REPRESENTATION OF SIMPLE MOLECULES BY MOLECULAR ORBITALS

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Introduction

THIS account of the method of molecular orbitals is divided into five distinct sections :

(1) The method of atomic orbitals for the study of individual atoms.

(2) Diatomic molecules, leading to the characteristic differences between single and double bonds.

(3) Polyatomic molecules involving localised bonds, leading to the theory of stereochemistry and valence angles.

(4) Polyatomic molecules involving non-localised bonds, leading to the phenomenon sometimes referred to as resonance.

(5) Some general related topics, including hyperconjugation.

In an account of this length it is not possible to report anything like all the work that has been published in the last twenty years since the subject began ; and the situation is made worse by the fact that no satisfactory simple account of the method of molecular orbitals by itself has ever been given. Our method of approach, therefore, will be first to explain the general character of the theory, and then to illustrate its power by selecting a series of typical applications. For the benefit of those who wish to study any section in more detail, we include references to suitable literature.

Like all problems in theoretical chemistry, the detailed working out of any part of the theory requires a certain familiarity with mathematical methods. In this case the essential technique is that of solving the Schrödinger wave equation under certain given conditions ; but the fundamental ideas behind the theory are easily understood by experimental workers with little or no mathematical experience. For that reason we have avoided all mathematics, and have insisted everywhere upon the pictorial character of each step in the argument. It is the visual character of these steps that makes the method of molecular orbitals so fundamentally simple, but this situation must not blind us to the fact that in practically every case quantitative as well as qualitative predictions have been made. Indeed, a study of recent literature shows that this method, originally rather neglected, is now receiving more attention than the alternative method of valence-bond structures, first introduced by W. Heitler and F. London [1] and so lucidly developed by L. Pauling in his book " The Nature of the Chemical Bond ".[2] A comparative study of the two methods,

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[1] *Z. Physik*, 1927, **44**, 455.　　　　　　[2] Cornell Univ. Press.

to which the present account is much indebted, has been given by J. H. Van Vleck and A. Sherman.[3]

1. *Atomic Orbitals*

General Principles.—Before we can profitably describe the motions of molecular electrons we must briefly review the simpler problem of how electrons move in isolated atoms. We need to study this, not only because molecules are built out of atoms, but also because the method of molecular orbitals runs closely parallel to the atomic problem and, as we shall see in Section 2, molecular orbitals are themselves compounded out of atomic orbitals.

If we make use of the self-consistent-field theory introduced by W. R. Hartree,[4] we may summarise the behaviour of the electrons in atoms by the following three principles :

(*a*) Each electron is assigned to a definite particular orbit. In the older quantum theory of Bohr, this orbit was as precise and clear-cut as the orbit of a planet round the sun ; but in the newer wave-mechanical theory, where such precise measurements of position are not possible, and a statistical description has to be used, the orbit is described by a wave function ψ. Not all wave functions are possible, but only those which are found as solutions of the Schrödinger wave equation. As ψ defines the orbit, we call it an *atomic orbital* (A.O.). The value of ψ for any electron varies from point to point, and ψ^2 at any place measures the probability that the electron will be found at that place. Thus if ψ is large anywhere, irrespective of its sign which has no physical meaning, the electron is likely to be found there. For many purposes a more pictorial (though less strictly accurate) interpretation of the wave function may be given as follows : the electron may be regarded as spread out in the form of a cloud (charge-cloud), the density of this cloud at any point being proportional to ψ^2. In places where ψ^2 is largest, the charge-cloud is most dense and most of the negative charge is to be found. The objection to this interpretation is that a single electron cannot possibly be distributed over regions of the size of one or two Bohr radii. Only the statistical, or probability, interpretation is really valid, but the charge-cloud picture is a useful one. Thus we shall often have occasion to represent atomic and molecular orbitals diagrammatically by boundary surfaces ; these surfaces are such that, if they are drawn to the right scale, almost all the electronic charge (*e.g.*, 90%) lies within the contour drawn, and for most purposes we may say that the electron is confined within this boundary. Examples of these contours are given in Figs. 1—4.

(*b*) Each wave function has its own appropriate energy, and if this is suitably determined, the total energy is approximately the sum of the energies of the constituent orbitals.

(*c*) In addition to its space wave function ψ, each electron has a spin, which must have one of two values ($\pm \frac{1}{2}$ in normal units), and the Pauli

[3] *Rev. Mod. Physics*, 1935, **7**, 168.
[4] *Proc. Camb. Phil. Soc.*, 1928, **24**, 111, 426.

" exclusion principle " tells us that in no case may two electrons have both the same ψ and the same spin. Two electrons may have the same ψ only by having opposed spins. In this case we speak of them as paired. Such electrons generally exert a repulsion upon other electrons near them.
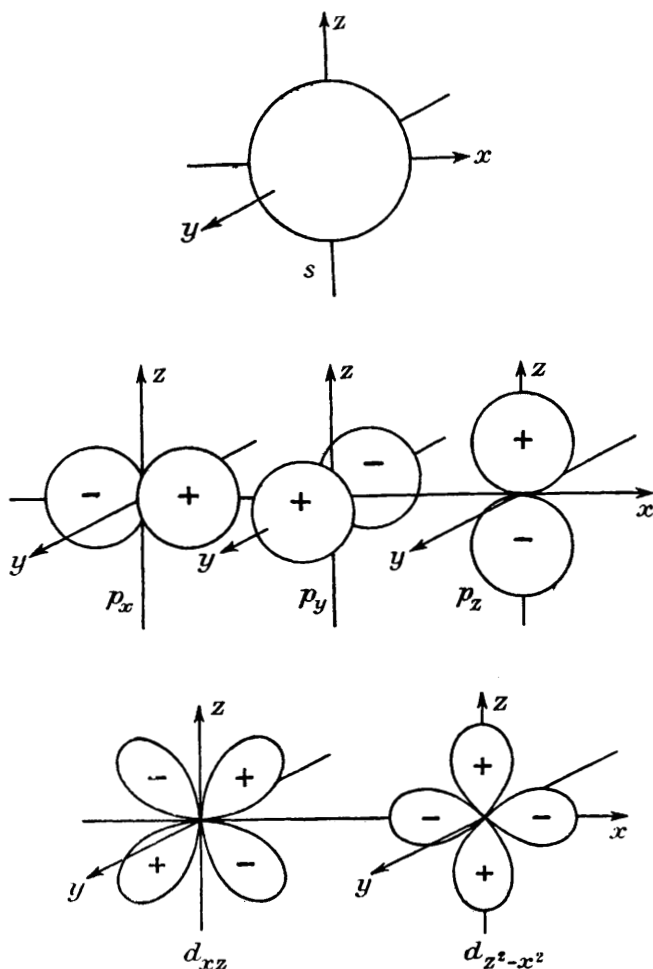

FIG. 1
Types of atomic orbital.

For our later purposes it is absolutely essential to have in our minds a clear picture of the appearance of the more common atomic orbitals. This picture must above all reveal the symmetry properties of the A.O. In ordinary atoms the A.O. are classified as s, p, d, . . . Fig. 1 shows the boundary contours for some of these orbitals. The s-type is spherically symmetrical, and the significance of the diagram is that the electron is

almost certainly to be found inside the sphere shown. There are three p-type orbits, in each of which the electron is practically confined to two regions together resembling a " dumb-bell ". In one half of the dumb-bell ψ is positive and in the other it is negative, as shown. There is a very marked directional character in these orbitals, which we exhibit by means of the suffixes p_x, p_y, p_z. An important fact about these A.O. is that the regions where ψ is of opposite sign are separated by a " nodal plane ", over which $\psi = 0$. For example, in the orbital p_x this nodal plane is the yz plane. The three p-type orbits are entirely equivalent except for their directional property. In a similar way there are five d-type orbitals, two of which are shown. In some respects a d orbit is like the superposition of two p orbits, for there are four similar regions of alternating sign, separated by two nodal planes. In the d_{xy}, d_{yz}, d_{zx} orbitals these are two of the co-ordinate planes. In the so-called $d_{y^2-z^2}$, $d_{z^2-x^2}$ orbitals, which are obtained by rotating the previous d_{xy}, . . . orbitals through $45°$, the nodal planes are, of course, also rotated. One might have expected a $d_{x^2-y^2}$ orbital as well as a $d_{y^2-z^2}$, $d_{z^2-x^2}$; and indeed it does exist. But it may be verified from a superposition of the appropriate diagrams, or else from the analytical form of the wave functions themselves, that the sum

$$\psi(d_{x^2-y^2}) + \psi(d_{y^2-z^2}) + \psi(d_{z^2-x^2})$$

is identically zero. This means that only two of these three are independent. Any pair of them, together with the previous d_{xy}, . . . make a total of exactly five independent, and equivalent, d-type orbitals.* More exact diagrams of these orbitals may be found in a paper by H. E. White.[5]

The full description of an A.O. requires, in addition to its s, p, d, . . . character, a knowledge of its principal, or total, quantum number, and its spin. The order of energies is well known to be

$$1s < 2s < 2p < 3s < 3p < 3d \ . \ . \ .$$

In giving the electronic state of an atom we adopt an " aufbau ", or building-up process, in which electrons are fed one at a time into the allowed levels, beginning with the $1s$, and satisfying the exclusion principle by allowing only two to each of the orbitals just described. Thus hydrogen in its ground state is represented by $(1s)$, helium by $(1s)^2$, nitrogen by $(1s)^2(2s)^2(2p)^3$, oxygen by $(1s)^2(2s)^2(2p)^4$, etc. In the cases of nitrogen and oxygen, however, and all other atoms containing incomplete groups or sub-groups, this still leaves undecided just which of the equivalent orbitals (here the $2p$ orbitals) are filled. For this we make use of Hund's rules.[6] These are that for equivalent orbits : (i) electrons tend to avoid being in the same space orbit, so far as is possible, and (ii) two electrons, each singly occupying a given

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* For the purposes of this account we have chosen always to use purely real wave functions. In such a case the five d orbitals are equivalent, and so are the three p orbitals. But for some purposes (e.g., magnetic) a different representation is used, in which the set of d orbitals splits into three groups according to the component of angular momentum in a particular direction (compare the σ, π, . . . classification in Section 2).

[5] *Physical Rev.*, 1931, **37**, 1416.
[6] See, *e.g.*, Herzberg, " Atomic Spectra and Atomic Structure ", Blackie, Chap. 3.

pair of equivalent orbits (e.g., $2p_x$, $2p_y$), tend to have their spins parallel in the state of lowest total energy. For instance, nitrogen in the ground state has the 1s and the 2s orbitals doubly filled, and each of the $2p_x$, $2p_y$, and $2p_z$ orbits singly filled, the three electrons concerned having parallel spins; and oxygen, with one more p electron, has one orbital (say $2p_z$) doubly filled, the other two being singly occupied, with parallel spins, as in Fig. 6. The $(2p_z)^2$ group, which as we shall see in Section 3 make no contribution to the bivalent character of the oxygen atom, are sometimes called the " lone pair " electrons. A similar name is used for the nitrogen $(2s)^2$ electrons.

Hybridisation.—All this is very well known. Yet we have mentioned it because it is not so well known that precisely equivalent rules describe the behaviour of electrons 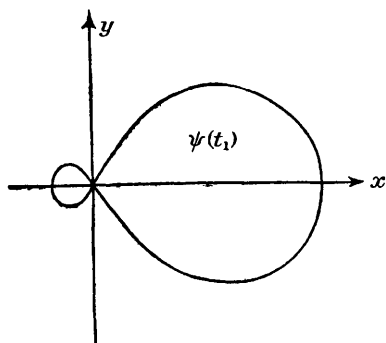in molecules ; but before we can deal with this, there is one new factor to be introduced. As it is of greatest importance in carbon, let us describe it for this atom. According to what we have just said, the normal state of carbon is $(1s)^2(2s)^2(2p)^2$, in which there are two unpaired electrons (e.g., $2p_x$, $2p_y$) and the spectroscopic state is ^3P. This corresponds to bivalency ; the characteristic quadrivalency can only be obtained if we start from a state with four unpaired electrons. A suitable state may be obtained if we excite one of the 2s electrons to the empty $2p_z$ orbit, making a ^5S state. Approximately 65 k.-cals./mole are required to

FIG. 2
A single tetrahedral orbital.

do this ; [7] but even now the four valence electrons are not equivalent, being 2s, $2p_x$, $2p_y$, $2p_z$. In order to get equivalent bonds we must mix these " pure " orbitals together and form " hybridised " orbitals. As Pauling [8] has shown, there are at least three such linear combinations that are of the utmost importance. They may be called tetrahedral, trigonal, and di-gonal (or diagonal, but neither word is particularly attractive !).

In the tetrahedral hybridisation we replace the four orbitals 2s, $2p_x$, $2p_y$, $2p_z$ by four others t_1, t_2, t_3, t_4 ; $\psi(t_1)$ is shown diagrammatically in Fig. 2. [With these axes $\psi(t_1) = \frac{1}{2}\psi(2s) + \frac{\sqrt{3}}{2}\psi(2p_x)$.] Evidently the electron cloud is greatly concentrated along a particular direction, here the positive x axis, and the wave pattern is cylindrically symmetrical around this direction. The other three orbitals t_2, t_3, and t_4, are entirely equivalent to t_1, except that they point in the three remaining directions of the vertices of a regular tetrahedron surrounding the carbon atom. We may anticipate that the characteristic quadrivalency of carbon is associated with the fact that,

[7] L. H. Long and R. G. W. Norrish, *Nature*, 1946, **157**, 486 ; **158**, 237 ; *Proc. Roy. Soc.*, 1946, *A*, **187**, 337.

[8] (a) *J. Amer. Chem. Soc.*, 1931, **53**, 1367 ; (b) *ibid.*, 1932, **54**, 988, 3570.

when it is prepared for the formation of a saturated molecule like CH_4 or C_2H_6, there is one electron in each of the four orbits $t_1 \ldots t_4$.

In the trigonal hybridisation, $2s$, $2p_x$, and $2p_y$ are compounded to give three equivalent coplanar orbitals I, II, III, somewhat similar in shape to t_1, and pointing at angles of 120° in the xy plane, as in Fig. 3. [Here $\psi(\text{I}) = \sqrt{\frac{1}{3}}\psi(2s) + \sqrt{\frac{2}{3}}\psi(2p_x)$.] The remaining orbital is the undisturbed $2p_z$, generally referred to in this connection as the π orbital. This form of hybridisation is evidently associated with the aromatic state of the carbon atom (*e.g.*, ethylene, benzene) where the three valence angles are known to be exactly, or approximately, 120°.

The third, or di-gonal, type leaves $2p_y$ and $2p_z$ unchanged, merely mixing the $2s$ and $2p_x$ orbitals in the forms $\psi(a) = \sqrt{\frac{1}{2}}\{\psi_x(2s) + \psi(2p_x)\}$, $\psi(b) = \sqrt{\frac{1}{2}}\{\psi(2s) - \psi(2p)\}$. As shown in Fig. 4, these hybrids point in opposite directions along a straight line. They are obviously related to the state of the carbon atom prepared to form compounds such as C_2H_2 and CO_2.

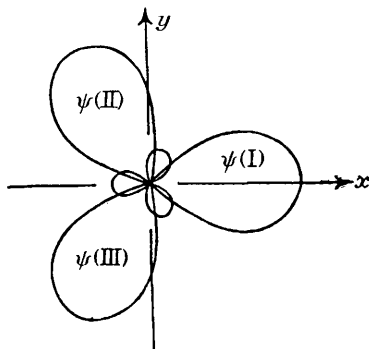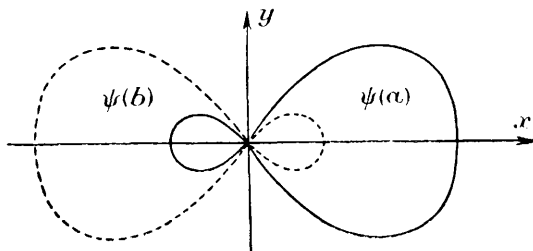Small variants of these three fundamental types occur in molecules

Fig. 3
Trigonal orbitals
[not including $\psi(p_z)$ which is as in Fig. 1].

Fig. 4
Di-gonal hybridisation
[not including $\psi(p_y)$ and $\psi(p_z)$ which are as in Fig. 1].

such as CH_3Cl, where all four bonds are not quite equivalent : but they do not differ appreciably from the above and we shall not discuss them here.

When electrons of the carbon atom (or other atom) have been placed in these new, hybridised orbits, which replace the old s and p orbits, we speak of the atom as being in a " valence state " (see particularly J. H. Van Vleck [9] and R. S. Mulliken [10]). The advantage of the valence state

[9] *J. Chem. Physics*, 1933, **1**, 177, 219 ; 1934, **2**, 20.
[10] *Ibid.*, p. 782.

is that the various orbitals have a very strongly directed probability function. The disadvantage is that energy is required to form the hybridisation, though this energy is less in the case of carbon, where $\psi(2s)$ and $\psi(2p)$ have more nearly equal energy, than in oxygen, where the difference is greater. But we reap our reward later when we find a correspondingly greater gain in energy through the formation of stronger bonds.

2. *Diatomic Molecules ; Single and Double Bonds*

General Principles.—There is absolutely no reason why we should not use exactly the same principles for describing the electron states in a diatomic molecule as in a single atom. However, on account of the fact that the electrons move in the presence not of one, but of two, nuclei, there are certain extra features to be considered. We may therefore start as follows :

(a) Each electron in a molecule is described by a wave function ψ, and the value of ψ^2 at any point represents the probability of finding the electron in unit volume around that point. These wave functions may appropriately be called *molecular orbitals*,[11] abbreviated to M.O., to distinguish them from atomic orbitals (A.O.), and to remind us that they are no longer monocentric, but are polycentric, since an electron which takes part in molecule formation must not be confined to one nucleus alone.

(b) Each ψ has its own appropriate energy, and if this is suitably determined, the total electronic energy is approximately the sum of the energies of the occupied orbitals.

(c) Each electron has a spin, and Pauli's exclusion principle must be satisfied just as in the case of an atom.

Characteristic molecular features occur in the following way. A strict calculation of ψ ought to be made by solving the appropriate Schrödinger wave equation. However, except for H_2, this is a mathematical task of too great complexity ; but we avoid the difficulty by noting that when an electron is in the neighbourhood of any one nucleus, the forces on it arise mainly from that nucleus and the other electrons on the same nucleus ; this means that both the wave equation and its solution must resemble the corresponding equation and solution for an isolated atom. The molecular orbital therefore resembles a series of superposed atomic orbitals, one at each of the constituent nuclei. We may describe this by a new principle :

(d) Each M.O. is compounded out of atomic orbitals. This fundamental idea, on which the whole of the structure of molecular orbital theory ultimately rests, is due to J. E. Lennard-Jones,[12] who applied it to the case of homonuclear systems H_2, N_2, etc. In the form just stated, which Mulliken [13] calls the L.C.A.O. approximation (linear combination of atomic orbitals) this principle is not an exact truth ; for the best possible M.O. for a diatomic molecule are not simply combinations of two A.O. However, as a detailed

[11] R. S. Mulliken, *Physical Rev.*, 1932, **41**, 49.
[12] *Trans. Faraday Soc.*, 1929, **25**, 668.
[13] *J. Chem. Physics*, 1935, **3**, 375.

study for the more manageable case of H_2 shows,[14, 15] the approximation is pretty good : and without some sort of approximation no progress could be made. Consequently, this technique of representing M.O. as L.C.A.O. has now become perfectly standard, and we shall adopt it throughout.

There is, in fact, a particular significance in the L.C.A.O. relation between a molecular orbital ψ in a molecule AB and its component atomic orbitals ψ_A and ψ_B. This is seen most clearly when the two electrons that occupy the orbital ψ are valence electrons contributing to the bond A–B. Normally, one of these electrons comes from each atom, and if the interaction between the atoms could be prevented, these electrons would be in orbitals ψ_A and ψ_B. Thus the molecular orbital ψ, which will accommodate two electrons, is correlated with the two atomic orbitals into which we might expect the molecular electrons to go when interaction between the atoms was artificially prevented, as, *e.g.*, by separating them to infinite distance. In a loose kind of way we could therefore speak of " the electron originally in state ψ_A " and " the electron originally in state ψ_B " being paired to form molecular electrons in state ψ for the bond A–B. So we might imagine ourselves bringing up the atoms A and B towards one another, without allowing any interaction, and then pairing together suitable electrons in A and B. This rather crude, and certainly not completely accurate, description of molecule formation reveals a link between M.O. theory and both the Lewis shared-electron-pair-bond, and the Langmuir octet theory. But the L.C.A.O. theory is not much use to us unless we have some criterion for deciding which of the possible orbitals ψ_A is to be combined with ψ_B. This brings us to another principle :

(*e*) The energy of a M.O. is lowest (*i.e.*, binding energy is greatest) when the component atomic orbitals overlap one another as much as possible. This is the " criterion of maximum overlapping ", originally introduced by J. C. Slater [16] and L. Pauling [8a] to explain the origin of directional valence. Although these writers developed the criterion for use in a different kind of treatment from ours, we shall find, in Section 3, that it applies beautifully to M.O. theory, and provides an ultimate explanation of all the fundamental rules of stereochemistry. A proof of the validity of the criterion is given by C. A. Coulson.[17]

An example will explain this principle most easily. In HCl there are two unpaired electrons which form a bond. In the separate atoms they are the $H(1s)$ and the $Cl(3p_x)$ atomic orbitals. The molecular orbital will be found by a combination of these : but the overlap of the two is greatest when the x direction from Cl points directly towards the H atom. This means that the H atom will lie along this direction, and the two sets of lone-pair electrons on the Cl atom $(3p_y)^2(3p_z)^2$ will point in directions at right angles to the bond H–Cl.

(*f*) Mathematical calculation [17] shows that, other things being equal,

[14] C. A. Coulson, *Trans. Faraday Soc.*, 1937, **33**, 1479.
[15] *Idem, Proc. Camb. Phil. Soc.*, 1938, **34**, 204.
[16] *Physical Rev.*, 1931, **37**, 481 ; **38**, 1109.
[17] *Proc. Camb. Phil. Soc.*, 1937, **33**, 111.

the binding energy is greatest if the component A.O. have as nearly equal energies as possible. Indeed, if these energies (for a diatomic or a polyatomic molecule) are not of comparable magnitude, no significant combination occurs. Thus, in the HCl molecule just discussed, the binding energy of $H(1s)$ is vastly less than that of any of the K- or L-shell electrons in Cl, so that these latter are practically unaffected by the association with H. Only the $3p_x$, $3p_y$, and $3p_z$ are of approximately equal energy with the $H(1s)$ and, as we have seen, the criterion of maximum overlapping picks out which of these co-operates with $\psi(H : 1s)$ in the formation of a M.O. For this reason we need only consider together atomic orbitals from the valence shells of the various atoms, the inner-shell electrons retaining atomic character. The same is true even when, as in homonuclear molecules such as Cl_2, the inner electrons of the one atom have identical energies with those of the other. Here it may be shown, on account of the fact that the A.O. for these inner-shell electrons scarcely overlap at all, that the result of compounding them to form M.O. gives a final distribution of charge effectively indistinguishable from that when they are not compounded. This clears up an earlier difficulty [12] regarding the use of atomic or molecular orbitals for inner-shell electrons. Our conclusion is that only the valence-shell electron orbitals are combined together, all the others being given their non-bonding atomic character. This is, of course, in complete accord with chemical behaviour.

Homonuclear Diatomic Molecules.—Let us consider the application of the above principles to diatomic molecules in which the two atoms are identical —homonuclear diatomics, as we may call them. If the nuclei are A and B, then molecular orbitals may be obtained by combining together atomic orbitals ψ_A and ψ_B, one from each atom. But the condition (f) of equal or nearly equal energy makes it clear that ψ_A and ψ_B must refer to orbitals of the same kind around their respective nuclei. Thus they may both be $1s$ orbitals, as in H_2, or $2s$ orbitals, as in Li_2 : or both may be $2p_x$ or both be $2p_z$ orbitals, etc. Suppose for the moment that they are both $1s$ orbitals $\psi(A : 1s)$ and $\psi(B : 1s)$. This will make our discussion apply particularly to the case of H_2. Then the L.C.A.O. principle (d) provides us with the molecular orbital

$$\Psi = \psi(A : 1s) + \lambda\psi(B : 1s) \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where λ is a constant. Quantum theory interprets such a wave function by saying that the relative probabilities of $\psi(A : 1s)$ and $\psi(B : 1s)$ are in the ratio $1^2 : \lambda^2$. Now by symmetry (Pauling [18] seems to have been the first to notice this particular point, but the more general discussion is due to Lennard-Jones [12]) the electron must be equally divided between A and B, so that $\lambda^2 = 1$. There are therefore two possible L.C.A.O. which we can form, and they are

$$\Psi_g = \psi(A : 1s) + \psi(B : 1s) \qquad . \qquad . \qquad . \qquad . \qquad (2a)$$
$$\Psi_u = \psi(A : 1s) - \psi(B : 1s) \qquad . \qquad . \qquad . \qquad . \qquad (2b)$$

[18] *Chem. Reviews*, 1928, **5**, 173.

The subscripts g and u are short for gerade (even) and ungerade (odd). All M.O. with subscript g are such that ψ has the same value at pairs of points diametrically opposite with respect to the centre of symmetry in the molecule. We may say that Ψ_g is even for reflection in the origin (or mid-point) ; Ψ_u is odd, so that it changes sign on reflection in the origin. These subscripts may be applied either to individual M.O., as here, or to the whole molecule. The importance of such a classification may be seen from the fact that the only allowed transitions are such as change the character ; i.e., $u \rightarrow g$ or $g \rightarrow u$. With heteronuclear molecules such as HCl, where the two nuclei are different, this type of symmetry about the mid-point no longer exists and separation into g and u orbitals is no longer possible.

Let us look a little more closely at the nature of (2a) and (2b). Fig. 5 (a) shows the two boundary surfaces (somewhat schematically) for the two cases. On the left we show the two separate atomic orbitals, and on the right the two M.O. Ψ_g and Ψ_u compounded from them. Both boundary surfaces have complete symmetry around the axis (this corresponds to zero component of angular momentum in this direction) ; when this happens we call the molecular orbitals σ-type. But Fig. 5 shows very clearly that in the Ψ_g M.O. the electrons are drawn into the region between the atoms, and in the Ψ_u case they are thrown away from the bond. Accurate calculations [15], [13], [20] can be made both of the shape and of the energy of these two orbitals ; and it appears that the symmetrical Ψ_g orbital gives rise to bonding, the antisymmetrical Ψ_u to antibonding. These two particular orbitals are usually denoted $\sigma 1s$ and $\sigma^* 1s$ (sometimes $1s\sigma$ and $1s\sigma^*$), a star denoting the antibonding character of the orbital.

We are now in a position to apply the " aufbau " principle to molecules, just as we have seen it applied to atoms. Thus the ground state of H_2 would be $(\sigma 1s)^2$, and that of He_2^+ would be $(\sigma 1s)^2(\sigma^* 1s)$. Similarly the lowest state of He_2 would be $(\sigma 1s)^2(\sigma^* 1s)^2$, but here the antibonding power of $(\sigma^* 1s)^2$ cancels the bonding power of $(\sigma 1s)^2$, with the familiar result that two unexcited helium atoms do not combine together. It may be regarded as a general rule that a combination of two unstarred and two starred M.O. compounded out of the same atomic orbitals, will give no appreciable net binding.

This type of argument is easily extended. If we use two s-type atomic orbitals we form a σs and $\sigma^* s$ M.O. with patterns substantially the same as in the $\sigma 1s$ and $\sigma^* 1s$ cases of Fig. 5 (a). If we combine together two p_x A.O. we get a somewhat similar pair of M.O. As these have the same symmetry about the axis of the molecule we call them σp and $\sigma^* p$. However, a new feature comes in if we combine a pair of p_z A.O. The general shape of the p_z A.O. in Fig. 1 makes it easy to see that the corresponding M.O., shown in Fig. 5 (b), are of rather different appearance from our previous σs and σp M.O. It is still true that out of the two atomic orbitals shown on the left we are able to form two molecular orbitals. The top one on

[19] O. Burrau, *Kgl. Danske Vid. Selskab.*, 1927, **7**, 1.
[20] E. Teller, *Z. Physik*, 1930, **61**, 458.

the right, which is bonding, consists of two ribbon, or streamer-type regions, in which Ψ has different signs, and the original nodal plane (xy plane) remains a nodal plane for the molecular orbital. It is important to realise that the two parts of this streamer go together; they are one unit and quite inseparable; together they represent the M.O. But there is no longer symmetry around the bond direction; there is, in fact, a component of angular momentum around the bond direction amounting to one unit. Such M.O. are called π orbitals. In the case of the upper, bonding M.O.

Atomic orbitals	Molecular orbitals	Wave function	Symbol
(a)	•B + A•	$\Psi_g \equiv \psi(A:1s)+\psi(B:1s)$	$\sigma 1s$
	B• •A	$\Psi_u \equiv \psi(A:1s)-\psi(B:1s)$	$\sigma^* 1s$
(b)	•B A•	$\Psi_u \equiv \psi(A:2p_z)+\psi(B:2p_z)$	$\pi_z 2p$
	•B A•	$\Psi_g \equiv \psi(A:2p_z)-\psi(B:2p_z)$	$\pi_z^* 2p$

Fig. 5

(a) *Formation of σ and σ^* molecular orbitals.*
(b) *Formation of π and π^* molecular orbitals.*

of Fig. 5 (b) it would be written πp (*e.g.*, $\pi_z 2p$, or $2p\pi_z$, or sometimes just $p\pi$); and the lower antibonding orbital in this same figure is written $\pi^* p$.

If we combined together two p_y atomic orbitals, we should get two molecular orbitals entirely equivalent to those shown in Fig. 5 (b) except that they are rotated through 90° around the axis. The superposition of a π_y and a π_z M.O. is symmetrical around the bond axis.

Similar schematic diagrams of several other molecular orbitals, as depicted by Weizel, are given by G. Herzberg [21] (but care is needed because the naming of the states is somewhat different from the more modern system described above).

[21] " Molecular Spectra and Molecular Structure ", Prentice-Hall, 1939, p. 348.

The " aufbau " principle of Section 1 may now be used to describe the states of homonuclear diatomic molecules, as soon as we know the relative order of the various M.O. energies. These can be determined [22] from a study of molecular spectra. The lower molecular orbital energies, arising from K- and L-shell atomic orbitals, are normally in the order shown below ; but the $\sigma 2p$ and $\pi 2p$ M.O. have rather similar energies and occasionally interchange places in the table. Note also the degeneracy between $\pi_y 2p$ and $\pi_z 2p$, which have, of course, identical energies.

Full notation :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p < \pi_y 2p = \pi_z 2p < \pi_y^* 2p = \pi_z^* 2p < \sigma^* 2p$$

Abbreviated notation :

$$z\sigma \qquad y\sigma \qquad x\sigma \qquad w\pi \qquad v\pi \qquad u\sigma$$

By this stage we have completed the second molecular shell. A somewhat similar scheme holds for the M.O. formed from atomic 3-quantum orbitals. In the second row of the table above we have shown an abbreviated notation introduced by Mulliken : [22] the advantages of this notation are that it may be made to apply to heteronuclear molecules where any particular M.O. may be compounded from A.O. of different atomic shells [e.g., H($1s$) and Cl($3p_x$) of HCl] and for which the former notation is not adequate : and it also enables us to discard the assumption that, for example, the $\sigma 2s$ molecular orbital is entirely composed of atomic $2s$ orbitals. Thus the notation $z\sigma$ means the lowest M.O. of σ-type, which will, in fact, normally be compounded almost entirely, but not completely, of $2s$ A.O. The most serious disadvantages of the abbreviated notation are that the $x, y, z, \ldots$ introduced in it have no relation whatever to the Cartesian x, y, z co-ordinates used in the top row of the table, and the new notation disguises the simple pictorial relationship between the M.O. and the two A.O. into which, as a rule, it reverts on separating the two atoms to infinite distance. For that reason we shall generally use the older notation in the top row of the table. Both notations are given in Fig. 6 for O_2.

With this order of molecular energies it becomes fairly easy to use the " aufbau " principle to describe the electronic states of whole molecules. Thus Li_2 has two valence electrons and they occupy the $\sigma 2s$ (or $z\sigma$) M.O., allowing us to write

$$Li[1s^2 2s] + Li[1s^2 2s] \longrightarrow Li_2[KK(\sigma 2s)^2]$$
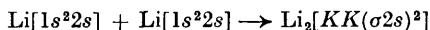
The notation KK implies that the two K-shells of the atoms are filled by non-valence electrons. Other examples are :

(i) $F[1s^2 2s^2 2p^5] + F[1s^2 2s^2 2p^5] \longrightarrow F_2[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^4]$
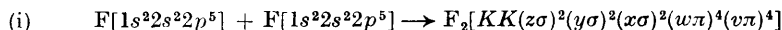
Here the $(z\sigma)^2$ and $(y\sigma)^2$ practically cancel one another's bonding, being $\sigma 2s$ and $\sigma^* 2s$, and so do the $(w\pi)^4$ and $(v\pi)^4$. This implies that although all 14 electrons take part, the bond is effectively due to the $(x\sigma)^2$ pair. As two electrons are primarily responsible, it may reasonably be called a single bond. On account of its symmetry it is a σ-bond.

(ii) $N[1s^2 2s^2 2p^3] + N[1s^2 2s^2 2p^3] \longrightarrow N_2[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4]$
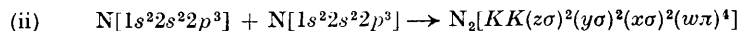
[22] *Rev. Mod. Physics*, 1932, **4**, 40.

Here the binding is effectively due to $(x\sigma)^2$ and $(w\pi)^4$. This amounts to a σ-bond plus two π-bonds, at right angles to each other. As six electrons are involved we may call this a triple bond.

(iii) $O[1s^2 2s^2 2p^4] + O[1s^2 2s^2 2p^4] \rightarrow O_2[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^2]$
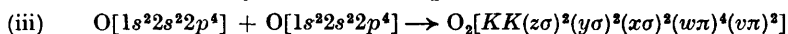
This is a double bond O=O, but the interesting point about O_2 is that there are two electrons in the $(v\pi)$, or (π^*2p), molecular orbital. Now, on account of the degeneracy between π_y and π_z this M.O. will accommodate four electrons ; it is therefore only half-full. So we appeal to Hund's rule (p. 147), indicating that these electrons will go one each in (π_y^*2p) and
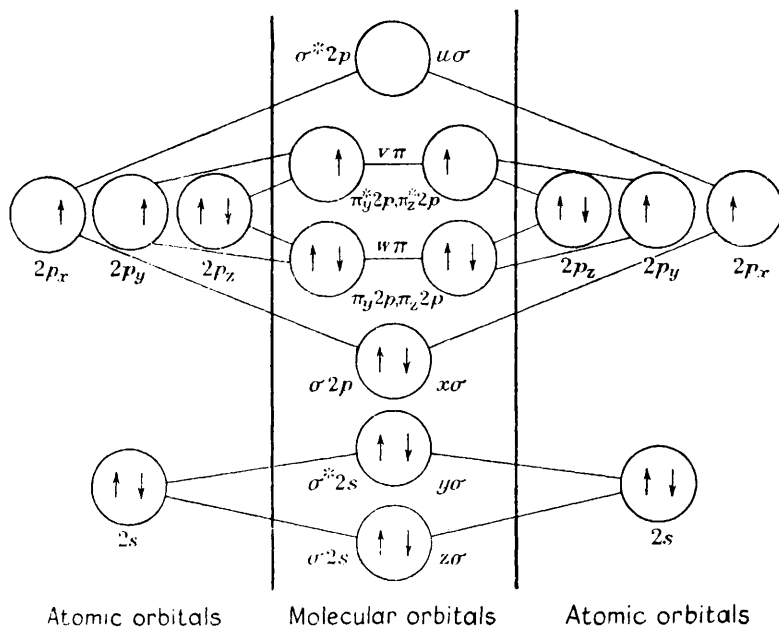

FIG. 6
Molecular orbitals for O_2.

(π_z^*2p), and will have parallel spins. In this way we see that the ground state of O_2 should be a triplet $(^3\Sigma_g)$, and should show paramagnetism. It was one of the earliest triumphs of the M.O. theory that it accounted for this somewhat unusual situation so very neatly.

The combination of A.O. into M.O. may be exhibited in a convenient pictorial way as follows. Let us take $O + O \rightarrow O_2$ (Fig. 6) as an example. On the left and right of the figure we show the various L-shell orbits of the separate atoms, and in the centre are the allowed molecular levels. Lines are drawn connecting the molecular orbitals to the atomic orbitals from which they are compounded. Energy is plotted upwards, so that $\sigma 2s$ is the lowest and σ^*2p the highest of the molecular levels. If a particular orbital is occupied by one electron, we put one arrow in the corresponding

cell, parallel arrows denoting parallel spins. In a doubly-occupied orbital the two arrows must point in opposite directions on account of the Pauli principle. Not more than two electrons may occupy any cell. In an unoccupied cell there are no arrows. Fig. 6 reveals at once how in the O_2 molecule all the levels up to $w\pi$ are completely filled, and it also shows why the parallel spins in the degenerate $v\pi$ level lead to a triplet ground state. Similar diagrams to this can, of course, be drawn for all molecules.

When, as is Li_2, the binding is due to two electrons in a σ-type M.O., we call it a σ-bond : similarly two electrons in a π-type M.O. constitute a π-bond. Consideration of the examples (i), (ii), and (iii) above enable us to say that (a) a single bond is normally σ-type, (b) a double bond is normally a σ-bond and a π-bond together, (c) a triple bond is normally a σ-bond and two π-bonds together. It is of great importance to recognise that a double bond is not merely two single bonds in a state of some strain.[23] Our analysis shows that a double bond is obtained from a single bond by superposing two electrons in a quite different type of orbit. Incidentally, as is a reasonable deduction from Figs. 5 (a) and 5 (b), the overlap of the component A.O. in a π-type M.O. is less than in a σ-type M.O. According to the criterion of maximum overlapping, this implies that the π-bond is weaker than the σ-bond, and it gives us a theoretical explanation of the high reactivity of a double bond. For it is easier to disengage the π electrons from each other and link them up with other approaching atoms.

Heteronuclear Diatomic Molecules.—There is not much difficulty in generalising these arguments to deal with heteronuclear molecules. Exactly the same principles operate, but the criterion of nearly equal energies implies that the two atomic orbitals which combine to form a M.O. will usually be different, though they must always have the same symmetry (component of angular momentum) around the bond axis. Thus for the bonding electrons in HCl, which we have seen are compounded out of $\psi(\text{H} : 1s)$ and $\psi(\text{Cl} : 3p_x)$, the M.O. is, by analogy with (1) :

$$\Psi = \psi(\text{H} : 1s) + \lambda\psi(\text{Cl} : 3p_x) \quad . \qquad . \qquad . \qquad . \quad (3)$$

but now the constant λ no longer satisfies $\lambda^2 = 1$, and must be calculated mathematically. There are two values of λ, as in (2a) and (2b), one of which gives a bonding orbital and the other an antibonding orbital. We could, if we wished, call these $\sigma 3p$ and $\sigma^* 3p$, remembering all the time that they are combinations of $H(1s)$ and $Cl(3p_x)$. If $\lambda > 1$, the M.O. has more of the chlorine atomic orbital in it, and may be said to lean on to the one side of the bond. This is exactly what does happen in HCl, for the greater electro-negative character of Cl than of H attracts the valence electrons towards the Cl. The corresponding boundary surface is sketched in Fig. 7. Accurate calculations of the shape of this M.O. (particularly its nodes) have not been made, and so Fig. 7 must be regarded as largely schematic. It is, however, sufficiently accurate for our purposes, and shows how closely the M.O. resembles a $3p_x$ atomic orbital for a hypothetical atom in which the H and the Cl nucleus have coalesced. This is an important idea, known

[23] W. G. Penney, *Proc. Roy. Soc.*, 1934, *A*, **144**, 166.

as the united-atom viewpoint.[11] Together with the separated-atom viewpoint, in which we consider what happens to the M.O. as we separate the nuclei from one another, it has proved most useful in correlating molecular orbitals and energies with known atomic ones. (A full account is given in ref. 22, pp. 19–73 ; see particularly the diagrams on pp. 40, 41 ; or else ref. 21, pp. 350, 351.) Because of their shape one sometimes says colloquially that M.O. such as in Figs. 5 (a) and 7 are " sausage type ", but the sausage is " fatter " at the Cl end than at the H end. This drift of electrons to the Cl atom gives rise to the dipole moment of the HCl bond. This moment depends almost entirely on λ, and Mulliken [24] (but see Coulson [25] for a correction in certain cases) has shown how an experimental determination of the dipole moment may be used to estimate λ.

According to this argument, the full description of HCl in its ground state is

$$\mathrm{HCl}[KL(3s)^2(\sigma 3p)^2(3p_y)^2(3p_z)^2]$$
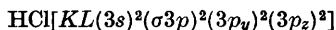
The orbitals are arranged in ascending order of energy, so that K and L denote chlorine K- and L-shells, and only the $\sigma 3p$ orbitals are genuinely molecular ; the others are atomic in character, though presumably the 3s
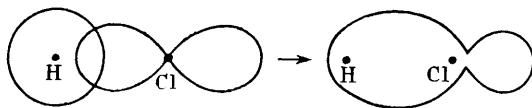

FIG. 7

Formation of molecular orbitals for HCl.

will partake very slightly of the H(1s) and the 3p_y and 3p_z of the H(2p_y) and H(2p_z) atomic orbitals.[26] This will imply a small drift of electrons towards the H nucleus, and partly cancel the dipole moment of the $(\sigma 3p)^2$ group. All this is, of course, simply the wave-mechanical description of the polarisation of non-bonding electrons.

Here is to be noticed, however, one of the strongest virtues of the M.O. viewpoint. The wave function (3) is a particular case of the general L.C.A.O. type of molecular orbital

$$\Psi = \psi_\mathrm{A} + \lambda \psi_\mathrm{B} \quad . \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

The coefficient λ, which measures the polarity of the orbit, may have any value ranging from 0 to infinity, according to the nature of the combining atoms. Thus the decreasing dipole moment in the series HF, HCl, HBr, HI is automatically included right from the start in the corresponding values of λ. Compare this with the alternative valence-bond viewpoint, where we are required to introduce a so-called pure-covalent wave function $\Psi_{\mathrm{cov.}}$(H–Cl) and a pure-ionic wave function Ψ_{ion}(H$^+$Cl$^-$), and then to superpose them in the complete wave function. Neither of these two

[24] *J. Chem. Physics*, 1935, **3**, 573.

[25] *Trans. Faraday Soc.*, 1942, **38**, 433.

[26] R. S. Mulliken, *J. Chem. Physics*, 1935, **3**, 514.

pure-wave functions corresponds to anything that can be found experimentally, so that their introduction is, in a sense, redundant.

With these principles as a background, it is not difficult to write down the M.O. representation of the electrons in most diatomic molecules (see refs. 21, p. 366, and 22, p. 78) ; and by the same method it is possible to discuss the possible excited states and deduce selection rules, very much as for atoms. In many cases these predictions may be verified by observation of ultra-violet spectra, band spectra, and ionisation potentials.

In most cases this qualitative description of the M.O. presents no great difficulty : but there are occasions when all available resources of knowledge must be used, even for a qualitative discussion. Such a case is carbon monoxide, CO. It is perhaps not surprising that this molecule, which has evaded a precise formulation for so long, provides a good example of the type of reasoning common to many M.O. arguments. In view of its intrinsic importance and its illustration of the way in which experimental evidence is absorbed into the M.O. description, we close this section by an account of the electronic structure of CO, similar in many ways to that of A. D. Walsh.[27]

Since carbon monoxide has the same number of electrons as N_2, we might expect, by the isoelectronic principle,[22] that it would formally be described just as in (ii) above (p. 155) ; i.e., we should write

$$C[1s^2 2s^2 2p^2] + O[1s^2 2s^2 2p^4] \longrightarrow CO[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4]$$
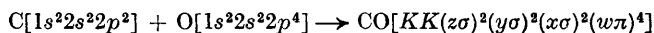
Let us see in more detail what the individual M.O. look like. It is convenient to regard the CO molecule as developed from N_2 by taking one positive charge from the first N nucleus and putting it on the second : we ask how the M.O. change in this process. It is quite clear that $z\sigma$ must represent very largely the O(2s) electrons, since these have an energy much lower than any others present ; $y\sigma$ would then be a M.O. formed from C(2s) and O($2p_x$), so that $(y\sigma)^2$ would provide one σ-bond. This uses up almost all the allowed σ-type orbits round O, leaving $x\sigma$ as mostly, but not entirely, C($2p_x$) electrons. There still remain the $(w\pi)^4$ orbits ; now a study of the spectrum of CO shows that if one of these π electrons is removed by ionisation the binding is slightly increased (as judged by inter-nuclear distance and force constant of CO$^+$ relative to CO). In this it differs from N_2 and suggests that at least two of the π electrons are practically non-bonding. Call them π_y, though there is no way of telling if they are π_y or π_z : indeed, we should expect resonance between the two possibilities. Presumably the two remaining π orbitals are binding, being compounded out of C($2p_z$) and O($2p_z$). These two electrons will convert the single bond into a double bond. It seems likely that the $y\sigma$ and $w\pi_z$ M.O. are approximately equally divided between C and O, so that there is only a small resulting dipole moment, in agreement with observation. It will be noticed how much more reasonable this is than the alternative valence-bond treatment which regards CO as a hybrid between C=O, C$^+$–O$^-$ and C$^-$≡O$^+$ in approximately equal proportions. It will also be

[27] Trans. Faraday Soc., in the press.

observed that the precise meaning to be attached here to the words " double bond " is rather hazy, since a total of 10 electrons contribute, in various degrees, to the binding between C and O ; it is to this fact that the confusion between double bond, triple bond, and semi-polar double bond has arisen.

3. *Simple Polyatomic Molecules*

Localised or Non-localised Bonds.—When we pass to polyatomic molecules we find ourselves in an immediate difficulty. We can best illustrate it by means of an example. Consider therefore the molecule of methane, CH_4. If we attempt to apply the principles of the last section, which have proved so effective for diatomic molecules, we shall argue that the ten electrons of methane are distributed so that two of them complete the carbon K-shell, and the remaining eight occupy molecular orbitals embracing all five nuclei. It is possible to calculate qualitatively [9, 28, 29] and quantitatively [30] the forms of the allowed M.O. : but the difficulty lies in this fact—it is well-known that the C–H bond has characteristic properties, such as its length, force constant, and polarity, which are effectively constant, with but small changes, from molecule to molecule. Since these properties depend upon the detailed distribution of electric charge, it is hard to see why the C–H bond should be so reproducible in character, and so independent of other substituents around the carbon atom, when the M.O. must themselves be quite sensitive to these substituents. The quandary is resolved [31] by a mathematical analysis which shows that in the ground state an alternative, and equally valid, set of M.O. can be written down, supposing that each single bond is due to two paired electrons in an orbital almost completely localised between the two nuclei concerned. Following F. Hund,[32] we may call these *localised molecular orbitals*. In this way the bonds of a polyatomic molecule each separately resemble a bond such as those discussed in Section 2 for a diatomic molecule.

The distinction that we have made between localised and non-localised M.O. is of great importance. If localised M.O. can be used, it is better to do so, for they are vastly easier to imagine and handle than are non-localised M.O. : and in addition they preserve the idea of a bond connecting two of the atoms in a polyatomic molecule. If we do not use them for those simple cases where they can be used, we do violence to the long chemical tradition dating from G. N. Lewis's famous 1916 paper on electron-pair bonds. Whenever possible, therefore, we shall use localised M.O., though the discussion at the end of Section 4 shows how, if we wish, we may translate the whole problem into the language of non-localised M.O. This language is essential when we come to aromatic and conjugated compounds, as the early part of Section 4 shows ; and it is to all intents and purposes equally essential to any discussion of the excited states (as opposed

[28] R. S. Mulliken, *J. Chem. Physics*, 1933, **1**, 490.
[29] *Idem, ibid.*, 1935, **3**, 586.
[30] C. A. Coulson, *Trans. Faraday Soc.*, 1937, **33**, 388.
[31] *Idem*, unpublished.
[32] *Z. Physik*, 1931, **73**, 1, 565 ; 1932, **74**, 1, 429.

to the ground states) of molecules such as H_2O, NH_3, and CH_4 where there is a certain amount of geometrical symmetry.

It is possible to give a plausible justification for the use of localised M.O. if we invoke the criterion of maximum overlapping (p. 151). Let us illustrate it in terms of the water molecule, H_2O. The available atomic orbitals for formation of.M.O. are the oxygen $2p_x$, $2p_y$ and the two hydrogen $1s$. Let us place the H atoms as shown on the left in Fig. 8, directly along the directions of the $2p_x$ and $2p_y$ orbitals of O. Then there is strong overlap between H_1 and $O(2p_x)$, and very little overlap between these and any of the others. The theorem referred to earlier shows that we may use H_1 and $O(2p_x)$ to form a localised M.O. of the form $\psi(I) = \psi(H_1) + \lambda\psi(O : 2p_x)$ and similarly H_2 and $O(2p_y)$ form a M.O. $\psi(II) = \psi(H_2) + \lambda\psi(O : 2p_y)$. These two M.O. are shown on the right of Fig. 8 and, to a first approximation, are quite independent of one another. It is now fairly clear that if we
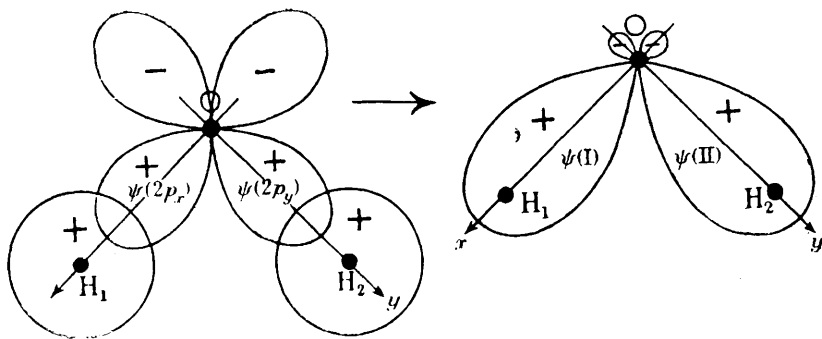

FIG. 8

Molecular orbitals for water, H_2O.

replace the hydrogen atom H_2 by some other group, *e.g.*, CH_3, we should change $\psi(II)$ but make little alteration in $\psi(I)$. In other words, the electrons in an O–H bond have characteristic wave functions ; but this general situation would not hold if the angle between the bonds was substantially altered, for if we moved H_1 towards H_2, their atomic orbitals would start overlapping with each other and with the other oxygen orbit [*e.g.*, $\psi(H_1)$ would start overlapping with $\psi(O : 2p_y)$]. Fortunately, we know from the criterion of maximum overlapping that the binding is strongest when the $H\hat{O}H$ angle is 90°, or thereabouts : it is precisely in such a condition that each O–H bond has a characteristic individual property.

Valence Angles of N *and* O.—The example of H_2O discussed above shows that if an atom has two p electrons with which to form bonds, these bonds will in general be at an angle of about 90°. This is the simplest example of the way in which stereochemical rules follow from the criterion of maximum overlapping ; but it is not the only example, for the nitrogen atom, in its ground state, has three unpaired p electrons, and these point in mutually perpendicular directions. If we wish, we can call them the x,

y, z directions. Then there is best overlap and strongest binding in the NH_3 molecule if the three hydrogen atoms are placed along these x, y, z directions, showing that the ammonia molecule is a pyramid whose apical angle is in the region of 90°. The same should be true of phosphorus and arsenic.

The molecular orbitals formed by combination of a central p atomic orbital and an attached group, such as $H(1s)$, are symmetrical around the direction of the bond. They are therefore σ-type. Thus we could describe NH_3 as

$$N(1s)^2(2s)^2[N(2p) + H(1s),\ \sigma]^6$$

and H_2O as

$$O(1s)^2(2s)^2(2p_z)^2[O(2p) + H(1s),\ \sigma]^4$$
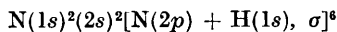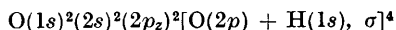
Valence Angles of Carbon.—It is not surprising that carbon introduces new features. In its ground state the C atom is $(1s)^2(2s)^2(2p_x)(2p_y)$, so that we might expect valence angles of the same kind as in oxygen, but such a scheme is obviously unable to account for the characteristic quadrivalence of a saturated carbon atom. To do this we must have four unpaired electrons ; and the importance of the hybridised orbitals introduced in Section 1 is now evident. If we may imagine a carbon atom to be "prepared" so that its four valence electrons are in the tetrahedral orbitals t_1, t_2, t_3, t_4, then we may mix these with the orbitals of four attached groups to form four localised M.O. Thus, in this scheme, methane would be described as

$$CH_4 \ .\ .\ .\ C(1s)^2,\ [C(t) + H(1s),\ \sigma]^8$$
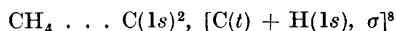
where $[C(t) + H(1s)]$ indicates that a M.O. is formed by linear combination of a carbon t orbital and the hydrogen $1s$ orbital chosen so as to ensure the maximum overlapping ; but we saw in Section 1 that the four orbitals $t_1 \ .\ .\ .\ t_4$ were very strongly directed tetrahedrally, so the valence angles in methane should have the characteristic angle 109° 28'. Needless to say, this conclusion, which finds such a neat explanation in the theory, is in complete accord with the experimental investigation of infra-red and Raman spectra. We may refer to these as tetrahedral bonds. A careful theoretical investigation [9] shows that no other type of hybridisation yields such a good binding energy, and even in molecules like CH_3Cl, where the four tetrahedral bonds are not quite equivalent, deviations from the tetrahedral angles are probably not very large.[33] The notation $[C(t) + H(1s)]$ used above must not be construed to imply that equal amounts of $C(t)$ and $H(1s)$ are used in forming the M.O. in question ; it simply means that these are the A.O. from which the M.O. is compounded. With non-polar or slightly polar bonds, to be sure, the amounts of the two components will be exactly, or approximately, equal ; but, as we have seen, a characteristic feature of the M.O. description is that it allows for any degree of relative importance in the two component atomic orbitals.

This gives a straightforward account of all the saturated carbon compounds. For example, in ethane C_2H_6, each carbon atom is in the tetrahedral state, and the carbon–carbon bond is formed by two electrons sharing

[33] W. G. Penney, *Trans. Faraday Soc.*, 1935, **31**, 734.

a M.O. compounded from two t-atomic orbitals pointing directly towards one another.   Each of the six C–H bonds is similar to a C–H bond in methane just described (for a diagram of this, and of a few other molecules, see ref. 34).   In this way we can see why the C–C and C–H bond energies are more or less constant, and we have an explanation of the additivity of bond energies, on which the whole basis of the calculation of resonance energies (Section 4) rests.   It is true that the situation is not quite so simple as this present account might lead one to believe,[35] but this is the essence of the theory.

We are now in a position to approach the ethylene molecule.[23, 36, 37] If the two carbon atoms are prepared in a trigonal state (cf. Fig. 3), we can form localised C–H bonds by combination of a H($1s$) A.O. and one of the trigonal orbitals pointing towards it : and a C–C localised M.O. arises from the combination of two of the trigonal orbitals directly facing each other.   The criterion of maximum overlapping makes all the angles 120°, in agreement with experiment, but, so far, says nothing about the relative orientation of the planes containing the two CH_2 groups.   This orientation is determined in such a way that the remaining $2p_z$ A.O. of each carbon atom join to form a π-bond, as in Fig. 5 (b).   If the two p_z orbitals are to overlap as much as possible, they must point in parallel directions, and work must be done to turn them away from this situation when we rotate one CH_2 group around the bond.   In this way the normal double bond $>C{=}C<$ is seen to consist of a σ-bond and a π-bond superposed.   We also see that the origin of the potential restricting internal rotation lies in the decreased overlap of the p_z orbitals when one end group is rotated out of coplanarity with the other.

Now the π-bond has a lower binding energy than the σ-bond ; and it may therefore be asked whether it would not be wiser to retain the tetrahedral hybridisation and let the carbon–carbon bond arise from the somewhat less efficient overlap of two pairs of tetrahedral orbitals, rather as in the pictorial scheme where two adjacent atomic tetrahedra share an edge when forming a double bond, and a vertex when forming a single bond, in the manner described by Langmuir.   W. G. Penney [38] has shown that such a scheme yields a smaller binding energy than that based on trigonal hybridisation, a result already anticipated by E. Huckel.[39]   This conclusion fits better with observations of valence angles, since tetrahedral hybridisation would favour HĈH angles of 109° 28', considerably different from the angle of 120° predicted for all aromatic carbons (except for possible strain) and verified in many distinct ways.

In acetylene the hybridisation is of the di-gonal type of Fig. 4.   This means that each C–H bond is of σ-type, the M.O. being a linear combination of H($1s$) with a carbon orbital $\psi(a)$ or $\psi(b)$ pointing directly towards it.

[34] W. C. Price, *Ann. Reports*, 1939, **36**, 47.
[35] R. Serber, *J. Chem. Physics*, 1935, **3**, 81.
[36] R. S. Mulliken, *Physical Rev.*, 1933, **43**, 279.
[37] *Idem, J. Chem. Physics*, 1935, **3**, 517.
[38] *Proc. Roy. Soc.*, 1934, *A*, **144**, 166.   [39] *Z. Physik*, 1930, **60**, 423.

The $C\equiv C$ bond arises from two di-gonal A.O. pointing at each other (a σ-bond), supplemented by two π-bonds. These latter are formed by combination first of the two $2p_y$, and then of the two $2p_z$ orbitals of the carbon atoms. This makes the whole molecule linear, and cylindrically symmetrical around the axis.

Hybridisation in Water, Ammonia, and Other Systems.—Hybridisation occurs to some extent in other atoms, though carbon is its supreme example. Let us return for a moment to the water molecule (p. 161). The HÔH angle is not exactly equal to the value 90° predicted for pure p binding because (i) the H atoms repel one another—and ordinary long-range repulsion between two separately bonded atoms is here increased on account of the fact that the O–H bonds are polar, so that there are positive charges on the two hydrogens—and (ii) a small amount of s-p hybridisation takes place. Both of these effects, which are small, conduce to an increase of the central angle, which becomes about 103°. In NH_3 the angle is increased to 109° [34] for a similar reason. During the " inversion " type of vibration, however, where the N atom passes right through the plane of the H_3 group, the hybridisation changes gradually from almost pure p to the sp^2 trigonal orbitals previously dealt with for carbon. In this way we see that there may be a gradual transition from one type of hybridisation to another. A second example of such a gradual transition occurs in the Walden inversion, when the sp^3 tetrahedral orbitals change to sp^2 trigonal ones at the half-way stage. (For further work see refs. 9 and 40.)

Hybridisation occurs in other compounds, and particularly in the transition group. For instance, Pauling and others [8a, 41, 42] have shown that sd^3 will give four tetrahedral hybrids, sp^3d^2 will give six orbitals of octahedral type (*i.e.*, directed to the six face-centres of a cube), and sp^2d will give four square-type orbitals directed to the vertices of a square, and lying in one plane. In this way the octahedral character of FeF_6^{---} and the plane tetragonal character of $Ni(CN)_4^{--}$ are nicely explained.

Bonds of σ-type which involve hybridised A.O. instead of pure s or pure p have sometimes been called q-type orbitals ; [32] however, in this account we shall continue to call them hybridised M.O.

Degree of Localisation.—We have assumed that the M.O. used above are all localised, and may be represented as L.C.A.O. of the type $\psi_A + \lambda\psi_B$. This means that Mulliken's rules [24, 25] may be used to correlate λ with the dipole moment. If the bond in question is highly polar, then λ will differ considerably from unity and the valence electrons will tend to congregate on either A or B. This will occur, for example, in the carbonyl group $>C=O$ of formaldehyde, treated by Mulliken and McMurry.[43, 44, 45] A further correlation with experiment is now possible, for the increased charge

[40] R. S. Mulliken, *J. Chem. Physics*, 1935, **3**, 506.
[41] R. Hultgren, *Physical Rev.*, 1932, **40**, 891.
[42] G. E. Kimball, *J. Chem. Physics*, 1940, **8**, 188.
[43] R. S. Mulliken, *ibid.*, 1935, **3**, 564.
[44] H. L. McMurry and R. S. Mulliken, *Proc. Nat. Acad. Sci.*, 1940, **26**, 312.
[45] H. L. McMurry, *J. Chem. Physics*, 1941, **9**, 231, 241.

on the O atom will repel the lone-pair $O(2p_y)$ electrons already there, and thus reduce their ionisation potentials. There ought therefore to be some simple relationship between the coefficient λ and the ionisation potential, as suggested by Walsh. In the case of formaldehyde the reduction in ionisation potential [34] is of the order of 2 volts.

It is very important to know just how reliable is the assumption of complete localisation. The author has made some unpublished calculations for the C–H bond in methane. These show that the wave function

$$\Psi = \psi(C : t_1) + \lambda\psi(H_a)$$

is not a completely satisfactory description of an electron in the bond between C and H_a ; for we ought to include in the wave function a small amount of $\psi(H_b) + \psi(H_c) + \psi(H_d)$ to allow the electron a small chance of migrating from the region C–H_a to the hydrogens H_b, H_c, and H_d. Numerical calculation shows that the chance of being found on H_b is about 1 in 50. We might describe this by saying that there is a small *delocalisation*, and it is likely that the order of magnitude of the effect is much the same in the other molecules of this section. To the extent that we may neglect this delocalisation, our previous descriptions are adequate.

4. Non-localised Molecular Orbitals

Non-localised Bonds.—In our earlier work we have tacitly assumed that the valence electrons can be represented by localised M.O., *i.e.*, molecular orbitals chiefly localised between two nuclei. This is almost always true for the ground states of molecules containing not more than one double bond, but it ceases to be true for excited states and for systems containing conjugated double bonds. We can illustrate the first of these situations for the particular case of methane. In the ground state (p. 162) there are four M.O. each doubly filled, and each localised in the region of one of the C–H bonds. Suppose one of these electrons is excited ; how can we say in which bond the excitation is to be found ?—for there is nothing to distinguish one bond from another. We might say, in different words, that the excitation (or " exciton ") is able to move to any of the four bonds. If this is so, our molecular orbitals must allow for the possibility of the excited electron's being on any of the five nuclei, and we are compelled to abandon our previous description in terms of localised M.O. Our molecular orbitals (see later) must now exhibit the complete symmetry of the whole molecule.

There are, however, other cases where localisation breaks down. For we have seen that localisation is possible if, when we form our M.O. from various atomic orbitals (including hybridised ones), each A.O. overlaps significantly with only one other A.O. In that case those two A.O. form a M.O. and the bond is localised. In fact, it is clear that one great merit in the various *s-p* hybridisations of carbon is that they provide A.O. from the carbon atom which are so strongly directed that they overlap very little with any A.O. other than those immediately in their direction. However, this pairing of A.O. is not by any means always possible. Consider,

as an example, the M.O. which could be compounded out of four equivalent $2p_z$ A.O. on four adjacent atoms, which we suppose (Fig. 9) to be collinear and equally spaced ; this makes all the $2p_z$ A.O. point in parallel directions at right angles to the common nuclear axis. If we call the atoms A, B, C, D and the $2p_z$ A.O. ψ_a, etc., it is perfectly obvious that ψ_b overlaps ψ_a just as much as it overlaps ψ_c. Evidently we cannot form a localised M.O. from ψ_a and ψ_b alone : we must include ψ_c and, for the same reason, ψ_d. This means that the M.O. which are compounded from these four A.O. must be of the form

$$\Psi = c_1\psi_a + c_2\psi_b + c_3\psi_c + c_4\psi_d \qquad . \qquad . \qquad . \quad (5)$$

where $c_1 \ldots c_4$ are certain constants. There are definite rules for finding these constants,[46, 47] which we shall not reproduce here ; what is important is that these electrons cannot be localised : they are therefore " mobile " electrons [48] or " unsaturation " electrons.[49] It turns out that the four A.O. $\psi_a \ldots \psi_d$ give rise to four M.O. of type (5), two of which are bonding and two anti-bonding. The wave functions have measurable values over the whole system : a typical boundary surface is shown very schematically in Fig. 9 (b). The double streamers
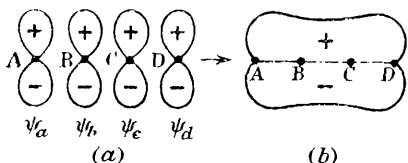

$\psi_a \quad \psi_b \quad \psi_c \quad \psi_d$
(a) $\qquad\qquad\qquad (b)$

FIG. 9

Butadiene π-orbitals.

that we described in Section 2 have now spread out to cover four atoms instead of two.

This delocalising may be expected to produce two new effects. In the first place, if the electrons " swarm " over the complete molecule somewhat like the conduction electrons of a metal, any electrical influence in one part of the system is easily propagated to any other, so that we have a basis for discussing directional substitution in conjugated compounds.[50, 51] In the second place, the fact that the electrons now have greater space in which to move implies that, in general, they have lower total energy, *i.e.*, greater binding energy, than when paired in localised bonds. This increase of binding energy could very properly be called the " delocalisation energy ", for that completely describes its origin. But on account of the fact that the M.O. theory grew up rather later than the valence-bond theory, it is more usual to call it the " resonance energy ". This energy is calculated by first determining the total energy of the mobile electrons in their completely delocalised orbits, and then subtracting from this the energy that would have been expected if the electrons had been paired in the most sensible way possible to give localised bonds, and we were able to use the principle of the additivity of bond energies. If, as a result of delocalisation,

[46] E. Huckel, Int. Conf. Phys., London Physical Soc., 1934, p. 9.
[47] J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, 1939, **35**, 811.
[48] J. E. Lennard-Jones, *Proc. Roy. Soc.*, 1937, *A.*, **158**, 280.
[49] R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41.
[50] G. W. Wheland and L. Pauling, *ibid.*, 1935, **57**, 2086.
[51] G. W. Wheland, *ibid.*, 1942, **64**, 900 ; *J. Chem. Physics*, 1934, **2**, 474.

the bond lengths in the actual molecule differ substantially from those associated with the pure single or double bonds to which the additivity rule applies, we ought to make a further allowance for " compression, energy " due to changes in bond length ; but such a correction is seldom made.[48, 49] Explicit calculations [46, 51, 52] show that the resonance energy is considerably greater for cyclic systems than for open-chain ones, in complete agreement with experiment (see ref. 2, Chap. 4).

In our discussion of the non-localised M.O. for four atoms A, . . . D we made the assumption that the nuclei were collinear ; but this is obviously a more stringent condition than is necessary, for, in order to get non-localised M.O. and the corresponding resonance energy, all that is needed is that ψ_b should overlap both ψ_a and ψ_c, and similarly for ψ_c with ψ_b and ψ_d. This may be achieved by making all the atoms coplanar, and not necessarily collinear, with the z-direction perpendicular to the plane. It is precisely this factor which causes the coplanarity in larger conjugated systems such as benzene and naphthalene. In the case of four atoms we could make the angles $A\hat{B}C$ and $B\hat{C}D$ each equal to 120°, and we should then be discussing the butadiene molecule $H_2C=CH\!-\!CH=CH_2$. In fact, a complete description of butadiene would be that each of the four carbon atoms was prepared in the trigonal state, with its valence angles all equal to 120° : and two electrons each were allotted to localised bonds C–H and C–C. This leaves four electrons, the $2p_z$ electrons of the carbon atoms, from which we compound the non-localised M.O. in the manner previously described. Two of these latter— the two most strongly bonding ones—are each doubly filled, giving a delocalisation, or resonance, energy of between 5 and 8 k.-cals./mole.

Benzene.—It is worth while discussing the benzene molecule a little more fully, since this is the classic example of non-localised bonds. A variety of evidence [e.g., 53, 54] tells us that all twelve atoms, six carbon and six hydrogen, lie in a plane, and that the carbon skeleton is a regular hexagon. This implies that the carbon atoms are in the trigonal state, where the bonds are directed in the plane of the molecule at angles of 120°. Herein, as W. G. Penney has shown,[55] lies the peculiar stability of benzene compared with other cyclic molecules C_nH_n : for if the carbon atom is to provide three bonds in a plane, there must necessarily be sp^2 hybridisation, and the strongest binding in the resulting σ-bonds occurs when the angles are each 120°, a situation that can only arise when $n = 6$. The trigonal A.O. and the hydrogen 1s atomic orbitals pair up to form localised bonds as indicated in Fig. 10 (a) (after A. L. Sklar [56]) : and each pairing of two overlapping A.O. provides a M.O. that will accommodate two electrons. Simple counting shows that this leaves us with six unused electrons, namely, the $2p_z$ electrons from each of the six carbon atoms. These are shown somewhat diagrammatically in Fig. 10 (b), where, for pictorial convenience,

[52] J. K. Syrkin and M. E. Diatkina, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1946, 153.

[53] C. K. Ingold *et al., J.*, 1936, 912.   [54] C. K. Ingold *et al., J.*, 1946, 222.

[55] *Proc. Roy. Soc.*, 1934, *A*, **146**, 223.

[56] *J. Chem. Physics*, 1937, **5**, 669 ; M. G. Mayer and A. L. Sklar, *ibid.*, 1938, **6**, 645.

the " dumb-bell " orbitals have been drawn quite separate from each other : they really overlap more than the diagram shows. Indeed, this overlapping leads to completely non-localised M.O., in which the double streamers formerly drawn for ethylene [Fig. 5 (b)] and butadiene [Fig. 9 (b)] stretch right round the ring, one streamer above and the other below the plane of the nuclei, as in Fig. 10 (c).

Out of the six $2p_z$ A.O. we can compound six distinct molecular orbitals of the form

$$\Psi = c_1\psi_1 + c_2\psi_2 + \ . \ : \ . \ + c_6\psi_6$$

where ψ_1 is the A.O. at nucleus 1, etc. Three of these M.O. are bonding and three are anti-bonding.[57, 58] As we have exactly six mobile electrons
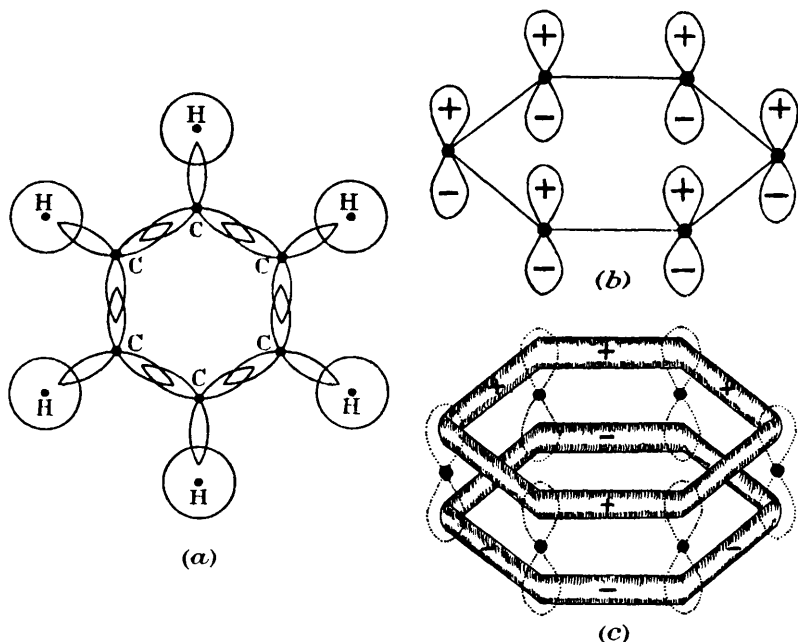

FIG. 10

(a) σ Orbitals ; (b) π atomic orbitals ; (c) π molecular orbitals.

to allot to the molecular levels, they will completely occupy the bonding orbits, and make their contribution to the energy of binding. The delocalisation, or resonance, energy is large, and amounts to rather less than 40 k.-cals./mole.

It is obvious that all this throws new light on the old idea of Kekulé, in which the benzene ring was regarded as being in a state of dynamic oscillation between structures containing alternate single and double bonds.

[57] E. Huckel, Z. Physik, 1931, **70**, 240 ; Z. Elektrochem., 1937, **43**, 752, 827.
[58] C. A. Coulson, Proc. Roy. Soc. Edin., 1941, A, **61**, 115.

There is nothing in the M.O. account that remotely resembles the separate Kekulé structures : indeed, every bond is always entirely equivalent to every other bond, and explicit calculation shows that the electrons are uniformly distributed on all the nuclei and bonds. We have, in fact, neither single nor double bonds, but a state in between the two (mesomeric state).

This account of benzene may be tested in three ways. First, all the bonds are found to be equal in length by X-ray analysis, and the length agrees with that calculated theoretically.[59] Second, electronic transitions among the mobile levels, called by Mulliken N $\rightarrow$ V transitions, give rise to characteristic absorption which may be calculated, and for which quite good agreement with experiment is found.[60, 61] Third, there are anomalous magnetic properties : for the mobile electrons may be regarded as tiny currents flowing round the ring. Normally they flow equally in both directions, but under the influence of a magnetic field there is a preference for one direction rather than the other, giving rise to a large diamagnetism when the magnetic field is perpendicular to the plane of the molecule. This is precisely what is found experimentally. (For further work on this subject see refs. 62—64.)

Other Molecules, especially CO_2.—The calculations for benzene are typical of many others, and they explain the characteristic properties of naphthalene, diphenyl, and many other similar condensed and aromatic systems (see, *e.g.*, refs. 46—48, 51, 52, 59). They may also be used for systems, such as pyridine, containing a hetero-atom.[51, 65] Here also the mobile electrons flow round the ring, but the greater electronegativity of the N atom is shown by a greater concentration of charge there than on the other atoms of the hexagon. They may also be applied to CO_2, and here, because of the intrinsic interest of this molecule, it is worth giving the description rather more fully. We follow fairly closely, but not exactly, the account given by R. S. Mulliken.[66]

Let us call the molecule, which is known to be linear, A–C–B, where A and B are oxygen atoms, and imagine ourselves to be progressively filling the allowed electronic levels. First, we complete the three K-shells, and then the $(2s)^2$ groups on A and B. The carbon atom -C is prepared in the di-gonal form of hybridisation (Fig. 4), and overlap between one of these orbitals and the $2p_x$ orbital of the appropriate oxygen atom gives two almost localised σ-type bonds, which we might write $\sigma_A 2p$ and $\sigma_B 2p$. These use four electrons, and leave us eight. These eight fit into four M.O., two of which are composed of atomic $2p_y$ orbitals and the other two, entirely equivalently, of atomic $2p_z$ orbitals. These four M.O. are non-localised,

[59] J. E. Lennard-Jones and J. Turkevich, *Proc. Roy. Soc.*, 1937, *A*, **158**, 297.
[60] R. S. Mulliken and C. A. Rieke, *Rep. Prog. Physics*, 1941, **8**, 231.
[61] A. Maccoll, this vol., p. 16.
[62] F. London, *J. Physique*, 1937, **8**, 397.
[63] H. Brooks, *J. Chem. Physics*, 1940, **8**, 939.
[64] *Idem, ibid.*, 1941, **9**, 463.
[65] H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, 1947, **43**, 87 ; M. J. Dewar, *ibid.*, 1946, **42**, 764.
[66] *J. Chem. Physics*, 1935, **3**, 720.

very much as in the case of butadiene (Fig. 8), except that we have three nuclei instead of four : the more bonding (written $\pi + \pi + \pi$) is a double-streamer extending over all three nuclei, and probably fairly equally divided among them, the less bonding (written $\pi - \pi$) is associated solely with the oxygen atoms A and B, and is very nearly without bonding power at all. Thus the molecule is cylindrically symmetrical around the axis, and, apart from its K-shell electrons, is :

$$(O_A : 2s)^2(O_B : 2s)^2(\sigma_A 2p)^2(\sigma_B 2p)^2(\pi_y + \pi_y + \pi_y)^2(\pi_z + \pi_z + \pi_z)^2(\pi_y - \pi_y)^2(\pi_z - \pi_z)^2$$

Group Theory : Non-localised M.O. in General.—We conclude this section with an explanation of the way in which the symmetry properties of a molecule determine the possible types of M.O. when we remove the restriction to being localised between two adjacent nuclei. We have already seen that the excited states of molecules compel us to think in terms of M.O. covering the whole nuclear framework. Indeed, it is in the study of excited states, transition moments (*i.e.*, intensities), and selection rules that the work we are about to describe is particularly valuable. It will be simplest to describe it in terms of an example. Consider therefore the allowed M.O. for tetrahedral methane, CH_4.

The M.O. for the valence electrons of methane must be compounded from carbon $2s$, $2p_x$, $2p_y$, $2p_z$ (this automatically includes hybrids of these, if they are necessary) and the four hydrogen $1s$ A.O. Let us think first of the hydrogen orbitals. If one of these (call it ψ_a) forms part of a M.O., then by symmetry all the others must be involved equally. Thus, one possible combination is

$$\psi_a + \psi_b + \psi_c + \psi_d . \qquad . \qquad . \qquad . \qquad . \qquad (6)$$

since this obviously gives equal weight to all hydrogen atoms. This is a particularly symmetrical combination, or grouping, of the H_4 group. We may say that it possesses the complete symmetry of the molecule, since any interchange of nuclei leaves it unaltered, but it is not the only possible grouping ; for example,

$$\psi_a + \psi_b - \psi_c - \psi_d . \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

is acceptable, since the weights (or probabilities) of the component hydrogen orbitals are in the ratio $1^2 : 1^2 : (-1)^2 : (-1)^2$; that is, they are all equal. It is not difficult to see that all permitted groupings of this kind are included in the expressions $\pm \psi_a \pm \psi_b \pm \psi_c \pm \psi_d$. Now, only four of these can possibly be independent, for we only started with four atomic orbitals $\psi_a \ldots \psi_d$. Mulliken [36, 67] has shown that the most sensible combinations to choose are (6) and the three of type (7) where there are two positive and two negative signs. The latter have less fundamental symmetry than (6), but they are evidently entirely equivalent among themselves, and may be shown to be approximately of the same symmetry type as the three co-ordinates x, y, z. For example, as Fig. 11 shows, the wave function (7) changes sign when we reflect it in the yz plane, and so does the co-ordinate x.

A convenient name for these combinations of the H_4 atomic orbitals is *composite orbitals*, or *group orbitals*. It is important to realise that these

[67] R. S. Mulliken, *J. Chem. Physics*, 1933, **1**, 492.

particular groupings are forced upon us by the symmetry of the molecule. In NH_3, for example, where there are only three hydrogens, the groupings are not the same as in (6) and (7) ; but they are the same in CCl_4, where ψ_a, etc., now refer to the chlorine $3p$ A.O. directed towards the central carbon atom. Mulliken [36] has shown how the mathematical apparatus of group theory may be employed to sort out the permitted composite orbitals, and arrange them in so-called " symmetry classes ". These symmetry classes include at the same time both the composite orbitals of the attached atoms and also the A.O. of the central atom (ref. 3, p. 219). This analysis is somewhat complicated, and we shall not develop it here : suitable accounts of the theory, which is useful in studying vibration frequencies as well as electronic levels, are found in refs. 68—72.

The importance of the sub-division into symmetry classes cannot be exaggerated. It enables us to introduce a seventh fundamental principle to be added to the six enunciated in Section 2 (a)—(f) ; for it may be shown that

(g) M.O. can only be formed by linear combination of atomic and group orbitals of the same class : and allowed transitions are only from one class to another class.

It will be recalled that when we were discussing homonuclear diatomic molecules such as H–H (p. 152), we introduced the g and u classification, and we stated that allowed transitions w e r e necessarily $g \rightarrow u$ or $u \rightarrow g$. This is, of course, merely an example (actually the simplest possible molecular example) of the way in which the geo-metrical shape of the molecule determines symmetry classes for the allowed M.O.

FIG. 11
Methane.

In the case of CH_4, the group orbital (6) and the carbon orbital $C(2s)$ are the only ones in their particular class, so that they alone combine to form a M.O. Linear combinations of this kind, which have very great symmetry, are called a-molecular orbitals. They have the analytical representation

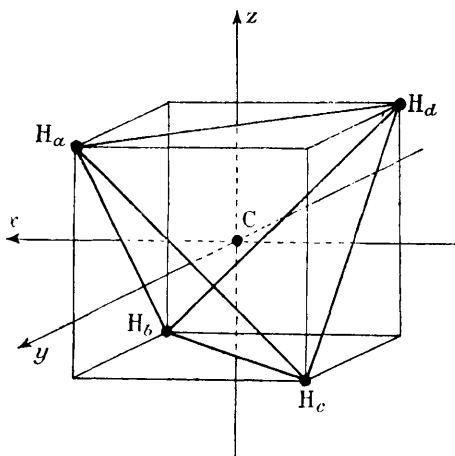$$[a] = \lambda C(2s) + \mu(\psi_a + \psi_b + \psi_c + \psi_d)$$

[68] H. Margenau and G. M. Murphy, " Mathematics of Physics and Chemistry ", Van Nostrand, 1943, Chap. 15.

[69] J. Rosenthal and G. M. Murphy, *Rev. Mod. Physics*, 1936, **8**, 317.

[70] H. Eyring, J. Walter, and G. E. Kimball, " Quantum Chemistry ", Wiley, 1944.

[71] A. G. Meister, F. F. Cleveland, and M. J. Murray, *Amer. J. Physics*, 1943, **11**, 239.

[72] A. G. Meister and F. F. Cleveland, *ibid.*, 1946, **14**, 13.

where λ and μ are certain constants. Similarly the type (7) group orbitals of H_4 combine only with $C(2p_x)$, etc., and a glance at Fig. 11 will show that these combinations (called t-type) must be

$$[t_x] = \lambda'C(2p_x) + \mu'(\psi_a + \psi_b - \psi_c - \psi_d)$$

λ' and μ' are two new constants, and $[t_y]$ and $[t_z]$ are just like $[t_x]$, apart from the change in direction. Values of the constants λ, μ, λ', μ' have been calculated by Coulson.[30] The ground state of the molecule, omitting the carbon K-shell, would be simply $[a]^2[t_x]^2[t_y]^2[t_z]^2$, and there would be excited states where, for example, one of the $[a]$ electrons moved to another, more excited, M.O. of type $[t]$.

A similar analysis could be used for any other symmetrical molecule : the greater the symmetry, the greater is the value of this group theory analysis in sorting out the allowed types of M.O. and the allowed transitions between them. It will be recognised that division into symmetry classes is the molecular parallel to the division of atomic orbitals into s, p, d, ... types. Indeed the likeness is sometimes very close, as in $[a]$ and $[t_x]$ above, which are very similar to atomic s and p_x states. But there is one important comment to be made—group theory tells us what types of M.O. may occur, but it does not tell us the coefficients (*e.g.*, λ, μ above) that occur in them, or the relative order of the energies of various M.O. of different symmetry types. It is possible, however, to estimate these by various empirical rules,[24, 29] so that reliable descriptions of the ground state and the allowed transitions may be obtained qualitatively : a quantitative study is usually quite prohibitively complicated, as some recent work on diphenyl shows.[73]

5. General Topics

Hyperconjugation.—When we were discussing the M.O. for methane (p. 165) we showed that it was not quite correct to describe a particular bond (*e.g.*, $C-H_a$ in Fig. 11) by two electrons having a localised M.O. :

$$\Psi = \psi(C : t_1) + \lambda\psi(H_a) \qquad . \qquad . \qquad . \qquad . \qquad (8)$$

but a small degree of delocalisation was necessary. Thus (8) was replaced by

$$\Psi = \psi(C : t_1) + \lambda\psi(H_a) + \mu[\psi(H_b) + \psi(H_c) + \psi(H_d)] \; . \qquad . \qquad (9)$$

in which μ was a constant considerably smaller than λ. At the time we interpreted (9) to mean that electrons in the bond $C-H_a$ had a small chance, of about 1 in 50, of being found on one of the other hydrogens such as H_b. Our introduction of group orbitals (p. 170), however, shows that another interpretation could be given as follows : If it were not for the $H_bH_cH_d$ group the bond $C-H_a$ would indeed be localised with a wave function (8) ; but the other three hydrogens are able to attract the electrons from the region $C-H_a$, behaving for this purpose not primarily as individual atoms but as a group. That is because the last terms of (9) are a group combination. In fact, we could say that the combination $[\psi(H_b) + \psi(H_c) + \psi(H_d)]$ was of the right symmetry to interact with $\psi(H_a)$ and $\psi(C : t_1)$. It is obvious

[73] A. London, *J. Chem. Physics*, 1945, **13**, 396.

from what we have said in earlier paragraphs that the last two atomic orbitals are symmetrical around the bond direction C–H_a ; but a glance at Fig. 12 (a) shows that this is also approximately true for the group orbital $[\psi(H_b) + \psi(H_c) + \psi(H_d)]$. This figure shows contours of constant ψ for this group orbital, the plane of the paper being the plane through the three nuclei b, c, d shown in the diagram. The direction of the C–H_a bond is perpendicular to this plane through the point marked with a cross. It is clear that there is approximate symmetry around the bond direction. [More precisely we should say that all three parts of (9) were unchanged by a rotation of $\pm 2\pi/3$ around the axis of symmetry ; they are therefore in the same symmetry class for a rotation described as C_3.] Thus all three parts of (9) are needed in the M.O. for the bond C–H_a. Fortunately, there is relatively little overlap between the composite orbital for $H_bH_cH_d$ and $\psi(C : t_1)$, for the tetrahedral orbital points directly away from the carbon towards H_a. Thus the delocalisation is not large. This type of interaction has been called σ-hyperconjugation.

In this way we may infer yet another principle—the eighth and last one—to guide us in the formation of molecular orbitals ; this principle shows the effect of a group of atoms, or a radical, upon an adjacent bond.

(h) When a group of atoms, adjacent to a bond but not actually part of it, is able to provide a composite M.O. of the right symmetry to combine with the electrons of the localised bond, a measure of delocalisation takes place. This delocalisation, like all delocalisations, is associated with a lowering of the total energy, $i.e.$, increased binding.

It is difficult to estimate the magnitude of this delocalisation energy ; but there is evidence that in diamond, where every C atom is surrounded by four other C atoms occupying the positions taken up by the H in methane, the delocalisation energy amounts to about 5 k.-cals./mole out of a total binding energy of 124 k.-cals./mole. This, if correct, is a reasonably important fraction of the whole.

Its importance, however, lies more in this conclusion—the fundamental properties of any one bond, as, $e.g.$, C–H or C–Cl, are not entirely independent of the adjacent bonds, but influences are propagated from one bond to another. In recent years there has been accumulating a large variety of experimental evidence for these small but significant changes. Now we can understand them a little more clearly from the theoretical side.

There is, incidentally, another way in which the $H_bH_cH_d$ group that we have described above can function. In Fig. 12 (a) we showed the σ-type behaviour of this group, leading to interaction between it and C–H_a ; but it may also function with a group wave function

$$[\psi(H_b) - \tfrac{1}{2}\{\psi(H_c) + \psi(H_d)\}] \qquad . \qquad . \qquad . \qquad . \quad (10)$$

Contours of this function are shown in Fig. 12 (b), which should be compared with Fig. 12 (a). Evidently there is now a line of nodes running across from left to right, separating regions of positive and negative ψ. This combination is clearly of the same general symmetry (π-type) as the dumb-bell orbital of an isolated carbon atom, shown on the right [Fig. 12 (c)].

In this way the $H_bH_cH_d$ group can behave as a pseudo-atom with a π-orbital perpendicular to the C–H_a bond.   Such a composite orbital could enter into combination with other orbitals on adjacent atoms to form M.O.   It is true that in methane such interaction will not take place, for the simple reason that there is nothing in the C–H_a bond of the proper symmetry ; but if we have a —CH_3 group attached to a benzene nucleus, as in toluene C_6H_5—CH_3, the double-streamer orbitals of the benzene ring are of the required symmetry type π, and there will be interaction between them and the group orbital (10), leading to M.O. in which electrons from the methyl group can migrate into and out of the ring system.   It is the resulting delocalisation of the electrons that provides the dipole moment of toluene and contributes and additional stability of about 1·5 k.-cals./mole [49] found in branched-chain paraffins as well.   It is also the cause of the so-called " alkylation red-shift " in the absorption spectra of many dye molecules
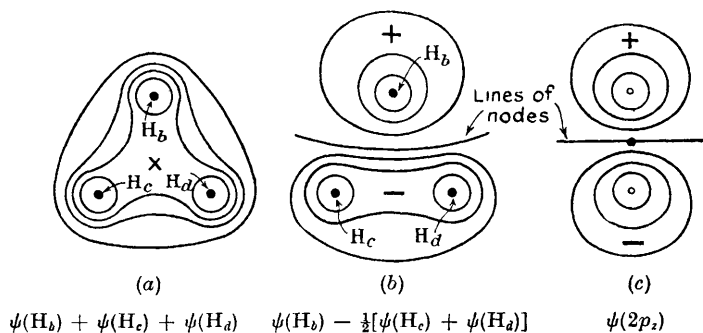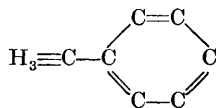

(a) (b) (c)

$\psi(H_b) + \psi(H_c) + \psi(H_d)$ $\psi(H_b) - \frac{1}{2}[\psi(H_c) + \psi(H_d)]$ $\psi(2p_z)$

FIG. 12
Group orbitals.

but as the relation between colour and chemical constitution is dealt with elsewhere in this volume [61] we shall not discuss this aspect further.   In a formal sort of way we could write a bond structure for toluene such as

This explains why the American workers refer to this phenomenon as π-hyperconjugation.[49, 74]   In the case of toluene we may expect the C–CH_3 bond to be somewhat strengthened by becoming an " acceptor " bond, drawing its new strength from the " donor " bonds on either side.   There are experimental grounds for believing that its length—and particularly that in the somewhat similar dimethyldiacetylene [75]—is reduced below the value appropriate to a normal single C–C bond.   Hyperconjugation of this

[74] R. S. Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265.
[75] G. W. Wheland, " Theory of Resonance ", Wiley, 1944, p. 286.

kind between a methyl group and an aromatic system may possibly be significant in the action of carcinogenic substances (for full references, see ref. 76).

The remainder of this report is devoted to a series of very brief introductions to other work involving molecular orbitals ; it is intended to help those who wish to follow any particular point in more detail, by indicating where such work may be found.

Partial Bond Order.—As a result of delocalisation in the electrons of aromatic and conjugated systems, the bonds are neither pure single nor pure double, but must be described in terms of a fractional bond order. Each one of the mobile electrons contributes a partial bond order to each of the bonds, the total order of any bond being the sum of all such contributions (*e.g.*, four in butadiene and six in benzene). Coulson [77] has shown how these bond orders may be calculated from the molecular orbitals, and finds values of $1\frac{2}{3}$ for all the bonds in benzene, and 1·894 and 1·447 for the so-called double and single bonds respectively in butadiene ═──═. Other bond orders are in refs. 47, 49, 65, 78. The idea of fractional bond order had earlier been introduced, under the title " percentage double bond character ", by L. Pauling and his collaborators,[79, 80] and by W. G. Penney [81] and others.[82, 83] If we know the fractional bond order of a bond we can calculate its length, as was first shown by J. J. Fox and A. E. Martin ; [84] these workers drew a smooth curve showing how the C–C bond length and bond energy varied with bond order. In this manner the theory may be tested experimentally.[47, 85] An alternative calculation of bond lengths by direct methods and without reference to bond order has been given by J. E. Lennard-Jones.[48] Substantially similar results are obtained in all cases. The partial bond order is also important when discussing vibrational frequencies, in ground and excited states, since evidently there must be a smooth relation between bond order and force constant (see, *e.g.*, ref. 58, and unpublished work of Longuet-Higgins and the writer). Partial bond order also enables us to discuss the time-honoured question of bond fixation, though on account of the fact that bonds are no longer pure single or pure double (in conjugated compounds) we can no longer think of complete fixation ; but if a particular bond order is high, we may say that a double bond is more nearly " fixed " in this position than if the order is low. In this way bond fixation in naphthalene,[86, 59] in quinones,[87, 88] and in nitrogen compounds such as pyrrole and carbazole [65] has been investigated, with

[76] R. Daudel; *Rev. Sci.*, 1946, 37.
[77] *Proc. Roy. Soc.*, 1939, *A*, **169**, 413.
[78] H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, 1946, **42**, 756.
[79] L. Pauling, L. O. Brockway, and J. Y. Beach, *J. Amer. Chem. Soc.*, 1935, **57**, 2705.
[80] L. Pauling, H. D. Springall, and K. J. Palmer, *ibid.*, 1939, **61**, 927.
[81] *Proc. Roy. Soc.*, 1937, *A*, **158**, 306.
[82] W. G. Penney and G. J. Kynch, *ibid.*, 1938, *A*, **164**, 409.
[83] C. V. Jonsson, *Arkiv Kemi, Min., Geol.*, 1942, **15**, *A*, No. 14.
[84] *J.*, 1938, 2106.   [85] C. A. Coulson, *Nature*, 1944, **154**, 797.
[86] *Idem, J. Chem. Physics*, 1939, **7**, 1069.
[87] *Idem, Trans. Faraday Soc.*, 1946, **42**, 106.   [88] M. G. Evans, *ibid.*, p. 113.

conclusions in substantial agreement with experimental evidence ; and some difficulties in the interpretation of the Mills–Nixon effect [78] have been elucidated.

Charge Distribution and Free Valence.—There are several calculations of the charge distribution and electronic energies in systems containing atoms other than carbon and hydrogen, though certain fundamental points still require to be cleared up : thus there seems no reasonably convincing method for calculating the absolute values of some of the resonance and Coulomb integrals that appear in the course of the work. These integrals have either to be guessed, or, alternatively, values are chosen to fit some molecules, enabling us to predict properties of other molecules and to correlate different properties of the same molecule. We have already referred to calculations for the carbonyl group,[43, 44, 45] the quinones,[87, 88] pyridine, etc. ; [50, 51, 65] to this list we ought to add the discussion of Wurster's salts,[89] the chlorobenzenes,[90] and naphthyls,[91] and a whole series of substituted benzenes.[92–95] H. C. Longuet-Higgins [96] has shown how the charge distribution in heteromolecules may be used to predict the so-called resonance-dipole moment (ref. 75 ; Section 5.4). Unfortunately, although experimental evidence is becoming increasingly available, a complete correlation between theory and experiment has not yet been achieved. A completely general molecularorbital treatment of conjugated systems, by which it is possible to study both the bond orders and charge densities, and to estimate how these are changed when the environment of any part of the molecule is altered, has been made by C. A. Coulson and H. C. Longuet-Higgins and is in course of publication. It seems likely that this type of treatment will prove useful in a study of reactions and reactive centres, along the lines indicated by M. G. Evans and E. Warhurst [97] and by G. W. Wheland and L. Pauling.[50, 51]

To some extent the reactivity of a particular atom in a molecule must be conditioned by the number and strength of the bonds that it is already forming. Indeed, this view is already latent in Werner's conception of " residual affinity ", and it is implicit in Thiele's famous " Theory of Partial Valence ". The author (ref. 98 and later work in publication) has shown how the idea of fractional bond order may be used to give a quantummechanical version of Thiele's theory, and to provide an absolute measure of the partial valence at each of the atoms in a conjugated molecule. This theory is of particular importance for deciding at what points polymerisation is likely to take place, and it may be used to justify R. Lutz's principle [99] of conjugate addition. Numerical results obtained for the partial free valence at different centres agree closely with those obtained in an alternative

[89] M. Goeppert-Mayer and K. J. McCallum, *Rev. Mod. Physics*, 1942, **14**, 248.

[90] J. Sherman and J. A. Ketelaar, *Physica*, 1939, **6**, 572.

[91] J. A. Ketelaar and G. W. Van Oosterhout, *J. Chem. Physics*, 1945, **13**, 448.

[92] A. L. Sklar, *Rev. Mod. Physics*, 1942, **14**, 232.

[93] *Idem, J. Chem. Physics*, 1942, **10**, 135.   [94] *Idem, ibid.*, 1939, **7**, 985.

[95] E. Huckel, *Z. Physik*, 1931, **72**, 310.   [96] Unpublished calculations.

[97] *Trans. Faraday Soc.*, 1938, **34**, 614.

[98] C. A. Coulson, *ibid.*, 1946, **42**, 265.

[99] *J. Amer. Chem. Soc.*, 1929, **51**, 3008.

treatment of this problem using the valence-bond method, and developed by C. V. Jonsson,[83] N. Svartholm,[127] and by R. Daudel and his collaborators.[128]

Systems with an odd number of electrons are usually free radicals. The energies, bond orders, electron affinities and free valences of several of these systems have been calculated by G. W. Wheland,[52] L. Pauling and G. W. Wheland,[121] C. A. Coulson,[100] W. E. Moffitt and C. A. Coulson,[101] W. J. C. Orr (quoted by J. L. Bolland and G. Gee,[102]) E. Huckel,[46, 57, 103, 104] and by Penney and Kynch.[82] The relation between the energies of free radicals and certain dissociation products has been discussed by these writers and by E. C. Baughan, M. G. Evans, and M. Polanyi,[105] and by G. W. Wheland (ref. 75, Section 7.6).

In a similar way one may discuss di-radicals,[126] particularly the so-called meri-quinones of which a typical example is Chichibabin's hydrocarbon

$$Ph_2C = \langle\!\!=\!\!\rangle = \langle\!\!=\!\!\rangle = CPh_2$$
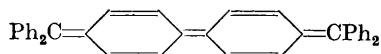
A. J. Namiot, M. E. Diatkina and J. K. Syrkin [106] have shown that at sufficiently low temperatures substances of this kind exist in a singlet diamagnetic state, but that as the temperature rises, some of them may acquire a paramagnetic condition to be interpreted as a di-radical state.

Exact Calculations.—Practically all the calculations described so far are approximate : *i.e.*, certain assumptions are made which, although physically reasonable, are not exact, or the values of certain quantities which occur in the analysis are obtained by correlation with experiment. So far as the author knows, the only complete straightforward M.O. calculations are for H_2^+ (a singularly simple case since an exact solution may be obtained if the correct types of co-ordinates are used ; see, *e.g.*, refs. 18—20, 107—109), H_2,[14, 15] H_3^+,[110] HeH^+,[111] LiH^+,[112] Li_2^+,[113] Li_2,[114] and CH_4.[30] This list makes no attempt to include a large number of other calculations in which ionic terms or polar terms are added : for this, while it certainly improves the accuracy of the result, destroys the genuine M.O. character of the final wave function. It is very doubtful whether exact calculations of other molecular systems are worth making by this method.

Electron Velocities.—Most of the work previously described has been concerned with the space distribution of molecular electrons, but in a series

[100] *Proc. Roy. Soc.*, 1938, *A*, **164**, 383.
[101] *Trans. Faraday Soc.*, in the press.
[102] *Ibid.*, 1946, **42**, 244.   [103] *Z. Physik*, 1933, **76**, 628 ; **83**, 632.
[104] *Trans. Faraday Soc.*, 1934, **30**, 40.
[105] *Ibid.*, 1941, **37**, 377.
[106] *Acta Physicochim. U.R.S.S.*, 1946, **21**, 23 ; *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **48**, 267.
[107] B. M. Dickinson, *J. Chem. Physics*, 1933, **1**, 317.
[108] E. A. Hylleraas, *Z. Physik*, 1931, **71**, 739.
[109] G. Steensholt, *ibid.*, 1936, **100**, 547 ; *Norske Vid. Akad. Avh.*, 1926, No. 4.
[110] C. A. Coulson, *Proc. Camb. Phil. Soc.*, 1935, **31**, 244.
[111] C. A. Coulson and W. E. Duncanson, *Proc. Roy. Soc.*, 1938, *A*, **165**, 90.
[112] J. K. Knipp, *J. Chem. Physics*, 1936, **4**, 300.
[113] H. M. James, *ibid.*, 1935, **3**, 9.
[114] C. A. Coulson and W. E. Duncanson, *Proc. Roy. Soc.*, 1943, *A*, **181**, 378.

of papers [115] C. A. Coulson and W. E. Duncanson have shown how the M.O. method may be used to describe electron velocities ; and they have related the resulting velocity distribution function to the shape of the Compton X-ray line, by means of which the theoretical predictions may be checked. The agreement is quite satisfactory. Similarly, C. A. Coulson and R. P. Bell [116] have shown that the virial theorem is satisfied by M.O. wave functions if the screening constant is suitably chosen.

Improved Calculations for Conjugated Systems.—Improvements in accuracy upon the early work on hyperconjugation [49] have been made by R. S. Mulliken and C. A. Rieke,[117] and have been applied to more complex conjugated systems and free radicals by G. W. Wheland.[118]   The self-consistence of the method of M.O. has been verified by C. A. Coulson and G. S. Rushbrooke,[119] and the author [120] has shown how the energy of such systems may often be evaluated with some facility by the use of complex integration.

   Group Theory.—Group-theory relations between the M.O. method and the valence-bond method have been considered by J. H. Van Vleck.[122]   A further comparison of the two methods, which shows that there are cases (*e.g.*, *cyclo*butadiene) when the simple M.O. theory is inadequate, has been given by Wheland,[123] and there are other comparisons by Hund,[32a] and Van Vleck.[9] Group theory has been applied to study the relation between diatomic and polyatomic molecules and to indicate some of their magnetic properties by J. E. Lennard-Jones.[124]   A discussion of the diamagnetism of methane has been given by C. A. Coulson.[125]

   In conclusion, the author wishes to acknowledge permission from the Council of the Royal Society of Edinburgh to reproduce certain figures from a paper (ref. 58).

[115] *Idem, Proc. Camb. Phil. Soc.*, 1941, **37**, 55, 67, 74, 397, 406 ; 1942, **38**, 100 ; 1943, **39**, 180.
[116] *Trans. Faraday Soc.*, 1945, **41**, 141.
[117] *J. Amer. Chem. Soc.*, 1941, **63**, 1770.   [118] *Ibid.*, p. 2025.
[119] *Proc. Camb. Phil. Soc.*, 1940, **36**, 193.
[120] C. A. Coulson, *ibid.*, p. 201.
[121] *J. Chem. Physics*, 1935, **3**, 315.   [122] *Ibid.*, p. 803.
[123] *Proc. Roy. Soc.*, 1938, *A*, **164**, 397.
[124] *Trans. Faraday Soc.*, 1934, **30**, 70.
[125] *Proc. Physical Soc.*, 1942, **54**, 51.
[126] E. Huckel, *Z. physikal Chem.*, 1936, *B*, **34**, 339.
[127] *Arkiv Kemi, Min. Geol.*, 1942, **15**, *A*, No. 13.
[128] R. Daudel and A. Pullmann, *Compt. rend.*, 1945, **220**, 889 ; **221**, 201, and other papers in this journal and *J. Physique* in 1945 and 1946.