1, χ_2, χ_3, and χ_4 orientated relative to one another in a tetrahedral manner, the orientation of the tetrahedron in space being arbitrary. The electronic structures of the other molecules of the series can now be discussed in terms of this basic system if we imagine unit positive charges to be removed successively from the nucleus.

If a single positive charge is removed to give HF, a preferred direction is established and the orbitals have to be referred to the internuclear line. Suppose we take this as the *z* axis. The orbitals will be somewhat distorted but their general arrangement will not be radically altered. One of the four localised neon orbitals will be pulled out into a localised bonding orbital; it can probably be expressed fairly accurately in the LCAO form as

$$\chi_{\text{bonding}} = \lambda(2s)_{\mathrm{F}} + \mu(2pz)_{\mathrm{F}} + \nu(1s)_{\mathrm{H}} \quad . \quad . \quad (28)$$

where λ, μ, and ν are numerical coefficients. This is a linear combination of an *s–p* hybrid on the fluorine atom directed along the *z* axis and the

1*s* hydrogen orbital (Fig. 3). The other three neon-like localised orbitals will not be distorted as much, so they will remain as three equivalent tetrahedral hybrids pointing in directions making an approximately tetrahedral angle with the bond. They are three equivalent lone pairs. It is interesting that the most important lone-pair direction (where the negative charge is most likely to be found) may not be directly at the back of the fluorine atom. As the lone-pair electrons play an important role as the negative end of hydrogen bonds, this is probably closely connected with the non-linear structure of hydrogen fluoride polymers.

The molecular-orbital description of HF can be obtained if we note that the three equivalent lone pairs can be obtained from a σ orbital and two π orbitals by a transformation similar to that used for obtaining the bent-bond description of N_2. In the LCAO form the σ lone pair will be another *s–p* hybrid and the two lone pairs will be $(2px)^2$ and $(2py)^2$. It is generally found that π lone pairs are less firmly bound than σ lone pairs so that the lowest ionisation potential would correspond to the removal of an electron from one of the last two orbitals.

We can now consider the structure of the water molecule by supposing

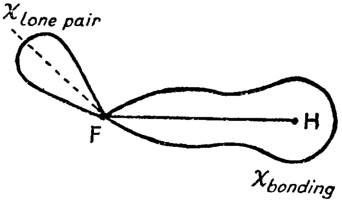

FIG. 3

Localised orbitals for hydrogen fluoride.

a further positive charge removed from the nucleus. The localised description gives some insight into the reason for the non-linear structure. Given that one positive charge has been removed, as in HF, the second charge will prefer to be pulled out in the directions where the remaining electrons are most likely to be found. As we have seen above this is in a direction at an approximately tetrahedral angle to the first bond. In the localised-orbital picture, therefore, the outer electrons of the water molecule occupy two sets of two equivalent orbitals. The first two are bonding orbitals concentrated mainly along the O–H bonds, and the other two are localised lone pairs which point in two equivalent directions towards the back of the molecule, above and below the plane of the nuclei.[3]

Once again this is a very useful description for understanding molecular interaction. The normal form of the ice crystal, for example, is held together by hydrogen bonds in such a way that each molecule is surrounded tetrahedrally by four others.[4] This is completely consistent with the electrostatic theory of the hydrogen bond according to which a proton is

[3] Pople, *Proc. Roy. Soc.*, 1950, *A*, **202**, 323.

[4] Barnes, *ibid.*, 1929, *A*, **125**, 670.

attracted by a localised lone pair of electrons on another molecule.[5] There is also considerable evidence that this structure persists to a large extent in the liquid.[6, 7]

To deal with the molecular orbitals for water it is useful to examine the effect of certain symmetry operations on the molecule. We choose a set of rectangular Cartesian axes (Fig. 4) so that the x axis bisects the angle between the bonds and the z axis is perpendicular to the nuclear plane.

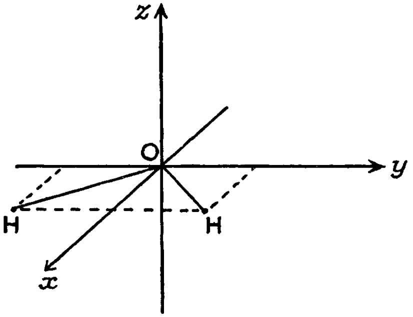

FIG. 4
Cartesian axes for the water molecule.

Then we can classify the molecular orbitals according to whether they are antisymmetric or not in the planes of symmetry. These are Oxy and Oxz. The molecular orbitals are summarised in the Table, together with LCAO forms.

TABLE. *Molecular orbitals for the water molecule.*

Symmetry	Description	LCAO form
ψ_1 Totally symmetric .	Oxygen inner shell	$(1s)_O$
ψ_2 Totally symmetric .	Symmetric bonding orbital	Mixture of oxygen hybrid of $(2s)_O$ and $(2px)_O$ with $(1s)_H + (1s)_{H'}$
ψ_3 Antisymmetric in plane Oxz	Antisymmetric bonding orbital	Mixture of oxygen $(2py)_O$ with $(1s)_H - (1s)_H$
ψ_4 Totally symmetric .	Symmetric lone pair	Hybrid of $(2s)_O$ and $(2px)_O$
ψ_5 Antisymmetric in plane Oxy	Antisymmetric lone pair	$(2pz)_O$

The localised equivalent orbitals are connected with these by the transformations

$$\begin{aligned} \chi_{\text{bonding}} &= (1/\sqrt{2})(\psi_2 \pm \psi_3) \\ \chi_{\text{lone pair}} &= (1/\sqrt{2})(\psi_4 \pm \psi_5) \end{aligned} \quad . \quad . \quad . \quad . \quad . \quad (29)$$

It is interesting that the molecular-orbital functions give an alternative

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[5] Lennard-Jones and Pople, *Proc. Roy. Soc.*, 1951, *A*, **205**, 155.
[6] Bernal and Fowler, *J. Chem. Phys.*, 1933, **1**, 515.
[7] Pople, *Proc. Roy. Soc.*, 1951, *A*, **205**, 163.

description of the lone-pair electrons which still distinguishes them from bonding electrons. There are two distinct lone-pair molecular orbitals, one of which, ψ_4, is an *s–p* hybrid on the oxygen atom directed along the negative *x*-axis, that is, backwards along the line bisecting the two O–H bonds. The other (ψ_5) is antisymmetric in the HOH plane and approximates to an atomic 2*p*-function. This is the orbital of lowest energy for the water molecule and corresponds to the lone-pair electron removed in the first ionisation process.

The structure of ammonia, the next molecule in the series, can be considered in a similar manner. If a further unit positive charge is removed from the nucleus in H_2O, the most favourable direction energetically will be towards one of the localised lone pairs. The ammonia molecule, therefore, will have a tetrahedral-like structure with three equivalent localised bonding orbitals and a hybrid lone-pair orbital in the fourth direction. The three bonding orbitals can be transformed into three delocalised orbitals, but here the lone pair is already symmetrical and approximates to a molecular orbital. It is interesting to consider the behaviour of the lone pair during the inversion of the molecule (this is known to occur with relatively high frequency). In the equilibrium configuration, the orbital is close to a tetrahedral *s–p* hybrid. As the molecule flattens, the amount of *s* character decreases until, in the intermediate planar configuration, the lone-pair orbital is a pure *p* function. After passing through this position, *s* character reappears, causing the lone pair to project in the opposite direction.

The final molecule of this series is methane, the tetrahedral structure of which follows if a fourth unit positive charge is removed from the nucleus in the ammonia lone-pair direction. There are now four equivalent bonding orbitals, which may be represented approximately as linear combinations of carbon *s–p* hybrid and hydrogen 1*s* functions. The transformation from molecular orbitals into equivalent orbitals or *vice versa* is exactly the same as for the neon atom.

Molecules with Multiple Bonds.—The double bond in a molecule such as ethylene provides a striking example of the transformation between equivalent and molecular orbitals.[8] The nuclear configuration of ethylene is known to be planar, so the molecular or symmetry orbitals can be divided into two classes according to whether they are symmetrical or antisymmetrical in this plane. By analogy with the classification for diatomic molecules, these are referred to as σ and π orbitals respectively. If we take the *z* direction to be normal to the plane, the LCAO forms of the σ molecular orbitals (apart from the carbon inner shells) will be constructed from the hydrogen 1*s* and carbon 2*s*, 2*px*, and 2*py* atomic orbitals. The only low-lying π atomic orbitals are 2*pz*. Two types of transformation are possible. In the first place, the σ orbitals may be transformed among themselves, so that all orbitals will retain the property of symmetry or antisymmetry in the nuclear plane. The occupied σ molecular orbitals could be transformed in this way into a set of localised σ orbitals which correspond to bonds of single axially-symmetric type. There will be five

[8] Lennard-Jones and Hall, *Proc. Roy. Soc.*, 1951, *A*, **205**, 357.

in all, four local C–H bonds and one C–C bond whose LCAO form will be approximately

$$\psi_{\text{C–C }\sigma\text{-bond}} = (1/\sqrt{2})(\text{tr}_A + \text{tr}_B) \qquad (30)$$

where tr_A and tr_B are trigonal *s–p* hybrids. The remaining two electrons will occupy the π-bonding orbital

$$\psi_{\text{C–C }\pi\text{-bond}} = (1/\sqrt{2})(2pz_A + 2pz_B) \qquad (31)$$

which will be antisymmetric in the nuclear plane. These two orbitals

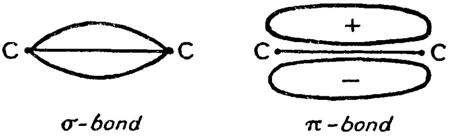


FIG. 5

σ and π Bonding orbitals in ethylene.

constitute the σ–π representation of the double bond (Fig. 5). If we now carry out a further transformation by writing

$$\begin{aligned} \chi_1 &= (1/\sqrt{2})(\psi_{\text{C–C }\sigma\text{-bond}} + \psi_{\text{C–C }\pi\text{-bond}}) \\ \chi_2 &= (1/\sqrt{2})(\psi_{\text{C–C }\sigma\text{-bond}} - \psi_{\text{C–C }\pi\text{-bond}}) \end{aligned} \qquad (32)$$

we get two equivalent orbitals, concentrated one above and one below the plane. This description corresponds to two bent bonds (Fig. 6). Each carbon atom takes part in four bonds in directions which are approximately tetrahedral, two being bent round towards the other carbon atom.

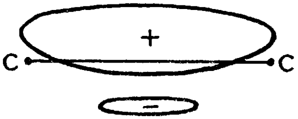


FIG. 6

Equivalent or bent bonding orbitals in ethylene.

Actually the HCH bond angle in ethylene is rather larger than the tetrahedral value. According to the equivalent-orbital picture, this can be attributed to the closing up of one pair of bonds leading to the opening of the other pair.

The carbon–oxygen double bond in aldehydes and ketones is similar and can be described in either of these two ways. If we adopt the localised-orbital description, formaldehyde will have two directed lone pairs in place of two of the C–H bonds in ethylene. In this case the axes of these hybrid orbitals will be in the molecular plane (unlike the oxygen lone pairs in water). Either the components of the double bond or the lone pairs can be transformed back into symmetry forms. The alternative description of the lone pairs would be one σ-type along the C–O direction and one π-type with axis perpendicular to the C–O bond but in the molecular plane. It is the latter orbital which has the highest energy, so that an electron is removed from it in ionisation or excitation to the lowest excited state.

The carbon–carbon triple bond in acetylene can be treated in a similar way to that in the nitrogen molecule.[8] The details of hybridisation may differ somewhat, but there will be a C–C σ bond and two perpendicular C–C π bonds. The alternative description is in terms of three equivalent bent bonds. The triple bond in hydrogen cyanide HC≡N is similar.

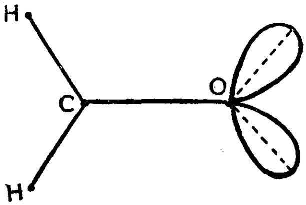
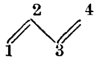


FIG. 7

Equivalent lone pairs in formaldehyde.

Resonance and Conjugation.—All the molecules described so far have been simple ones which can be described in terms of a single classical valence structure. For such systems we have seen how the molecular-orbital wave function can be expressed in terms of a set of localised equivalent bonding orbitals, each such orbital corresponding to a chemical bond or to a lone pair of electrons. In many more complex molecules, it is generally recognised that a single valence structure is insufficient and that the ground state should be represented as a mixture of several structures. This raises the question of what happens to the localised bonding orbitals when such mixing occurs.

This can be illustrated by the π electrons of buta-1 : 3-diene as an example (inset). This molecule is planar and its principal structure has two ethylenic-type double bonds. The correct equivalent-orbital description of this structure would be in terms of two localised bonding orbitals



$$\begin{aligned}\chi_A &= (1/\sqrt{2})(\phi_1 + \phi_2)\\ \chi_B &= (1/\sqrt{2})(\phi_3 + \phi_4)\end{aligned} \quad . \quad . \quad . \quad . \quad (33)$$

where ϕ_1, ϕ_2, ϕ_3, and ϕ_4 are the $2p\pi$ atomic orbitals. The corresponding symmetrical orbitals are obtained by taking the sum and difference of these two :

$$\begin{aligned}\psi_{\text{sym}} &= \tfrac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)\\ \psi_{\text{antisym}} &= \tfrac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4)\end{aligned} \quad . \quad . \quad . \quad (34)$$

Now actual calculations based on a simple model of a hydrocarbon such as this suggest that these molecular orbitals are better approximated by

$$\begin{aligned}\psi_{\text{sym}} &= 0{\cdot}3717\phi_1 + 0{\cdot}6015\phi_2 + 0{\cdot}6015\phi_3 + 0{\cdot}3717\phi_4\\ \psi_{\text{antisym}} &= 0{\cdot}6015\phi_1 + 0{\cdot}3717\phi_2 - 0{\cdot}3717\phi_3 - 0{\cdot}6015\phi_4\end{aligned} \quad . \quad . \quad (35)$$

The equivalent orbitals corresponding to these are obtained by applying the reverse transformation and are

$$\begin{aligned}\chi_A &= (1/\sqrt{2})(\psi_{\text{sym}} + \psi_{\text{antisym}}) = 0{\cdot}6882(\phi_1 + \phi_2) + 0{\cdot}1625(\phi_3 - \phi_4)\\ \chi_B &= (1/\sqrt{2})(\psi_{\text{sym}} - \psi_{\text{antisym}}) = -\,0{\cdot}1625(\phi_1 - \phi_2) + 0{\cdot}6882(\phi_3 + \phi_4)\end{aligned} \quad . \quad (36)$$

Thus it appears that the best equivalent orbitals in this molecule are not completely localised in the two double bonds but are to some extent distributed over the whole system. This failure to obtain localisation is the molecular-orbital analogue of resonance between valence structures.

Discussion

The main result that emerges from the discussions of particular cases is that it has proved possible to give a description of a molecule in terms of equivalent orbitals which are approximately localised, but which can be transformed into delocalised molecular orbitals without any change in the value of the total wave function. The equivalent orbitals are closely associated with the interpretation of a chemical bond in the theory, for, in a saturated molecule, the equivalent orbitals are mainly localised about two atoms, or correspond to lone-pair electrons. Double and triple bonds in molecules such as ethylene and acetylene are represented as bent single bonds, although the rather less localised σ–π description is equally valid.

Another property of these equivalent orbitals is that they include in themselves effects of delocalisation. Such effects are most important in conjugated molecules, although they are present in all molecules to a greater or lesser extent. In a highly conjugated system such as benzene only a limited amount of localisation can be achieved by transforming the orbitals.

For large molecules, the equivalent-orbital analysis is the most convenient starting point for a molecular-orbital treatment. In a molecule such as a long-chain paraffin it is possible to write approximate equivalent orbitals corresponding to each bond and then to apply a transformation to obtain the delocalised molecular orbitals. Simple assumption about the interaction of neighbouring bonds will then lead to estimates of the relative stability of the various energy levels.[9]

[9] Hall, *Proc. Roy. Soc.*, 1951, *A*, **205**, 541.