

RECENT DEVELOPMENTS IN VALENCE THEORY

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ABSTRACT

In the early 1930s valence theory was confused by a conflict between molecular-orbital and valence-bond approximations. But during the 1940s a reconciliation between the two methods was found; and from that time until now much the greater effort has been put into MO calculations. These calculations have been tremendously enriched in the 1960s by the widespread use of electronic computers, and package programmes.

A study of the charge distribution calculated for covalent bonds shows that the early picture of a bond as being associated with a build-up of charge between the nuclei is still valid. However, if bonding electrons are drawn into this region, other electrons tend to get forced out of it; recent studies show the importance of these two effects. The early representation of these charge-clouds in terms of hybridization was particularly fruitful in the 1940s, but is now recognized as too restrictive.

The development of the experimental techniques of photoelectron spectroscopy and x-ray spectroscopy now enables a direct verification to be made of the early ideas of individual molecular orbitals. In this way Mulliken's original theoretical descriptions have been triumphantly justified.

Another aspect of valence theory that has developed in recent years is that of the relation between σ and π electrons. No longer may the π electrons be treated as if they were independent of the σ electrons, but a close relationship exists between them.

The account concludes with a description of those situations where the number of valence electrons is either too few (electron-deficient molecules) or too large (electron-rich molecules) to provide the normal complement of two electrons per bond. In each case the simple concept of a bond needs to be modified. Attention is drawn to the remarkable way in which theoretical concepts have recently received experimental verification.

INTRODUCTION

Valence theory is much older than the fifty years referred to in the title of this Symposium. We should at the very least go back to 1861 when Odling, Crum Brown and others started using the horizontal line—which has been the symbol for a chemical bond ever since; and we should think of Kekulé only a few years later trying to use the symbol to indicate some sort of geometrical relationship between the various atoms of a polyatomic molecule; or Butlerov, with his early feeling for chemical structure. Moreover, for these last hundred years, as Mulliken and Van Vleck have shown in their

accounts, the mental picture of a valence bond has continually been changing. But in the last fifty years, under the influence of wave mechanics, it seems that we are reaching some more definitive conclusions. We can start talking seriously, and in a quantitative manner, about what is meant by a bond, and we can ask questions about its size and shape. Until questions such as these could be asked and answered, any account of valence theory was bound to be largely empirical or descriptive, and at best semi-quantitative. This is not to disparage the work of the early chemists, but rather to draw attention to the remarkable developments that have become possible since Schrödinger introduced the wave equation in 1926, and, in the following year, Heitler and London made the first, and famous, excursion into quantum chemistry, with a discussion of the binding forces in molecular hydrogen. Professors Mulliken and Van Vleck have given excellent accounts of the early part of this period, in which they themselves played some of the leading roles. It falls to me to bring their story up to date with an account of recent developments.

To summarize these adequately in one brief talk is manifestly impossible. I went up to Cambridge in 1928 and have therefore had the tremendous privilege of watching all these developments take place. As Lennard-Jones's first pupil when he moved from Bristol to the first (and for many years the only) chair of theoretical chemistry in Britain, I was very early introduced to molecular-orbital theory. I remember vividly my astonishment when Mulliken visited Cambridge early in the 1930s, and showed how to describe the double bond formed by bringing two CH_2 groups together in ethylene. How neat, and in a sense how obviously satisfying it was, to have this description in terms of σ and π molecular orbitals. Later—it must have been around 1934, but I do not remember precisely—I recall the sense of excitement that we shared with one another when the powerful methods of group theory were shown to provide an explanation of the symmetries of molecular states, and the allowed and forbidden transitions between them. Perhaps now we have become too blasé, and less easily thrilled than then. But (if I may be allowed a very personal reference) I remember discovering almost at the same time both the power of group theory and the existence of an ultra-violet-absorption spectrum for benzene. I talked about it for an hour or so with Lennard-Jones, and then went to my rooms in College and worked excitedly to interpret this spectrum by group theory right through the night and until midday on the following morning. It does not matter that this work was never published: for several others had been doing much the same thing. I mention it now to show the sense of really new insight and achievement of those years of discovery.

There is another debt that I must repay today—not just for myself, but for many others. I learnt more about valence theory from the three papers on methane and ammonia, by Van Vleck, published in 1933 and 1934 in the first two volumes of the *Journal of Chemical Physics*, to which he has modestly referred as only indicating some vague general ideas, and from that wonderful review article with Sherman a year later in the *Reviews of Modern Physics*, than from any other reading. I took this latter review on a summer holiday with my parents: it nearly ruined my holiday and gravely tested family forbearance!

THE IDEA OF A BOND

Valence Theory is about bonds: what they are, how many there are from each atom, and why they are directed in the way that they are. So fifty years of valence theory really means fifty years of changing ideas about a chemical bond. The first one-third of this period, so ably described by Mulliken and Van Vleck, was necessarily concerned with identifying the electronic nature of the bond, and in escaping from the thought-forms of the physicist, dominated by the centre of symmetry in an isolated atom, so that the chemical notions of directional bonding and localization could be developed. It soon became clear that the basic fundamental picture of a bond must be of two electrons, having opposed spins, and a charge cloud largely localized in the region of the bond. The existence of bond properties, such as length, energy, force constant, dipole moment, many of which were nearly additive to give appropriate values for the whole molecule, left us really with no option. It might be true, in a formal sense, that all the electrons in a molecule (CH_4 for example) must be able to move all over the nuclear framework; but chemistry forced us to interpret this by admitting that, with a proper allowance for the fact that all electrons are identical (i.e. we must adopt a determinantal form of the wave function), we must somehow have an effective localization in pairs. I confess, even now, to a sense of astonishment that if, in the water molecule, I replace one of the hydrogen atoms by some other group, such as methyl or phenyl, there will be hardly any change in the length of the remaining OH bond; this will remain at about 0.96 Å, and its energy will remain at about 110 kcal. This must mean that the O—H bond is chiefly constructed from some sort of localized pair of electrons.

The period from about 1930 to 1939 was spent in trying to elucidate the nature of this localization. We all learned about the molecular-orbital and valence-bond theories, and we became as partisan about them as, in Britain, we are partisan about the Oxford and Cambridge Universities' boat race on the Thames! The simple MO theory of H_2 gave a better bond length, but a poorer dissociation energy, than the VB theory. Which was better? Both could be improved—the MO theory by the inclusion of interaction between more configurations (electronic, not geometrical!) of the same symmetry; and the VB theory by the inclusion of resonance among other types of covalent pairing, and ionic structures. The VB theory got off to a better start here, due perhaps to the differing personalities of the leading protagonists. But, by 1945, it was becoming clear that the difficulties in handling the lack of orthogonality among atomic orbitals (AO) on different atoms were such that, whatever might or might not be the conceptual advantages of the VB scheme, the MO scheme, in which the important orthogonality was between MOs and not AOs and was automatically ensured by the way in which the MOs were determined, was far easier to handle. The last twenty years have seen an almost complete concentration on MO methods.

An illustration of this, which I borrow from the preface to Streitwieser's book on organic chemistry, will show what I mean. It was in 1930 that E. Hückel made the fundamental distinction between σ and π electrons; or, as he called them, electrons of the first and second kind. The next six to seven years were spent under the leadership of Pauling, Wheland, Hückel, Lennard-Jones, Penney and others in developing both the VB and MO

applications of this distinction. But when, in 1938, Hückel came to write his *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*, he described both theories, yet spent at least two thirds of the book on the MO account. In the 'thirties Streitwieser says that in MO theory a 'mere handful of papers (approximately twenty) was followed by approximately seventy papers in the 'forties, and . . . some six hundred papers in the 'fifties'. My own estimate is that before the 1960s are completed in five months time there will have been published about five thousand papers involving the MO π electron theory of organic molecules. At one time I tried to read and to keep a card index of every paper on the theory of molecular structure. Up to 1950 this was just about possible; since then I have abandoned the attempt as quite hopeless.

The 'conflict' between the exponents of MO and VB theory was resolved in several ways:

(1) It became clear that when the MO theory was improved by the addition of configuration interaction, it ultimately became identical with VB theory, supplemented by resonance among other covalent and ionic states. This was first brought out by Mrs Fischer-Hjalmars (then Miss Fischer) and myself, for two-electron systems such as H_2 , and then extended to all systems by Longuet-Higgins. There was no question therefore of 'right' and 'wrong' but of which had the more easily used technique, or was more reliable when used in a restricted form.

(2) Even in their simple forms both theories were much closer together than was at first realized. Thus at the equilibrium distance in H_2 , the overlap integral between the simple MO and VB wave functions, with appropriate orbital exponents, is no less than 0.9875 (Braunstein and Simpson, 1955). If its value was 1.0, the maximum possible, it would mean that the functions were identical. They are obviously much less different than had earlier been supposed.

(3) This similarity was brought out clearly by a study of the one-electron density matrix, whose diagonal element gives the total charge density as it is measured by the x-ray chemical crystallographer. The two densities, associated with the MO and VB approximations, were closely similar.

In retrospect it is clearly a great pity that these internal disputes ever took place. At the very least they distracted attention from the main problems—which were a better understanding of how to treat many-electron situations, and of how to cope with the exceedingly difficult many-centre integrals which are an inescapable part of any molecular calculation, and whose conquest had to await the arrival of modern high-powered computers. I shall not say anything more about molecular integrals, except to remind you that even Heitler and London's first paper on H_2 lacked a proper evaluation of the fundamental exchange integral, whose value was subsequently obtained by Sugiura: and that S. F. Boys of Cambridge, one of the pioneers in techniques appropriate to polyatomic integrals, once said that our inability to calculate molecular integrals had held up the subject for fifteen years. Perhaps the theoretician's need for better mathematical techniques is the counterpart of the experimentalist's familiar cry for better equipment, whose non-existence, or delay, hampers his work.

CHARGE DISTRIBUTION

At this stage I would like to pick out four chapters in the theory of valence, and briefly trace their story from earliest beginnings in the situations already described by Mulliken and Van Vleck to their present state. I have chosen these as follows: (1) charge distribution, (2) hybridization, (3) π -electron bonding, (4) systems in which there appear to be either too many or too few electrons to form the proper number of bonds: these are commonly called electron-rich or electron-deficient molecules.

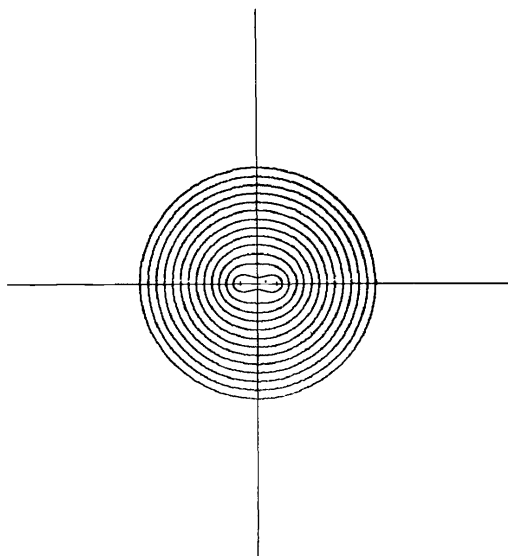


Figure 1. Total charge cloud density contours for H_2 [A. C. Wahl, *Science*, **151**, 961 (1966), by permission]

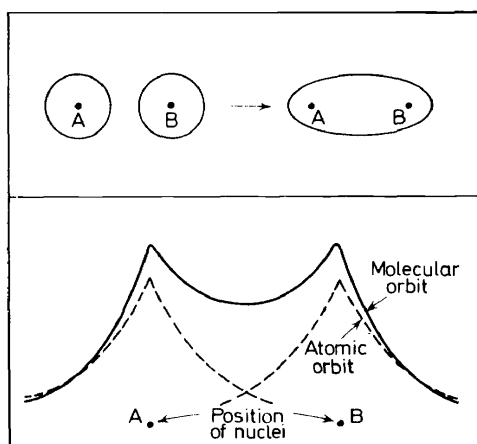


Figure 2. Charge density along the axis in H_2

First, let me deal with the total charge distribution in a molecule. Everyone is familiar with contour diagrams of total density such as that in *Figure 1* for H_2 . It is interesting to note that this diagram, though computed with a very complicated and elaborate wave function, hardly differs from a similar diagram which I obtained in 1938 in what were (I believe) the first self-consistent-field calculations for a molecule. This gives us some confidence that other s.c.f. calculations will provide satisfactory charge distributions. There are other reasons too to justify this hope: for the charge distribution is essentially a one-electron property, and it is known that s.c.f. wave functions give a much better account of one-electron properties than of two-electron ones, such as electron correlation. *Figure 2* shows the density in H_2 plotted along the axis of the molecule, and brings out the way in which, in a covalent bond, charge is brought from the outer parts of the molecule into the region between the nuclei. *Figure 3* shows the difference density, much beloved of

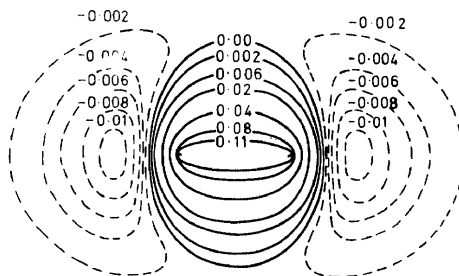


Figure 3 Difference density in H_2 (R. W. F. Bader, private communication.)

crystallographers, because it shows how the formation of a bond changes the undisturbed atomic charge-clouds. The concentration in the middle is shown clearly. As we are in Australia it is only right to mention that the clearest experimental proof of the existence of this overlap-charge has been provided by Barrie Dawson of the CSIRO, who has recently given numerical estimates for bonds between two carbon atoms.

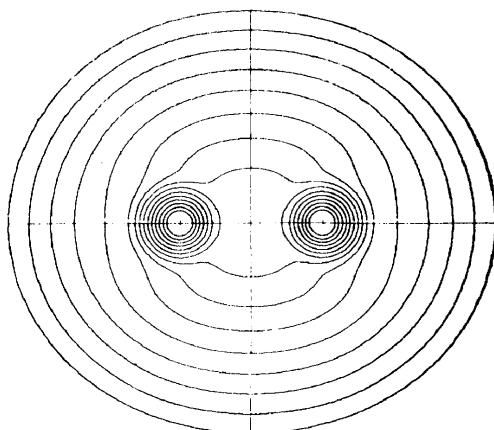


Figure 4 Total charge density for Li_2 (A. C. Wahl, loc. cit.)

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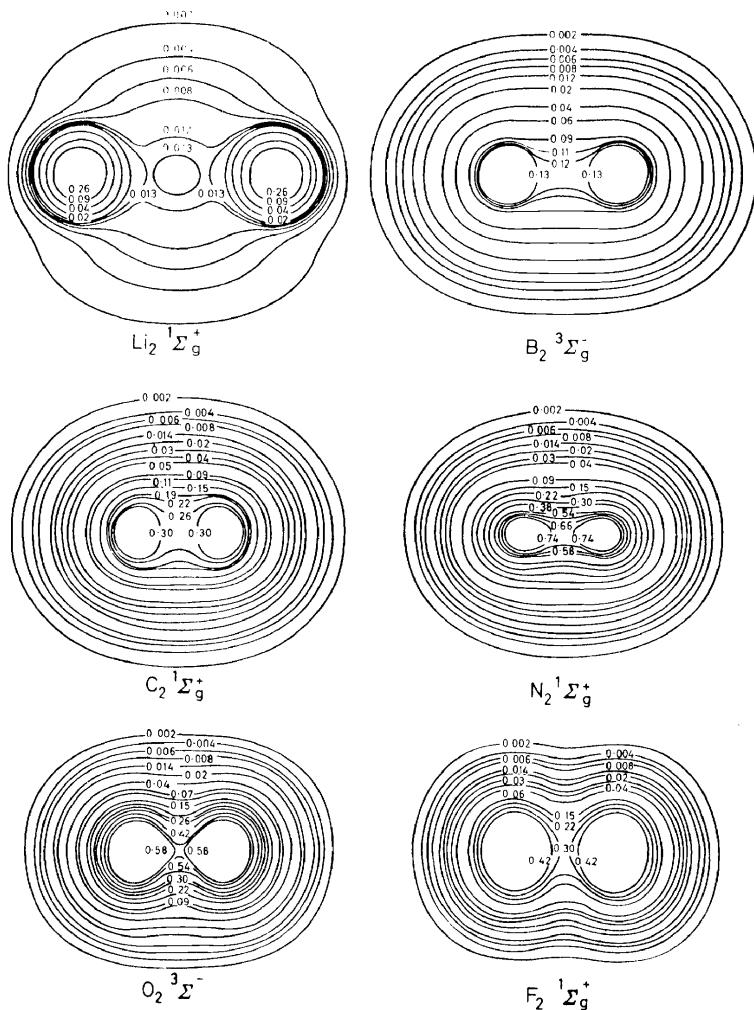


Figure 5. Total charge density for homonuclear diatomics Li_2 to F_2 [R. W. F. Bader, W. H. Henneker and P. E. Cade, *J. Chem. Phys.*, **46**, 3341 (1967), by permission.]

From H_2 we pass to Li_2 (Figure 4) and (Figure 5) to the diatomics Li_2 – F_2 . Notice how the bond shortens from the long and weak bond in lithium to the short and strong triple bond in nitrogen, and then the overlap charge diminishes as we go through oxygen to the single bond in fluorine. In diagrams of this sort there is a lot of chemistry, for they illustrate in a precise fashion what has been accepted in a qualitative way for about fifty years.

There is also a lot of chemistry in Figure 6, which shows the charge distribution for the series of hydrides, from LiH to HF . As we move along this series we start with hydrogen more electronegative than lithium, so that now charge flows from the alkali atom to the hydrogen: but we end with hydrogen much less electronegative than fluorine, so that charge flows from

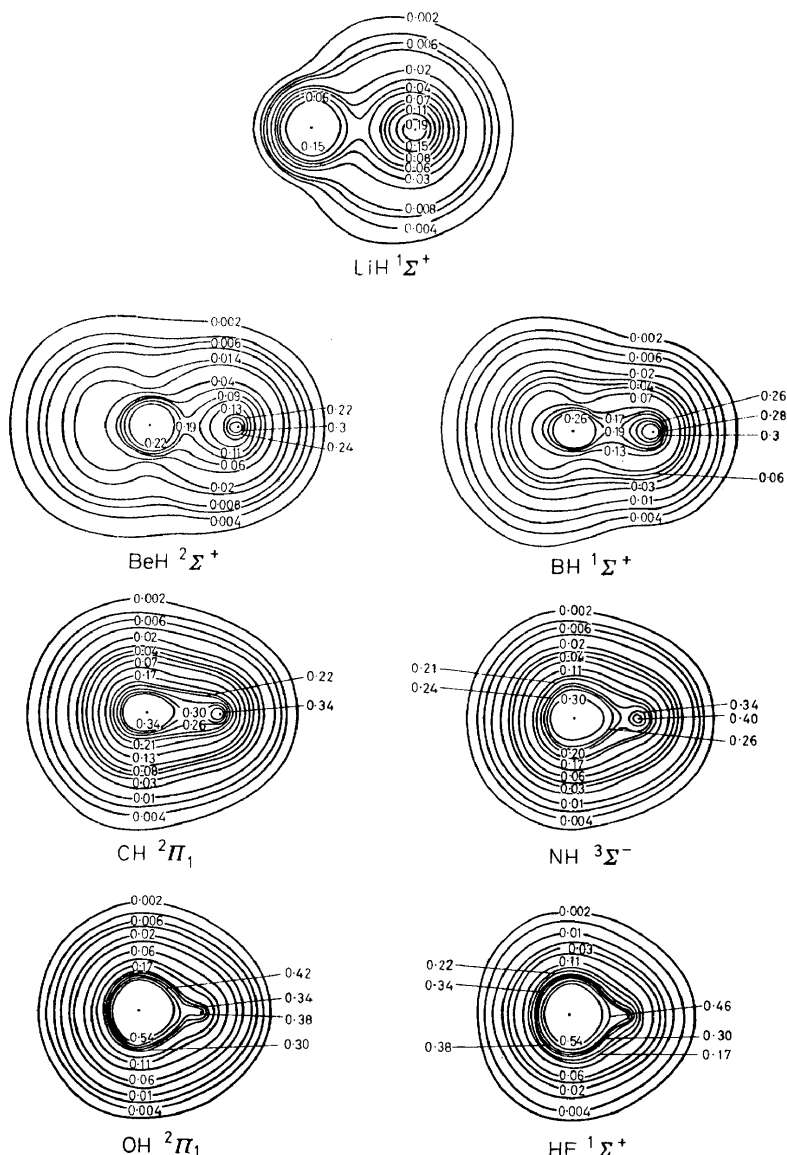


Figure 6. Total charge density for hydride diatomics LiH to HF [R. W. F. Bader, I. Keaveny and P. E. Cade, *J. Chem. Phys.*, **47**, 3381 (1967), by permission.]

the hydrogen to the fluorine, and the partly-bare proton is almost embedded in the spherical cloud of a fluoride ion. A closely similar diagram applies to the second-row hydrides NaH to HCl.

I should say that for many of these admirable contour diagrams we are indebted to the work of R. W. F. Bader, P. E. Cade, A. C. Wahl and their collaborators. It is quite astonishing to see in what detail we can now talk about the size and shape of a chemical bond.

HYBRIDIZATION AND INDIVIDUAL MOLECULAR-ORBITAL DESCRIPTIONS

The total charge-cloud densities just described refer to the totality of electrons. It is up to us to decide how we break it down into parts. One way—the early way of covalent-ionic resonance due to Pauling in the early 1930s—is to talk about the superposition of a covalent and one or more ionic structures. This method, though very appealing at first sight, proved to be almost impossibly difficult in practice, when high accuracy was required. This was because, even in the covalent part of the bond, it was not always easy to see just what orbitals on the two atoms were to be paired together in a Heitler–London sort of way. Here Pauling's concept of hybridization, later independently discovered by Slater, was a great help. For example, the tetrahedral character of methane could be associated with the possibility of forming four equivalent hybrids—combinations of the valence $2s$ and $2p$ orbitals of the carbon atom—which were strongly oriented in the appropriate directions. These hybrids could be paired with the corresponding hydrogen $1s$ orbitals to form four strong bonds.

The advantages of this description were several: (1) the hybrids were very much better at overlapping than their component s and p orbitals, so that what we might call the overlap energy increased (also the unfavourable interactions between electrons not paired together were reduced, for the simple reason that their charge-clouds were more separated than before); (2) the directions of the hybrids were just those required by the stereochemistry of the molecule. So far as the increased overlap is concerned the situation is well-represented by the curve in *Figure 7* due to Maccoll, which shows how the overlap of two carbon hybrids of s and p depends on the way in which they are mixed. The greater strength of hybrids, particularly the digonal ones with equal amounts of s and p , as compared with pure s or pure p , is very marked. It is not surprising that in a letter which Pauling wrote me some years ago he referred to his first paper on hybridization in 1931 as one of the papers of which he was most proud.

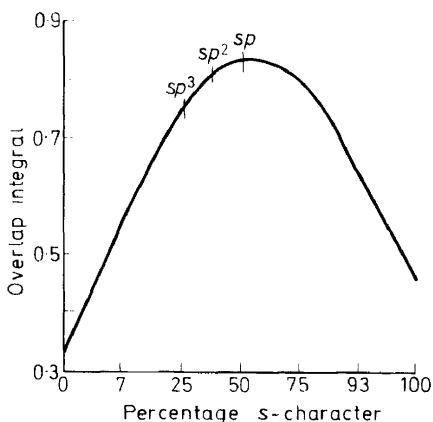


Figure 7. Overlap integral for two hybrid carbon atomic orbitals as a function of the extent of sp mixing [C. A. Coulson, *Valence*, p 209, Oxford University Press: London (1961)]

It was not long before hybridization was widely used to explain valence angles. The octahedral nature of sp^3d^2 hybrids, the square-planar nature of sp^2d , the trigonal sp^2 so important in aromatic systems: all these fall into place. The theory of valence angles could be described in terms of hybridization: stereochemistry was just one aspect of hybridization.

It is true that there were many notable successes in this area. As two further examples of this I would mention the idea of bent bonds, as in cyclopropane; and the variation of covalent radius with hybridization. In the first of these, developed by Moffitt when he was one of my students reading for his doctor's degree, we attribute strain in a molecule such as cyclopropane (*Figure 8*)

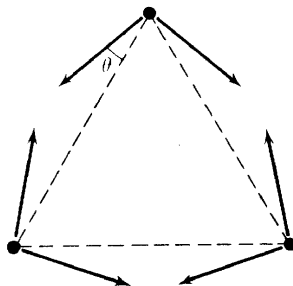


Figure 8. Bent bonds in cyclopropane [C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949)].

with unnatural valence angles, to the fact that no satisfactory hybrids can be formed to point directly from one carbon to another and have good overlapping. Some compromise has to be achieved: in this case the hybrids for the C—C bonds 'point' at mutual angles of 104° , and consequently the HCH angle is opened out, in agreement with experiment. This idea has recently had a very pleasant confirmation. If the overlap of the C—C hybrids does not occur primarily along the line joining the nuclei, but lies off this line, then the piling-up of charge which we previously discussed for H_2 , will itself occur outside the equilateral triangle formed by the three carbon nuclei.

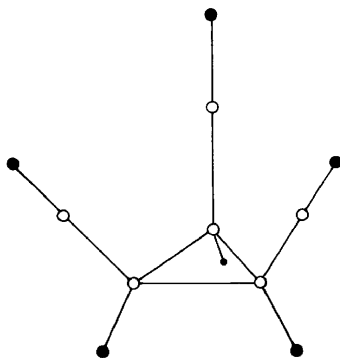


Figure 9. Tricyanocyclopropane.

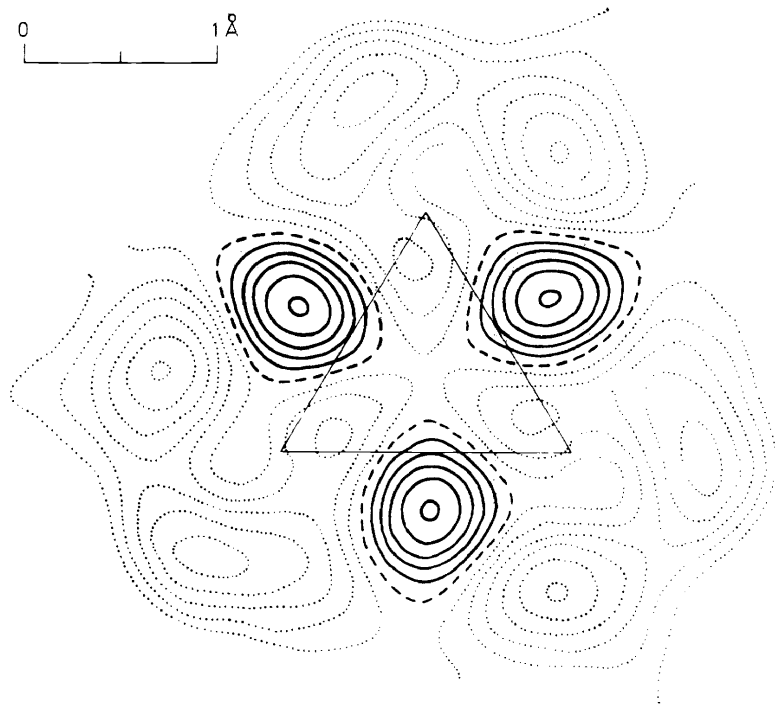


Figure 10. Experimental difference density in plane of ring [A. Hartman and F. L. Hirschfeld, *Acta Cryst., Camb.*, **20**, 80 (1966), by permission].

This is exactly what is found by Hartmann and Hirschfeld (*Figures 9 and 10*) for the tricyano compound $C_3H_3(CN)_3$. The difference density map for the charge density in the carbon plane shows this excess very nicely. Bent bonds are now part of our vocabulary.

The second example concerns the effect of a change of hybridization on bond length. It is easily seen that a hybrid of s and p projects out from the nucleus, and that the extent of this asymmetry will depend on the relative amounts of s and p (or d) in the hybrid. It is not difficult to use this to define a covalent radius; but of course it is a covalent radius for a particular hybrid of a particular atom, and not of the atom as a whole. *Figure 11* shows how the curve which I obtained in 1948 relates r_{cov} for carbon with the hybridization ratio of s and p . There are significant differences, which correlate with observed C—H distances when the carbon atom is in a tetrahedral trigonal or digonal form. The correlation is good, but not perfect, because by using a minimal basis set of functions we do not allow sufficient flexibility to our wave function. But at least we can say that we know why a carbon atom in methane appears a little bigger than in acetylene. We are learning more about the finer details of the bonds.

Naturally there were difficulties. I will mention one of these because it is an old problem which has only very recently been resolved. Soon after his arrival in London from Australia Allan Macoll showed very elegantly that

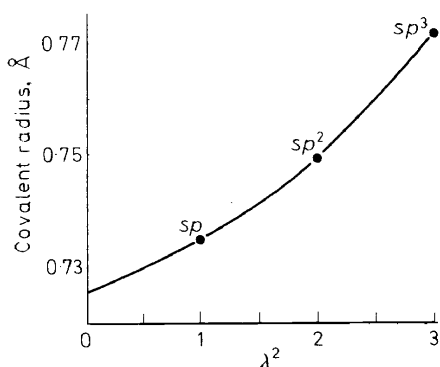


Figure 11. Variation of the covalent radius of carbon with hybridization ratio of s and p orbitals [C. A. Coulson, *Proc. Roy. Soc. A*, **207**, 66 (1951), by permission.]

hybridization of two atomic orbitals would be effective in increasing the net overlap, and hence the overlap binding energy, only if the two orbitals were of approximately the same size. This led to trouble with molecules such as SF_6 in which, following Pauling, it was supposed that the sulphur atom was in a state sp^3d^2 , out of which octahedral hybrids were formed. Here the orbitals were $3s$, $3p$, $3d$, all with the same principal quantum number 3. However, all the simple rules, such as Slater's rules, for estimating the size of the $3d$ orbital, and even the s.c.f. calculation of a wave function for sulphur with one electron excited to a d -orbital, showed that the resulting $3d$ orbital was far too big to be effective in hybridization with $3s$ and $3p$. It was referred to as an 'outer- d ', to distinguish it from the 'inner- d ' (e.g. $3d$, $4s$, $4p$) found in transition metal complexes. This difficulty remained as an argument against the octahedral-hybrid description of SF_6 until Professor Craig, now at

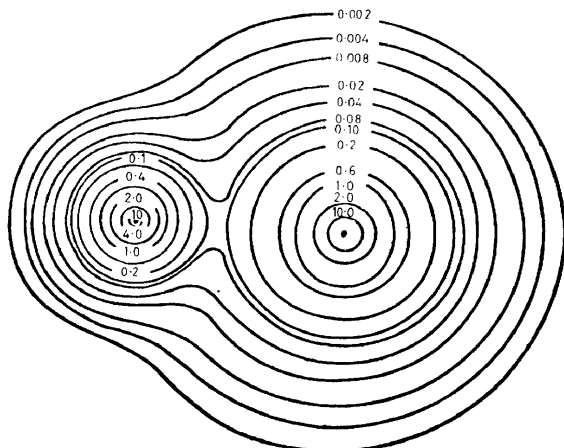


Figure 12. Total charge density for LiF (R. W. F. Bader, private communication.)

Canberra, and Professor Cruickshank, myself and others showed that if two d -type electrons were excited instead of only one, and if the ligand groups were sufficiently electron-attracting, then the mean radii of these d -orbitals became much smaller, and satisfactory hybridization became possible.

The variation of atomic size with degree of ionization is important in other ways. Consider, for example, the LiF diatomic molecule. In its neutral state the isolated lithium atom is very much larger than the isolated fluorine atom. So you would expect, when looking at the charge-cloud contours in *Figure 12* that the larger end of the molecule would be the lithium end. This is not so. The difference in electronegativity between the two atoms is so great that almost a whole electron goes from the lithium to the fluorine. This slightly increases the size of the fluorine, but drastically reduces that of the lithium atom, since when the solitary $2s$ electron has gone away, all that remains is the very compact ionic core. The calculations in *Figure 12* do indeed show very clearly the heavily polar nature of the bond, and corresponding reversal in sequence of atomic (or ionic) size.

We need not look only at the total charge density: and particularly when all the bonds are inequivalent, much insight can now be gained by considering the hybridization in each separate MO. *Figure 13* shows the contours for the valence-electron MOs in carbon monoxide. The 1σ is the most bonding of all these orbitals, the 2σ and 3σ are largely (but not of course completely) non-bonding hybrids around O and C respectively: and the two 1π orbitals are more polar towards the oxygen than the carbon atom. We could, of course, give a hybridization ratio for each such orbital. Such more detailed information considerably supplements the bare total shown in *Figure 14*.

Another example is molecular lithium, whose total density patterns we saw in *Figure 4*. This is the result of superimposing two electrons each in $1\sigma_g$, $1\sigma_u$ and $2\sigma_g$ molecular orbitals [*Figure 15* (a, b, c)]. Clearly the bond is due almost wholly to the $2\sigma_g$ pair: and if we wished to do so we could analyse this particular cloud in terms of s,p mixing. The difference map [*Figure 15* (d)] shows clearly the familiar pile-up of charge between the nuclei that we have met before. But this time it is a smaller pile-up, associated with the fact that the diffuse $2s$ atomic orbitals are not very good at overlapping, even when mixed with a little $2p$ character.

At this stage it may be helpful to look a little more carefully at the experimental evidence for these individual MOs. Professor Mulliken, to whom so much of the fundamental picture is due, has already described to us in this Symposium the lines of thought that led him to assign definite molecular orbitals with quantum numbers to the electrons of a molecule. For a long time after the development of the theory there was very little direct evidence for these MOs, except for the top-energy one or two, which could be studied by the ionization limit of Rydberg series in the ultra-violet. But in the last few years, two exceedingly important developments have taken place, to change this situation completely. First there is the photo-ionization technique, in the hands of D. W. Turner and W. C. Price, which uses a sharply defined high energy photon from an appropriate atom to ionize a valence electron of the molecule considered. By measurement of the energy of the emitted electron one can work back to the binding energy of the ejected electron. Second, there is the x-ray technique of Siegbahn and his collaborators in

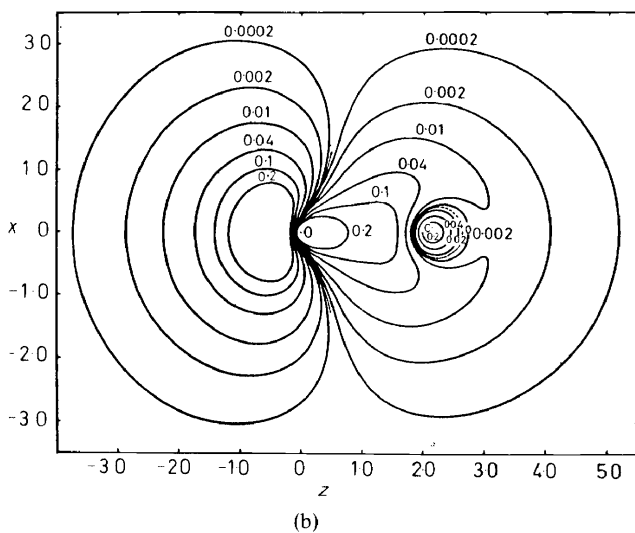
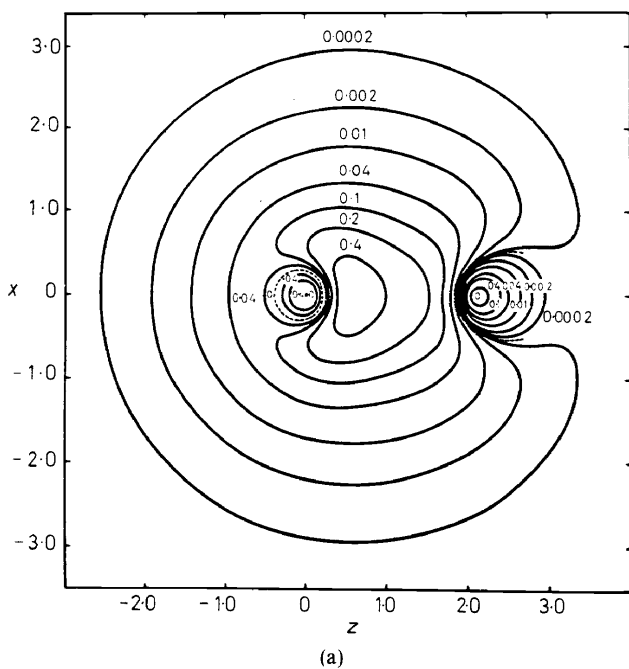
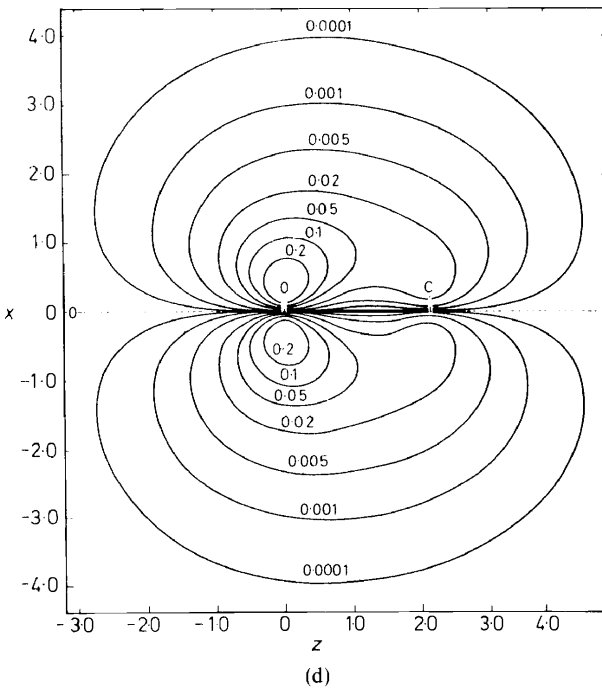
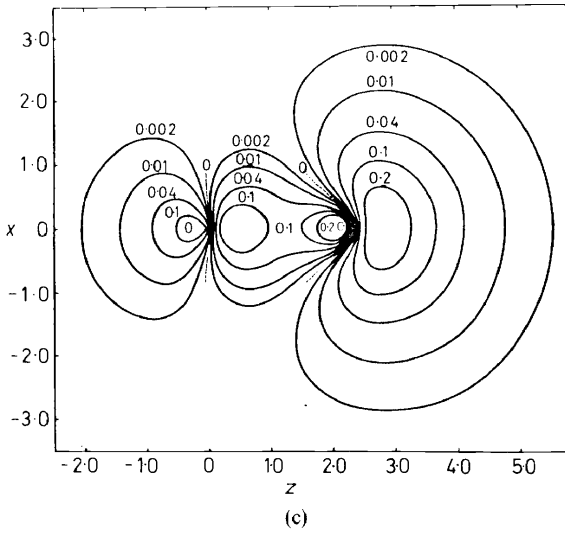


Figure 13. Charge contour diagrams for the valence orbitals of CO (a) 1σ , (b) 2σ , (c) 3σ , (d) 1π [adapted from W. M. Huo, *J. Chem. Phys.*, **43**, 624 (1965), by permission.]

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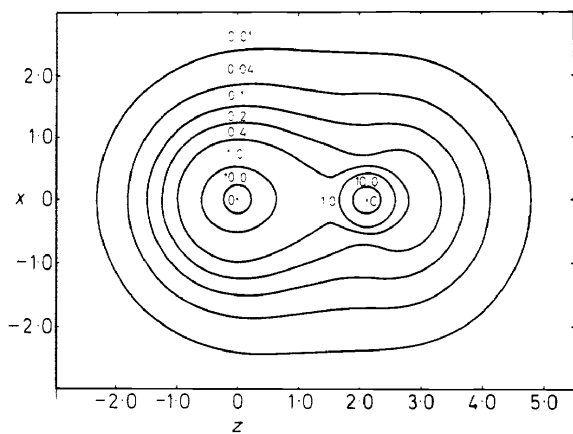


Figure 14. Total charge density in CO (W. M. Huo, loc. cit.)

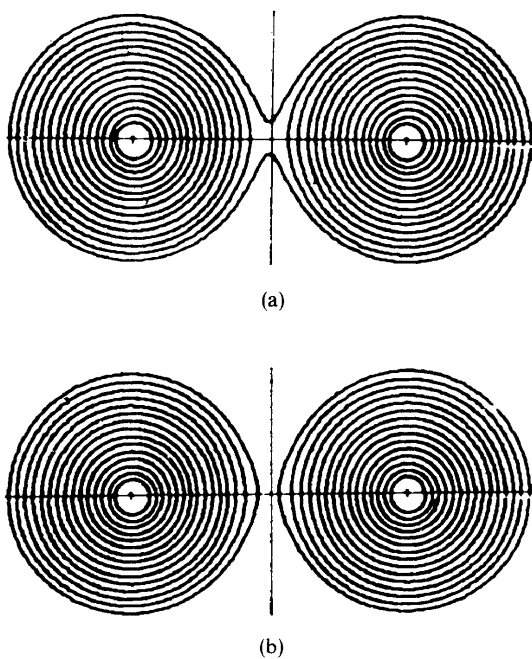
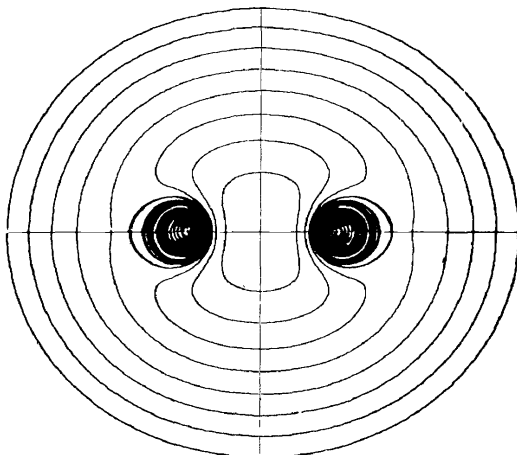
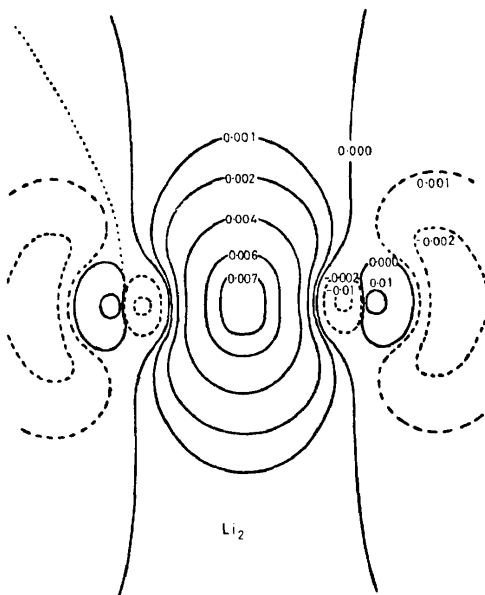


Figure 15. (a) (b) (c), Charge density of molecular orbitals in Li_2 (A. C. Wahl, loc. cit.)
 (d) Difference density in Li_2 (R. W. F. Bader, W. H. Henneker and P. E. Cade, loc. cit.)

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(c)



(d)

Uppsala, in which the energy comes from an x-ray level in an appropriate solid. This technique is now so important that it rejoices in its own symbolic name—ESCA (Electron Spectroscopy for Chemical Analysis). Both methods give similar results, with better definition from the photo-ionization method when both techniques are applicable.

The importance of these techniques for the study of molecules would be hard to exaggerate. If we have all the inner ionization potentials we can check with our theory, as in the case of CO (*Table 1*) referred to earlier and illustrated in *Figure 13*. The agreement is not bad, and certainly allows us to identify the MOs involved in all these ionization processes.

Table 1. Ionization potentials in CO (eV)

	3σ	1π	2σ
I.P. calculated	13.79	16.66	20.68
I.P. observed	14.01	16.58	19.70

An even nicer illustration is in *Figure 16*, which shows the photo-ionization spectrum of N_2 , O_2 and NO. There is no time here to go into the details: suffice to say that in all important respects we find agreement with the basic ideas of Mulliken and others. At last, therefore, we can claim to be well launched in our understanding of the behaviour of electrons in molecules.

What does all this mean? First, that it is right to speak of the motion of any one electron in a molecule, then that we can measure the energy to remove it, and by combination of theory and experiment, can say from what parts of the molecule the electron will mostly come. This provides an immediate link with chemical reactivity, and its character at different sites in the molecule, both in ground and excited states.

Before leaving this reference to the individual orbital motion of the electrons I must mention another type of discussion involving them. I am thinking of Walsh's rules. As long ago as 1953 A. D. Walsh started drawing correlation diagrams in which some geometrical property of the molecule, usually one of the valence angles, was varied. The ordinate was chosen to be the energy of any one of the MOs. *Figure 17* shows a typical Walsh diagram, this one being for triatomic molecules of the form AH_2 . By means of this diagram we can make certain conclusions regarding the result of a change in the electronic distribution due to ionization or excitation. For example, in *Figure 17*, if an electron in the orbital $2a_1$ is removed, we should expect that the valence angle would increase, since, according to this curve, an electron in the $2a_1$ orbital is tending to decrease the angle. Further, if the electron is excited from $2a_1$ to $1b_2$ we should expect an even larger increase in valence angle, since the orbital $1b_2$ tends to open out the molecule.

By means of these rules a large amount of experimental information about the normal- and excited-state valence angles of many molecules has been rationalized. But, despite its many successes, the method is still empirical, in the sense that no-one has yet succeeded in showing just what the ordinate—Walsh's binding energy—really represents. Here, despite the work of L. C. Allen and others, there is still work to be done. In fact, the MO theory of valence angles is much less straightforward than is the VB theory.

RECENT DEVELOPMENTS IN VALENCE THEORY

P.E. spectra from He 584Å

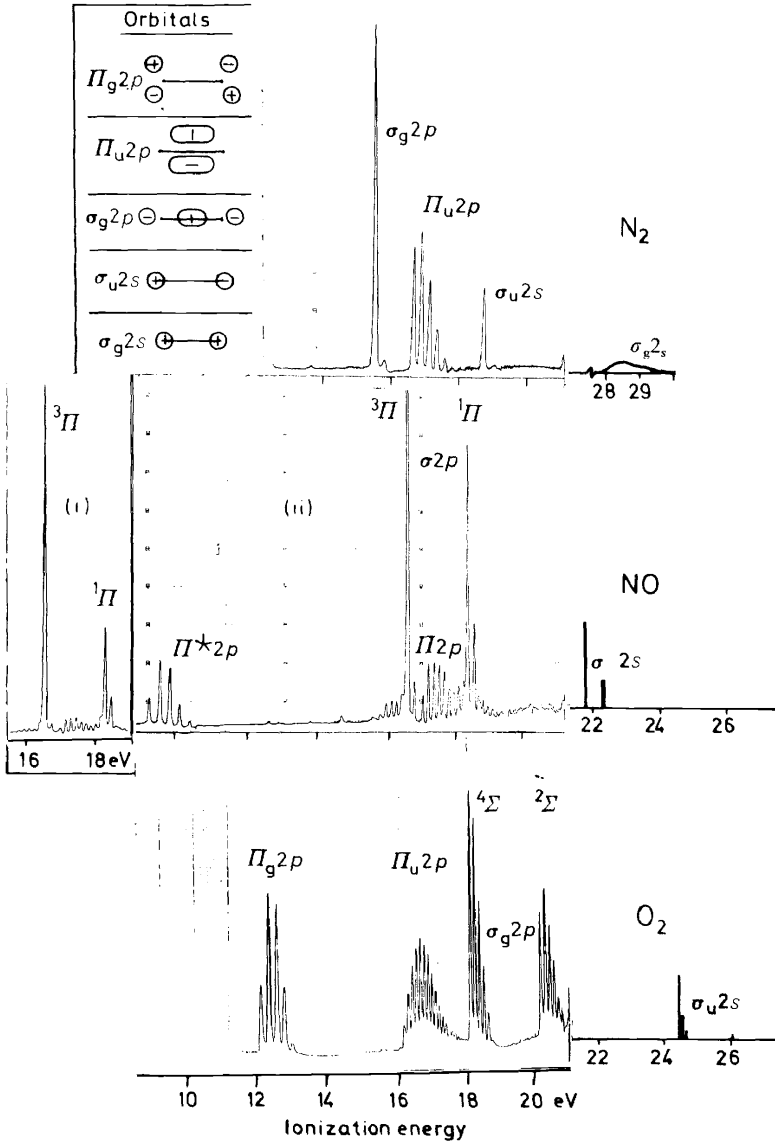


Figure 16. Photoionization spectrum of N₂, O₂, NO (W. C. Price, private communication)

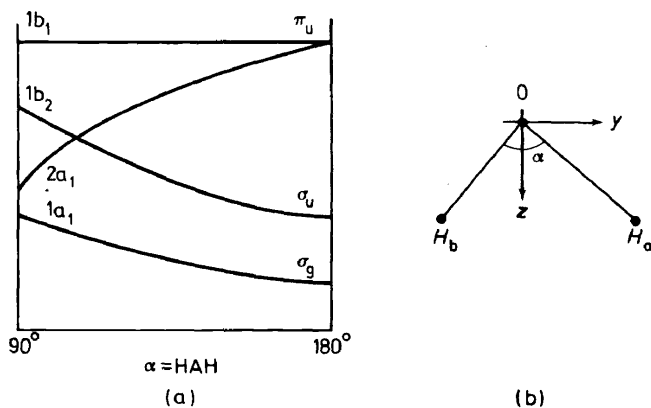


Figure 17. The Walsh diagram for molecules of type AH₂ [A. D. Walsh, *J. Chem. Soc. (London)*, 2260 (1953), by permission.]

π ELECTRONS

We must leave these discussions of small molecules, and turn to the history of our understanding of large ones. By this I mean the planar (or nearly planar) molecules whose characteristic properties, both as regards structure (bond lengths) and reactivity (directing property of substituents) are due chiefly to the π electrons. Here, as with diatomics, the VB method got off to a better start than the MO method. By 1933 Hückel's description of σ and π electrons had led Pauling and Wheland and Eyring to discuss the π electrons in terms of resonance among canonical structures. A canonical structure is really only a way of pairing electrons to give single and double bonds, and corresponds, in the case of benzene, to the Kekulé and Dewar models. Before long the resonance energies and double-bond character of many of these molecules, e.g. naphthalene, anthracene, styrene, had been computed. The idea of a fractional bond order goes back a long time, and can be said to have been implicit in the picture of partial valence and residual affinity of Thiele and Werner and others in the nineteenth century. But Pauling, Fox and Martin showed that it could be translated into wave mechanics as percentage double-bond character. Since double bonds are shorter than

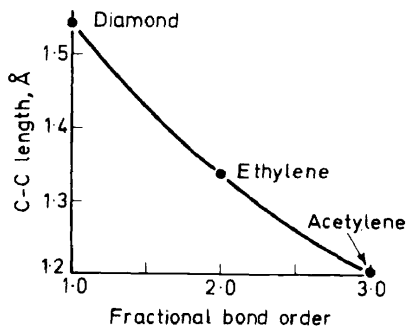


Figure 18. Order-length curve for carbon-carbon bonds

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single bonds, and triple bonds are even shorter still, a relation must exist between bond order and bond length. *Figure 18* shows an order/length curve for carbon-carbon bonds. By this means, if we can calculate the order of a given bond, we should be able to predict its length. In this way it could be shown, for example, that the 1—2 bond in naphthalene was much more close to being a double bond than was the 2—3 bond. Old ideas of bond fixation in aromatic molecules were restored to new life, though with this difference, that in the old days all bonds were of integral order—single, double, triple: but now they could have any fractional order. *Figure 19* shows a collection of results, dating from about 1951, in which x-ray-measured bond lengths were plotted against calculated bond order. Almost all the points lie within a band, indicating that there is a close relation between order and length. More recent and better experimental measurements have enabled us to refine this discussion, and of course to add improvements to the theory.

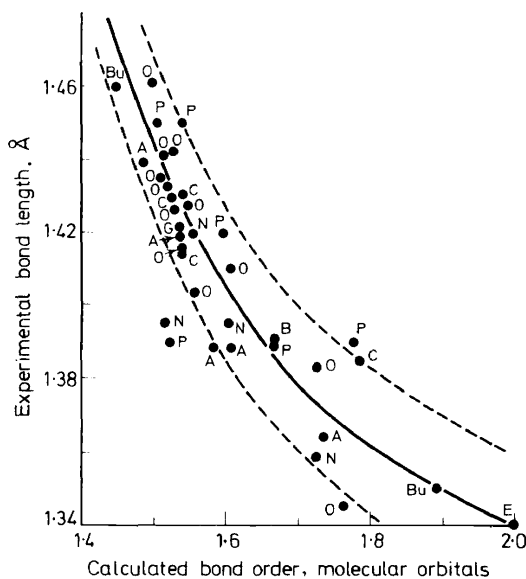


Figure 19. Experimental C—C bond lengths and corresponding Hückel π bond orders [C. A. Coulson. *Proc. Roy. Soc. A*, **207**, 95 (1951)].

But the important fact is that when π electrons are present bonds are no longer quite so constant in their properties as when only σ electrons are involved.

There were some unsatisfactory features in the early ideas of double-bond character. One of these was that if we included more possibilities of resonance, by incorporating additional structures, the bond orders dropped, although the stability increased. Here was a situation, not unfamiliar in science, where a simple theory may be more effective than a more sophisticated one. In this particular case it was shown by Penney, one of the early workers in this field, that a more elaborate definition could be provided of bond order. If two π electrons on adjacent atoms are perfectly paired together, so that their spins

are anti-parallel, they may be said to form a complete bond. If their spins are quite random they form a zero-order bond. So the mean value of the angle between their spins could be used to measure this fractional bond order in intermediate situations. There developed the so-called Penney–Dirac bond orders. These orders appeared rather more difficult to compute, and fell into disuse until, in the early 1960s, they were revived by myself and Dixon, taking account this time of variations in bond length to get the appropriate Coulomb and exchange integrals.

The valence-bond scheme is less and less satisfactory for very large molecules. Part of the reason for this is that the number of canonical structures rapidly increases with size of molecule, being 5 for benzene, 42 for naphthalene and 429 for anthracene. It soon becomes out of the question to include them all: and, moreover, the total weight of the chemically less satisfactory structures containing one or more long bonds increases so that it appears to dominate the chemically more satisfactory structures of Kekulé type. It was almost inevitable that, just as with smaller molecules, the initial popularity of the VB scheme should yield to the more powerful techniques of the MO scheme. But before describing this I should perhaps recall a rather unsatisfactory period, from about 1935 to 1945, during which experimental organic chemists, having come across the concept of resonance, used it quite indiscriminately to justify any idea that came into their heads. The technique of resonance among canonical structures does have a sound mathematical basis in the Rayleigh–Ritz form of the variation principle. But it was appealed to by people who knew nothing of this, in such unsatisfactory ways that by the end of 1945 resonance had become almost a ‘dirty’ word.

An example will show what I mean: ‘Since there is more resonance in nitronaphthalene than in naphthalene, the long wavelength absorption of naphthalene is shifted to the red on nitration.’ Statements of this kind appear to have forgotten that an electronic excitation refers to the difference in energy of the two states involved, so that only a comparison of changes in both states—and not the ground state only—could tell us anything about a possible blue or red shift.

As the VB method went out, so the MO method came in. Hückel’s pioneer calculations for polynuclear molecules were followed by Lennard–Jones’s allowance for the changing energy of the σ -bond framework when the bond lengths differed from some standard value. In 1939 I introduced a MO definition of fractional bond order, in which it was supposed that when a π electron was delocalized over the nuclear framework it would contribute to each bond order. The total bond order was then found by summation over all the π electrons. Some of these partial contributions were positive, others were negative, permitting us to discuss changes of bond length on ionization or excitation.

The success of this simple model was sometimes quite astonishing. As an example consider (*Figure 20*) the large unsaturated molecule called ovalene on account of its oval shape. The bond orders could be calculated, and hence the bond lengths predicted. Quite independently of our calculations, J. M. Robertson in Glasgow made x-ray measurements. The x-ray diagram is shown in *Figure 21*, from which the various bond lengths A–L could be estimated. *Figure 22* shows the remarkable agreement between the calculated

RECENT DEVELOPMENTS IN VALENCE THEORY

and observed sequence of lengths. One cannot always get agreement of this kind; but at least we can begin to feel confident that we understand the reasons for these differences in bond length, small though some of them may be.

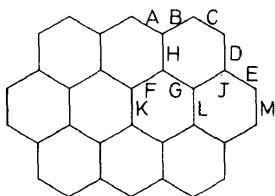


Figure 20. Ovalene.

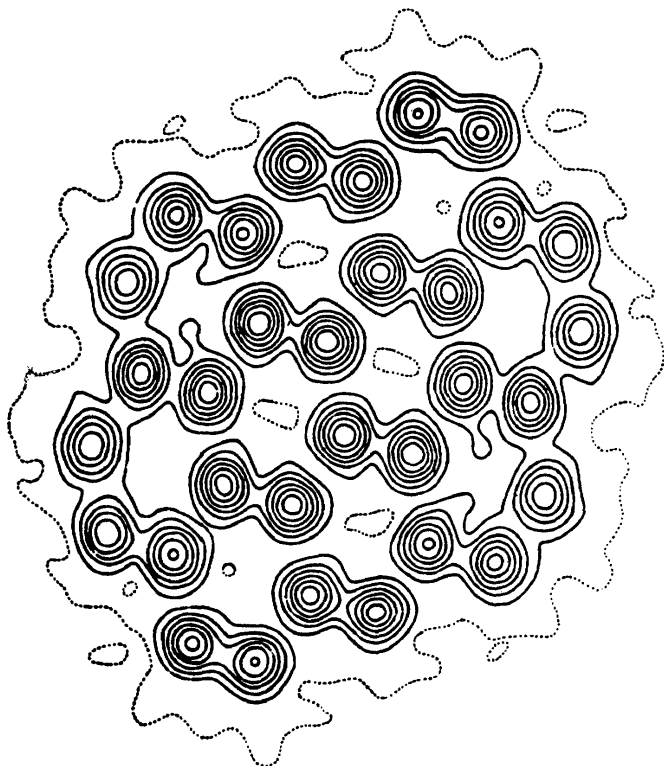


Figure 21. Experimental x-ray density diagram for ovalene [J. M. Robertson, *Proc. Roy. Soc. A*, **207**, 105 (1951), by permission.]

It may be asked whether there are any significant differences between the bond orders as calculated by VB and MO methods. Since the definitions in the two cases are not identical we cannot expect that the two measures would coincide. However, as *Figure 23* shows, there is indeed a close correlation; the bonds fall into three types, and within any one type an almost strict linear relationship holds. Our confidence in the use of fractional bond orders is thus much enhanced.

C. A. COULSON

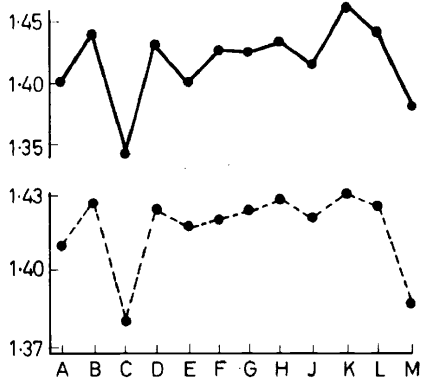


Figure 22. Calculated (above) and measured (below) bond lengths in ovalene (J. M. Robertson, loc. cit. p 106, by permission).

In the early days of π electron chemistry it was frequently stated that the reason why it was possible to deal with the π electrons alone, and without reference to the underlying σ electron core, was that this core was indeed inside the π electron cloud. It is certainly true that a π electron orbital has zero density on the central plane, so that in a two-dimensional projection in this plane we should find no evidence of the π electrons. Moreover it was urged that the overlap of σ atomic orbitals, leading to the piling-up of charge, would occur along the line of the 'bond', and the π electron cloud

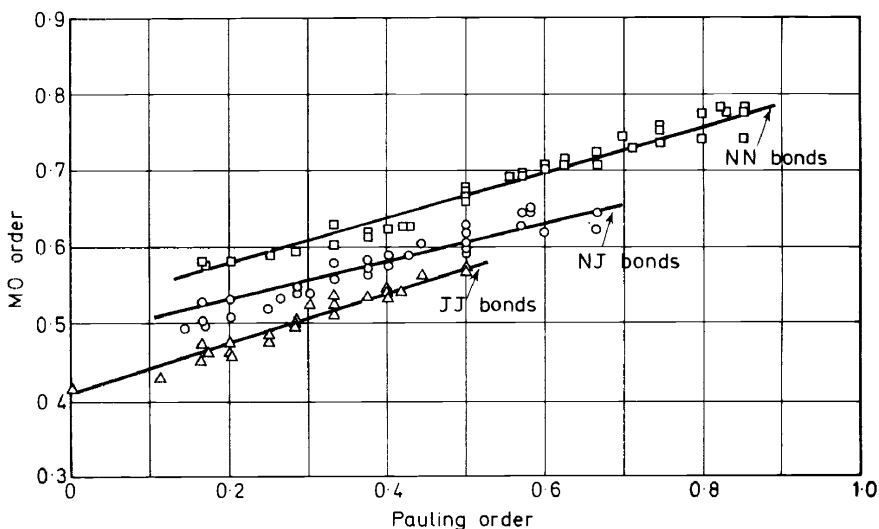


Figure 23. Comparison of π bond orders calculated in the VB and MO approximations: NN bonds, in which neither atom is at the junction of two rings. NJ bonds, in which one atom is at a ring junction. JJ bonds, in which both atoms are at a ring junction

[D. W. J. Cruickshank, *Tetrahedron*, 17, 155 (1962), by permission.]

would lie away from the bond axis, and so outside the σ -core. It is a matter for surprise that this naïve view was unchallenged for so long. In fact it grossly oversimplifies the situation. For when N. H. March, S. L. Altmann and I in 1952 came to look into the matter it soon appeared that over much the greater part of the volume of the molecule (benzene, say) the total σ density exceeded the total π density. This is not surprising if we remember that near a carbon atom there are on average three σ electrons but only one π electron. It might not be quite correct to put it this way, but it is not too far from the truth to say that the π electrons move within a sea of σ electrons. Then how does it come about that we can treat them separately with as much success as I have described? The answer is simply: symmetry. The simple difference, that a π electron orbital changes sign on reflection in the molecular plane, whereas a σ electron orbital does not, is decisive. Here we see once more the strange partiality that Nature shows for symmetry. We could almost say that nearly all the chemistry of these important molecules resides in this one symmetry factor!

There is, however, another aspect of this π , σ distinction which has only recently come to light, and which justifies me in stressing its importance. If the σ electrons were all lying inside the outer charge layer of the π electrons, then clearly the energies of the π electrons would all lie nicely above the energies of the σ electrons. This is just what was implicitly supposed for many years. Recent very accurate theoretical studies by Clementi and others have shown this to be quite wrong. There is a band of energies within which the σ MO energies lie, and another band within which the π MO energies lie. But these are not completely separate from each other: they overlap. The table below shows some of the calculated σ and π energies in pyrrole. The values listed refer to the top occupied nine MOs, grouped according to the proper symmetry of the orbital. It will be seen that the top two energies are of π -type, and that these are followed by three σ -type orbitals before we come to the lowest π orbital. Thus there is overlapping and interlacing of σ and π energies. Photo-ionization experiments confirm this general situation, even though a complete interpretation for many molecules is not yet available. It is really quite exciting to see one of our cherished convictions torn to shreds, and watch the process of remaking a better picture of the π electron cloud.

Table 2. Calculated orbital energies (a.u.) in pyrrole (after Clementi)

group symmetry label	σ -type		π -type	
	a_1	b_2	b_1	a_2
	- 0.577	- 0.602	- 0.425	- 0.388
	- 0.648	- 0.624	- 0.631	
	- 0.778	- 0.797		

I have already drawn attention to the remarkable successes of even the simplest π electron theories. It is worth spending a few moments asking how it comes about that so much more progress was made with organic than with inorganic chemistry. Part of the answer is that in inorganic molecules the range of bond energy is very great, and each molecule is in danger of having

to be treated on its own; part also is that the valence behaviour of inorganic molecules is related much more intimately to the interplay of s , p and d electrons, whereas in aromatic hydrocarbons we are able to limit ourselves to just one π orbital per atom. These are good reasons. But there is another: as (I believe) Professor R. G. Parr once put it, the trouble with diatomic molecules is that they are all 'ends' and have no 'middle'! So each electron is likely to 'see' a different environment from any other. But this is not so for a large planar aromatic molecule. So far as the π electrons are concerned these molecules have almost no 'ends', and a very large 'middle'. Any one π electron sees much the same average field as any other; so with an appropriate parametrization quite good predictions can be made with quite simple theories. The remarkable success of the simple Hückel model can be attributed to this: and, as recent much more sophisticated theories have shown, to improve on the Hückel theory demands an almost disproportionately large amount of computer time and programming.

A single illustration must do to show the great success of the simple theory. Let us suppose that we begin with a neutral π electron molecule, and then convert it to an ion by adding or subtracting a π electron. There is then one unpaired electron, and so an uncompensated spin. The distribution of this spin on the different nuclei of the molecule will depend chiefly (wholly so in the case of the simple Hückel theory) on the charge distribution of this odd electron. Hyperfine splitting in e.s.r. experiments allows us to test this predicted spin density against what actually occurs. The graph in *Figure 24*

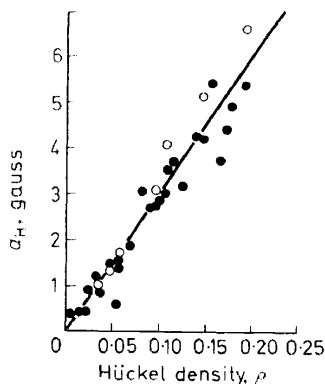


Figure 24. Calculated and observed spin densities in aromatic radicals and ions [A. Carrington, *Quart. Rev. Chem. Soc. London*, **17**, 67 (1963), by permission.]

shows how surprisingly good the predictions are. It was almost inevitable that with so many successes so relatively easily achieved, a disproportionate amount of effort went into π electron chemistry. Indeed, it was really only after 1945 that, in the hands of people like L. E. Orgel, C. J. Ballhausen and C. K. Jørgensen, any systematic pattern of inorganic chemistry and transition-metal complexes was established, and a further chapter in valence theory completed. But it is a sobering thought that this chapter had been started, in the early 1930s, by Van Vleck and his students. Sometimes the final harvest is delayed if everyone picks the plums most easily reached around the base of the tree.

BONDS WITH THE 'WRONG' NUMBER OF ELECTRONS

My final story concerns what we might call unnatural molecules—that is, molecules with either too few or too many electrons to allow us the conventional allocation of two electrons to each valence bond. Let me begin with electron-deficient compounds, where it seems that there are not enough electrons to constitute the bonds. Diborane B_2H_6 is the best known of these, and will serve as our example to illustrate the theory.

In the early days it was assumed that B_2H_6 had the same shape as ethane C_2H_6 . But, as G. N. Lewis recognized, in that case there would be only 12 valence electrons to form 7 bonds. In the early 1930s, he spoke of these as providing on average only 6/7 of a normal bond. The idea was not attractive: Nature does not seem to work that way. The first thing to be established, when seeking a satisfactory explanation, was that diborane was not like ethane; for two of the hydrogen atoms (*Figure 25*) acted as bridges between the two boron atoms. Moreover these bridge atoms lay symmetrically between the borons. It was natural to suppose that the four terminal B—H bonds were of conventional character, with two electrons each. This left only four electrons to bind together the two boron atoms and the two bridge hydrogens.

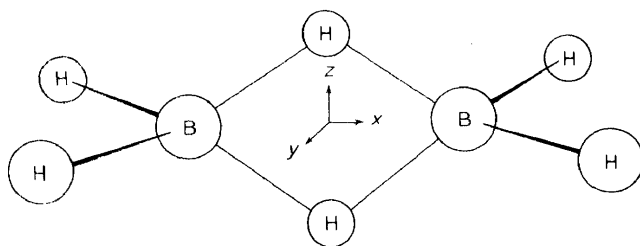


Figure 25. The diborane molecule B_2H_6 .

In 1945 K. S. Pitzer proposed that the analogy should not be with ethane, but with ethylene: he suggested that there were π and σ MOs in diborane, and that the bridge protons embedded themselves in the π cloud. Four years later Longuet-Higgins showed that a better interpretation was to suppose that the four electrons in question went into two MOs, but these MOs were three-centre ones, with a bent character similar to that shown in *Figure 26*.

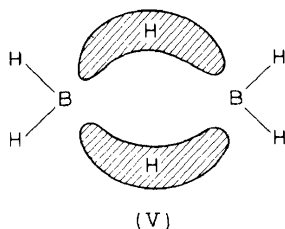


Figure 26. Three-centre bonds in diborane.

The idea proved almost magical: and, as often happens when an old concept is enlarged, an exciting and turbulent period followed, in which, at the hands of W. N. Lipscomb, a complete rationalization of the complete (and large) family of boron hydrides became possible. Up till that time a chemical bond consisted of two electrons binding two centres: now it was seen that although we were still dealing with two electrons, they could be used to form a three-centre or even a four-centre bond. In this way another cherished belief had to be abandoned—or, better, enlarged—to give a satisfactory account not only of the boron hydrides, but of a large and growing series of electron-deficient molecules.

The example of diborane will show the good chemical sense that came out of this. Let us call the boron atoms B_a, B_b ; and the bridge hydrogens H_1, H_2 . Then we may use the calculated MOs to compute overlap populations and net charges. An overlap population is a quantity introduced, as so many other quantities have been introduced, by Mulliken. It generalizes the bond order previously described, and is proportional to it. It is a measure of the number of electrons that bond two atoms together. This bonding, however, may be positive or negative, as the case may be. The situation in the diborane bridge is as shown in *Table 3*. Thus the direct bonding between the two boron atoms is very similar to that between a boron and a bridge hydrogen. We may say that each three-centre bond helps to bind all three relevant atoms together, and no simple old-fashioned bond diagram is adequate to express this.

Table 3. Overlap populations and net charges in the bridge atoms of diborane

	<i>Overlap populations</i>	<i>Net atomic charges</i>
(B_a, B_b)	0.338	B_a, B_b + 0.22
(B_a, H_1)	0.356	H_1, H_2 -0.22
(H_1, H_2)	0.306	-

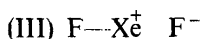
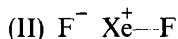
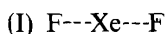
However, the two bridge hydrogens are in different three-centre bonds, and therefore repel each other. Further, the bridge hydrogens carry a net negative charge, balanced of course by a corresponding positive charge on the boron atoms. In various ways almost all of this has subsequently been checked experimentally.

From electron-deficient molecules we turn to electron-rich ones. Again the story is exciting. Most of us were brought up on the old adage, that the rare gases formed no bonds. Were they not called the noble gases, to show that they could resist all attack? However in 1962, both Höpfe in Germany, and Claassen in the U.S.A., with their colleagues, showed independently that xenon and radon could form compounds. Before long XeF_2 and XeF_4 became just the first and best-known of a series of such molecules, with bond energies up to 30 kcal/mol, and with known geometrical structures. There was consternation among the theoreticians, and excitement among the experimentalists.

In the old view of valence an atom such as xenon, with a closed-octet outer shell $(5s)^2(5p)^6$ had no unpaired electron with which to form a normal

chemical bond, nor was there any other low-lying orbital into which an additional electron or pair of electrons from some ligand groups could be accommodated. It seems at first as if the whole edifice of valence theory, so carefully built up during these fifty years, was to be shattered by one single group of molecules.

But of course there was an explanation. More precisely there was one explanation that could be put in terms either of the MO or the VB models. In the MO model it could be shown that by appropriate use of three-centre bonds, as with the electron-deficient molecules previously described, one could understand the situation. It turned out that there were just enough electrons in all cases to complete a shell of molecular orbitals. This explanation, though accurate, was not particularly helpful in a pictorial sense. Fortunately, however, this is a case where the VB model has great conceptual advantages. Let us consider XeF_2 (I) as our example. The neutral xenon atom



may indeed have a closed shell and be technically zero-valent. But if we remove an electron to form Xe^+ , we have an electronic structure isoelectronic with a normal iodine atom, leading to the possibility of a normal $\text{Xe}^+ \text{F}$ bond. To preserve neutrality we require a second fluorine atom, as in (II), to accept the electron ionized from the xenon atom. Having written (II) it is immediately obvious that there is another equivalent structure (III), that could be drawn. In VB language we expect resonance between (II) and (III), leading to a stable linear molecule. I was able, shortly afterwards, to show that the energetics of the process just outlined were such as almost certainly to lead to molecular stability. There was really no mystery at all, and none of the really fundamental rules of electronic behaviour had been broken.

Two aspects of this are worth mentioning. First, the formation of (II) and (III) will depend upon the ease with which an electron is removed from the rare gas atom in the centre. If it is too hard to remove an electron, so that insufficient energy is regained in the formation of the $\text{Xe}^+ \text{F}$ bond, and in resonance between (II) and (III), no stable molecule is formed. Now, as *Table 4* shows, the ionization potentials of the rare gases diminish as we go down the periodic table to heavier atoms. We should therefore expect that these molecules would be formed best with the heavy atoms. In fact no compounds are known with He, Ne, Ar; the compounds with Kr are not very stable, and those with Xe are more stable. Little can be said about Rn because it is such a difficult substance to handle on account of its radioactivity.

Table 4. The lowest ionization potentials of the rare gases

Atom	He	Ne	Ar	Kr	Xe	Rn
I.P. (eV)	24	22	16	14	12	10.8

The other aspect concerns the nature of the ligands to be attached to the rare gas. Experimentally fluorine and oxygen occur readily, chlorine with difficulty, and at present there are no others. But this is not surprising, since as (II) and (III) show, it is important to have as a ligand an atom with high affinity for the electron removed from the rare gas; and also—though I shall not give the proof here—as small a radius as possible. In these respects O and F are much better than S and Cl.

It is a very remarkable commentary on both theoretical and experimental chemists that although there is not one word of my description of XeF_2 and of the other rare-gas compounds, which could not have been spoken 35 years ago, it was not until 1962 that these molecules were constructed. In this Symposium we are thinking of 50 years of valence theory. If valence situations such as those of the rare-gas compounds had to wait so long to be discovered, who knows what else may be lying in wait for us in the next 50 years ahead?

CONCLUDING REMARKS

I am sure that it will have been noticed that I have said very little about the techniques used in the calculations that I have described. These merit a discussion of their own. Of course they have grown in complexity, from the days in 1935 when I could use my little £25 hand Brunsviga calculating machine somewhat laboriously to find the numerical values of a few three-centre integrals, to 1969, when a single large-scale calculation, such as that of Clementi on the energy surface for the system $\text{NH}_3 + \text{HCl}$, may involve three thousand million integrals, many of them three- and four-centred. Only the world's largest computers can handle this sort of thing. This is why so many attempts have been made to simplify the work by, if necessary, throwing out as many types of integral as possible in a systematic manner. One thinks of the Roothaan equations, and of Pariser and Parr, with Pople's modification of their method of the neglect of differential overlap: or of the CNDO or the INDO methods, and the Mataga formulation for the integrals that still remain. I have not spoken of them because, although they are necessary as tools to derive the sorts of contour diagrams that I have shown, they are only tools: and for us today the tools matter less than the building that they help to construct. Nor have I spoken of the great controversy, with alternating fortune on each side, whether to use Slater orbitals or Gaussians as building bricks. This also is a question of technique, necessary if we are to answer my opening question about the size and shape of a chemical bond, but not otherwise important for us. I have not spoken of the various effects, essential for a complete understanding of electronic distribution in space, such as spin-spin coupling, rotational magnetic moments, and quadrupole coupling constants. These, which arise from what are sometimes referred to as the small terms in the Hamiltonian, give us detailed information about such matters as the situation close to a nucleus, or the amount of *p*-character in a bond. They are important ancillaries to that broad pattern of which I have been speaking; and they give us excellent confirmation of particular features of the charge distribution. But, if we only had these, we should never have come to the concept of a chemical bond.

Now, as I close, this last remark leads me to my final question. The study of chemistry has been built up around the concept of a bond. Once this had been recognized as being associated with two electrons having paired spins, everyone realized the simplicity of the idea; and in one sense the story that I have been telling today is the story of continual adaptations in order to preserve this central idea. Covalent-ionic resonance permitted unequal sharing of electrons; hybridization explained observed stereochemical behaviour; fractional bond orders allowed the delocalization effects of π electrons to be related to this simple notion: ultimately three-centre bonds were found to be necessary, and—in the sandwich molecules such as ferrocene, of which there has been no time to speak—the role of an atomic orbital in bond formation was taken over by a complete molecular orbital of a π -electron in a five- or six-membered ring. So to the question: has the chemical bond now done its job? Have we grown to that degree of knowledge and that power of calculation that we do not need it? Certainly in the more elaborate of the calculations that I have referred to, the authors seldom if ever use the word 'bond'.

This is a tantalising question. And only a little can be said by way of comment. Chemistry is concerned to explain, to give us insight, and a sense of understanding. Its concepts operate at an appropriate depth, and are designed for the kind of explanation required and given. If the level of enquiry deepens, as a result of our better understanding, then some of the older concepts no longer keep their relevance. No one talks much now about the polarization of non-bonding electrons, of dynamic oscillation, or of bond fixation. From its very nature a bond is a statement about two electrons, so that if the behaviour of these two electrons is significantly dependent upon, or correlated with, other electrons, our idea of a bond separate from, and independent of, other bonds must be modified. In the beautiful density diagrams of today the simple bond has got lost. It is as if we had outgrown the early clothes in which, as children, we could be dressed, and now needed something bigger. But whether that 'something bigger' that should replace the chemical bond, will come to us or not is a subject, not for this Symposium, but for another one to be held in another 50 years time, and bearing for its title: the changing role of chemical theory.