

The Chemical Bond

Gilbert N. Lewis

Citation: *J. Chem. Phys.* **1**, 17 (1933); doi: 10.1063/1.1749214

View online: <http://dx.doi.org/10.1063/1.1749214>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v1/i1>

Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



Explore the **Most Cited**
Collection in Applied Physics

AIP
Publishing

The Chemical Bond

GILBERT N. LEWIS, *Department of Chemistry, University of California*

(Received November 10, 1932)

IT was not long ago that the physical and the chemical pictures of the atom and the molecule seemed almost irreconcilable. Indeed, when the quantum theory was young, it could not be surmised that the development of that strange theory would bring about the reconciliation. Yet the chemist has always assumed, without being fully aware of it, a sort of quantum theory. The battle fought in the early years of chemistry between the theory of a continuous gradation between chemical substances, and the theory of discrete states, resulted in a complete victory for the latter theory. Thus, in the development of organic chemistry it became necessary to recognize that a molecule of given composition might occur in a certain limited number of isomeric states, and such a set of organic isomers now affords one of the best examples of a given system in several distinct quantum states.

Structural organic chemistry, although developed without mathematics, except of the most elementary sort, is one of the very greatest of scientific achievements. An enormous mass of information was reduced to a well-ordered system through the aid of a few simple principles. It was this system of structural chemistry that served chiefly as my basis when I advanced my theory of valence. The main feature of this theory was a set of simple *electronic* structures of such sort that if one asks whether a given molecule has a given electronic structure, the answer must be yes or no. The molecule may snap from one structure to another but there are no continuous gradations such as would be expected from classical electromagnetic theory. Such an electronic structure was pictured as capable of changing its form, or its energy, or its electric distribution, without changing its essential type.

Thus I visualized a sort of articulated skeletal structure in which the different parts have some freedom without change of articulation, but which is also capable of an abrupt change of articulation to produce a new structural type.

Aside from the chemical behavior, this transition from one structural type to another was best evidenced by the magnetic susceptibility, for the change from a diamagnetic to a paramagnetic molecule is sudden and complete. More recently we have found other criteria of skeletal structure, especially in spectroscopy. Here we find differences in spectroscopic terms which could not conceivably be bridged by a continuum.

It seemed a little strange to attribute this essential skeletal structure to the electrons which have always been regarded, and are still regarded, as the most mobile part of a molecule. This view, however, is substantiated by modern spectroscopic analysis in which it has been found extremely useful to distinguish those vibrational and rotational levels which are due to the atoms from the levels which are due to the electrons, and it ordinarily requires far more energy to produce a transition from one electronic level to another, than it does to change the atomic level.

This idea of electronic structure, and, in fact, all the structural ideas which are used by chemists, were obtained by a method which may be called analytical, in the sense that from a large body of experimental material the chemist attempts to deduce a body of simple laws which are consistent with the known phenomena. The mathematical physicist, on the other hand, postulates laws governing the mutual behavior of particles and then attempts to synthesize an atom or a molecule. When the attempt is successful he has a weapon of extraordinary power which enables him to answer questions quantitatively which at best could be answered qualitatively by the other method. On the other hand, an inaccuracy in a single fundamental postulate may completely invalidate the synthesis, while the results of the analytical method can never be far wrong, resting as they do upon such numerous experimental supports.

It was a recognition of this fact, when I first deduced the idea of the electron pair bond from

an analysis of chemical facts, that emboldened me to accept this deduction; although it was obviously incompatible with the then accepted laws of electromagnetics and mechanics. The qualitative principles of molecular structure were presented, so to speak, as the minimum demands of the chemist which must eventually be met by the more far-reaching and quantitative work of the mathematical physicist. They have not been altered during the recent unprecedented period of discovery in mathematical and experimental physics; but it is now possible to amplify a little, and to express more nearly in the language of modern physics, these minimum demands, or qualitative specifications, to which we have reason to believe the quantitative results of mathematical physics must eventually conform.

I should have liked to show how, step by step, from the first investigations of Heisenberg and Schrödinger and Pauli, to the recent studies by Slater and by Pauling of the tetrahedral eigenfunctions, the physical picture has been brought successively nearer to meeting the qualitative chemical demands, and to point out some of the remaining gaps, but this I cannot do in any systematic way. There can be no question that in the Schrödinger equation we very nearly have the mathematical foundation for the solution of the whole problem of atomic and molecular structure, but there are two reasons why we cannot immediately deduce from this equation all the desired facts, and these two reasons are of very different character. In the first place, the equation is incomplete in that it ignores the phenomenon of spin, which is of such vital importance both to the chemist and to the spectroscopist. In the second place, even with a complete mathematical foundation, the intricacy of the problem usually prevents a satisfactory solution. When we remember the difficulty in Newtonian mechanics of solving the three body problem, and in relativistic mechanics even the two body problem, we see that the problem of the many bodies contained in the atom and the molecule cannot be completely solved without a great further development in mathematical technique. It is for this reason that the chemist and the spectroscopist must long be content with results that are qualitative, or only half quantitative.

THE STRUCTURAL FRAMEWORK

There is one set of conclusions arrived at both by chemists and by spectroscopists, which, while seeming not inconsistent with quantum mechanics, can hardly be said to have been deduced from the mechanical equations. Both agree in assigning to the atom or molecule a certain pattern or framework. The chemist says that in proceeding from the hydrogen atom through the atoms of successively higher atomic numbers, electrons fall into the first shell, then into the second, and when these are both filled they fall into the third shell, but before this is completely filled they begin to enter the fourth shell, leaving certain positions in the third shell *unoccupied*. The spectroscopist says that there are certain quantum states which he names by analogy to the possible quantum states of the hydrogen atom, and these states may be occupied or unoccupied by electrons. In both cases a pattern is assumed which sometimes is supposed to have spatial significance like a set of pegs upon which hats might be hung, or sometimes it is considered to have purely ordinal significance like the numbered and lettered cards in a library catalogue, some of which might contain the names of books, while others might be left blank until the entering of new books. In either case we have a framework of positions some of which may be empty.

Now we are convinced that the specifications for the quantum state should be specifications for the atom or the molecule as a whole, but since the total number of specifications necessary to fix completely the quantum state of a system of N particles is $3N$ (ignoring spin for the moment), one is tempted to divide the whole set of specifications into N sets of three specifications each, and then to ascribe each set of three to one of the particles. This, however, is not permissible. Anyone who has studied the beautiful treatment of the two-electron problem given by Heisenberg must see the impossibility of saying anything of one electron which is not at the same time said of the other. We can, however, avoid this difficulty. For example, in the case of N electrons, we may set up our framework or cataloguing system with N series, each series consisting of sets of quantum specifications, three to a set. Then we

can say, not that a given electron is in one position or another, but only that N positions are occupied and the rest are unoccupied.

This is essentially the classification resulting from Bohr's theory of atomic structure, which gave a spatial significance to the various orbits that might or might not be occupied by electrons. Formerly, in discussing the Bohr theory of chemical structure I stated that we should "refer to the position of the orbit as a whole rather than to the position of the electron within the orbit." The Bohr orbit has now been replaced by its less tangible counterpart in quantum mechanics. We may still maintain the notion of certain spatialized loci and we may, I think, without danger of misunderstanding, still refer to these loci as orbits, using the word in a generalized sense. We thus visualize a set of orbits which may be occupied by not more than one electron at a time, but which may also remain unoccupied. I feel that it is a mistake to identify these orbits with the spatial distribution corresponding to a given eigenfunction of quantum mechanics, for the eigenfunction ordinarily refers to a distribution either in the $3N$ -dimensional configuration space, or in some division of that space which cannot as a rule be identified with our physical space.

The orbits belonging to a single atom are ordinarily grouped according to the principle quantum number. Those having a principle quantum number of one are said to belong to the first, or K shell of the atom, those of principle quantum number two are said to be in the second shell, which may be divided into the s sub-shell and the p sub-shell. These two sub-shells together are equivalent to the octet. In the third and higher shells there is also the d sub-shell, which, however, is not often occupied by the valence electrons, so that the octet retains its significance even in elements of high atomic number. There are, however, numerous cases, especially among the so-called coordination compounds, in which Pauling has clarified a number of difficult questions by making use of d orbits merged with the s and p orbits, as the two latter are believed to merge in the formation of the octet.

PAIRS AND BONDS

In my original theory of valence, aside from the theory of the completed shells, which was advanced at the same time by Kossel, and which I shall presently have occasion to discuss more fully, the two most essential features were the electron pair and the chemical bond of shared electrons. Between these two phenomena there is no immediate connection. The pairing of electrons occurs in nearly all chemical substances, whether or not the pairs serve as bonds. Ten years ago I wrote, "there is nothing in the known laws of electric force, nor is there anything in the quantum theory of atomic structure, as far as it has yet been developed, to account for such pairing." This ceased to be true after the discovery of the remarkable principle of Pauli and of the phenomenon of electron spin. To our former quantum specifications we must add the new quantum specification of spin, so that in place of every one of our former orbits, each capable of being occupied by one electron, we now have a pair of orbits with opposite spins.

The change in energy of a system when one of its orbits becomes occupied depends largely upon what other orbits are already occupied. There is, however, a certain rough approximation to additivity of orbital energies which enables us to say, for example, that there is a wide difference of energy between the two $1s$ orbits and the two $2s$ orbits, that there is a considerable difference in energy between the two $2s$ orbits and the six $2p$ orbits, but that there is a small difference between the several $2p$ orbits. Therefore when electrons are successively added to the atomic nucleus the first electron enters a $1s$ orbit, the second enters the other $1s$ orbit, completing the pair and also the first shell. The next electron enters a $2s$ orbit, the fourth enters the second $2s$ orbit, completing the pair (and the sub-shell). Now we shall see that there is no "force" that draws two electrons into a pair. If we are to speak at all of a force between the two electrons of a pair, it is on the whole a repulsive force, for, as the electrons begin to enter the three pairs of p orbits, the first two do not enter the same pair of orbits, and they therefore do not form an electron pair. This is the state of affairs in the free carbon atom in its lowest energy state.

Numerous examples of this sort, when several pairs of orbits have nearly the same energy and the electrons consequently do not enter in pairs, have been found by spectroscopic research, and by the study of the magnetic properties of what I have called the transition elements.

There has been some tendency among physicists to speak of any two electrons as paired if they have opposite spins. This is far from my own idea. I think, rather, of a pair of occupied electronic orbits as fusing into a single entity, and claim that whenever it is permissible to assign separate quantum specifications to the several orbits, then the two orbits of a pair must be given the same four quantum specifications (for example n , l , m_l and m_s) except for sign. To the pair of electronic orbits we must unquestionably give opposite values of m_s and the same values of n and l . There may be some question regarding the other quantum number, m_l . Professor Latimer, to whom I am extremely grateful for many interesting discussions of the problems considered in this paper, suggests that if the two values of m_l are not zero, they should be taken to be opposite in sign. From this it would result that the electron pair would contribute neither spin-moment, nor angular momentum. As far as I am aware, there are no facts opposed to this view.

Not only is the pair of electrons not necessarily a bond, but the bond need not always be a pair. The simplest case of a molecule in which two atoms are held together by a single electron is the hydrogen molecule ion, H_2^+ , first discovered by J. J. Thomson. One might perhaps expect to find many examples of the one electron bond among the enormous number of known chemical substances, but on the contrary, it is a very rare phenomenon, and it is doubtful if there is a single known case of a stable chemical substance in which there is good evidence for the one-electron bond. There is one thing that we can say pretty certainly from chemical, and especially from spectroscopic evidence, regarding the single electron bond, and in fact regarding unpaired electrons in general. If an atom or a molecule contains one or more unpaired electrons, or in other words, if any orbit is occupied when the other orbit of the pair is unoccupied, then either in its lowest state or in a state which will appear at moderate temperatures, the atom or molecule

will exhibit paramagnetism. This is the most effective criterion for determining the existence of unpaired electrons.

In order to account for the structure of the hydrides of boron, which have too few electrons to assume the normal octet structure, Sidgwick proposed that two of the bonds between boron and hydrogen in B_2H_6 are single electron bonds. This idea has been amplified by Pauling through the assumption that it is no two particular bonds that permanently have this one-electron character, but rather that this character alternates among the several bonds in a sort of resonance. As far as I am aware, the magnetic properties of these substances have not been studied, but when they are, I shall be surprised if any paramagnetic behavior is observed. I shall propose presently another explanation of these structures which seems more probable.

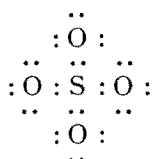
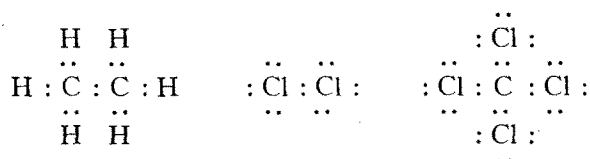
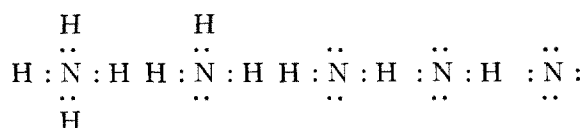
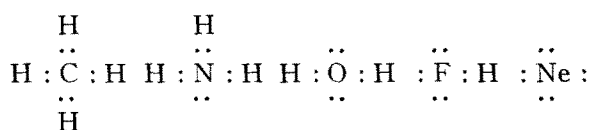
The reason for the scarcity of the one-electron bond is apparently two-fold. In the first place, most of our chemical substances have completely occupied shells or sub-shells, so that pairing is inevitable. In the second place it has been pointed out by Pauling that the single electron bond is not very stable, especially when two unlike atoms are thus bonded. On the other hand, the ordinary two-electron bond stabilizes the pair of electronic orbits which constitutes the bond. The work of Heitler and London made it possible to calculate the energy of some simple systems containing two electrons shared by two atoms. While their calculations were of the utmost importance as a step towards the quantitative study of such systems, I cannot admit that it threw any further light upon the phenomenon of pairing, since their method of calculation could be applied to any two electrons in any two quantum states, or even to a system of two atoms and three electrons.

Unlike the one-electron bond, the three-electron bond, which has sometimes been proposed, is, to my mind, unthinkable. We could, however, have a three-electron double bond with two occupied orbits in one bond, and one in the other. (So also we might have double bonds with only two unpaired electrons.) But all such molecules would exhibit the paramagnetic behavior to which I have referred, and I know of no case where there seems to be any reason to believe in

their existence, except possibly in such an ion as that of ethylene from which one electron has been removed.

THE STERIC IMPLICATIONS OF THE OCTET

We now come to a discussion of those simple electronic structures which are so important to chemists, and in which the valence shell of each atom is fully occupied, or in other words, is a completed shell. Let us write down some of the simple electronic structures with which we have to deal.



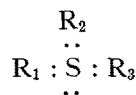
The first two rows illustrate the case of the single octet with or without protons bonded by the electron pairs. The remainder represent cases in which two octets share a pair of electrons, the bonding pair. We shall say that the dots represent, not individual electrons, but occupied electronic orbits.

One of the facts which chemists have been at greatest pains to establish is the fact of the perfect symmetry of the methane molecule. When, however, the present system of spectroscopic classification was introduced, this fact was doubted because the eight electrons of the valence shell of carbon were classified as two *s*-electrons and six *p*-electrons. It is now generally recognized that the two views may be reconciled by a sort of merger of the *s*-orbits and the

p-orbits in such manner as to give four equivalent pairs of orbits. Pauling effects such a merger by an expedient which, unfortunately, breaks the continuity of electronic structure between the methane molecule and the neon atom. The equivalence of these two electronic structures is a point which I insisted upon strongly in my first paper, and upon which I still think that I must insist. When we consider the series of structures from methane through ammonia, water, hydrogen fluoride, to neon, or still better, if we consider the next series obtained by successive removals of one proton from ammonium ion to give ammonia, amide ion, imide ion, and nitride ion, we see how arbitrary it would be to assume a discontinuity of electronic structure about the central atom in such series.

Now the chemist requires not only the equivalence of the four hydrogens in methane, but also a spatial, or steric, arrangement of these atoms. He requires a tetrahedral arrangement about the carbon atom,—a regular tetrahedron if the four entities attached to the central atom are the same, as in methane and carbon tetrachloride, and an irregular tetrahedron if any two of these entities are different. When all four of the entities are different he measures the asymmetry of a molecule by its optical rotatory power.

When one of the protons belonging to ammonium ion is removed, while the electron pair which served as bond remains in the molecule, does this non-bonding pair sink into an *s*-shell, leaving the six *p*-orbits to rearrange themselves in a triangular, or two-dimensional arrangement, as distinguished from the three-dimensional, or tetrahedral arrangement? The answer is decidedly in the negative. The non-bonding pair remains as one of the entities which determines the tetrahedral character of the molecule! It is true that when the three hydrogens of ammonia are replaced by three dissimilar groups, it has not yet been possible to resolve the two optical isomers. Nevertheless, the tetrahedral form about the nitrogen atom is the accepted explanation of the isomerism of the oximes, and in the quite similar structures of the sulphonium type,



numerous substances have been resolved into their optical isomers.

When we come to the next type, represented by water and imide ion, we can no longer hope to find the phenomenon of optical rotation, since two of the entities attached to the central atom are now alike, namely, the two non-bonding pairs; but their steric effect is still manifest in the departure of the molecule from a linear form. I realize that attempts have been made, both by chemists and by physicists, to show that two bonds might, in their normal state, assume an angle less than 180° , even in the absence of other bonds or pairs, but I have never seen any evidence, theoretical or experimental, that seems to warrant such a conclusion. On the contrary, I believe that whenever we have four electron pairs on the central atom, we have a tetrahedron, regular or irregular; that when we have three pairs we have a triangle, while two pairs give a linear structure. Thus in the case of such ions as CO_3^{--} and NO_3^- , in each of which, according to the structure first proposed by Latimer and Rodebush and since abundantly corroborated, there are only three electron pairs binding the three oxygens to the central atom, a structure in three-dimensions was at first suspected, but it is now agreed that the form of each is an equilateral triangle with the carbon or nitrogen atom centrally placed.

When we come to molecules such as HF and NH^- , we no longer have any means of determining the steric effect of the non-bonding electron pairs, but it seems hard to believe that the presence of one more non-bonding pair has produced a change in the essential structure of the molecule. Finally, by removing one more proton from the imide ion, we are left with the neon structure. There will be many who will grant the tetrahedral structure of methane, or even of ammonia, but who will be strongly averse to assigning any such structure to neon. Thus the student of quantum mechanics will show that in neon, with its completed shells, the electron cloud is distributed with perfect radial symmetry. But this, in fact, could also be shown to be true of the methane molecule. The distribution given by quantum mechanics is an average distribution over infinite time, and such a distribution, calculated for methane, would show a central

nucleus with spherical shells of negative electricity, and, mainly outside of these, a spherical shell of protons. This is simply because the tetrahedral atom would, in course of time, pass through all orientations, so that in the statistical average no directions would be unique.

If, instead of methane, we consider carbon tetraiodide, the same thing would be true, but owing to the large mass of the iodine atoms, the system would be more sluggish, and it would be less useful to speak of the spherical distribution of the atoms. We might compare carbon tetraiodide, methane, and neon, with the hour hand, the minute hand, and the second hand of a watch, a photograph of each of which, taken over a day, would show a uniform disk, but this would not be true for short exposures.

On account of the complexity of quantum mechanics in the problem of many bodies, it frequently happens that two investigators, basing their work upon this mechanics, are led to widely different physical views of the atom or molecule, but this is ordinarily because they are dealing with different first approximations, both of which are far removed from ultimate reality. On the other hand, even when an accurate solution of the Schrödinger equation is obtained, it is usually a special, and not a general solution, so that there may be another apparently quite different solution which is equally satisfactory. It is quite possible, if the average electric distribution about the neon kernel were accurately obtained by means of the Schrödinger equation, that we should find indications of two concentric, but largely overlapping shells, one of which might be called the *s*-shell, and the other the *p*-shell, but I see no reason for believing that two-electron orbits would be confined chiefly to the former and six to the latter. The same distribution might equally well be attained by four equivalent pairs of electron orbits. Nor do I see that there is anything in quantum mechanics to prohibit a schedule for the electrons upon their several tracks, or to put it less figuratively, phase relations within the several orbits, such as would give to the neon atom the pattern of a regular tetrahedron.

After all, however, I wish to lay no stress upon the tetrahedral character of the neon atom, and it is of no practical utility. There is no ques-

tion but that the tetrahedral character becomes greatly enhanced, and also becomes more important scientifically, when atoms are bonded by the four-electron pairs. I have only entered upon this discussion because I wish strongly to reaffirm my belief that the fundamental electronic structure, with respect to the central atom, is the same from methane to neon, inclusive, and that the tetrahedral character of methane is not caused by a promotion to a different quantum state from that represented by neon.

THE MOLECULE WITH COMPLETED ELECTRONIC SHELLS

In the study of atomic spectra there is peculiar significance to the completion of an electronic shell, or even of a sub-shell. The atom of neon has its first and second shells completely occupied. It has no uncompensated electronic spins, no angular momentum, no magnetic moment, and no electric moment. It is a singlet state indicated by spectroscopists as 1S . If now we consider that the electrons of a bonding pair help to fill the shells of both the bonded atoms, then we may say that in the molecule of methane the carbon is in a similar state to that of neon, while each hydrogen has its completed first shell. This molecule also has no resultant spin, no angular momentum, and no magnetic moment (but it may have an electric moment when the hydrogens are replaced by different groups). Since spectroscopists have decided to distinguish between atomic and molecular types, methane is said to be in a singlet state, known as the $^1\Sigma$. This is not true only of methane, it is probably true of all molecules that chemists call saturated.

Some spectroscopists, in discussing molecular states, have started with what seems to be a mistaken extension of the Pauli principle, and therefore have been led to the very unpromising idea that a molecule can have only two electrons in its first, or K , shell. It seems to me almost self-evident that when two chlorine atoms combine, the two K electrons of each atom are almost undisturbed. If this is admitted, we are led to consider the valence electrons also, or rather, the occupied electronic orbits, as belonging to the shells of individual atoms, and when this is done we have, at least in the case where all shells are

completely occupied, just the picture of electronic structure that I have presented.

In a molecule consisting of atoms A , B , and C , the several electronic orbits may be designated as A -orbits, B -orbits, and C -orbits, except that certain pairs of orbits should be designated as AB -orbits, or BC -orbits, if there is a bond between A and B , and between B and C .

Thus in the molecule $\begin{array}{c} \cdot\cdot \\ \text{Cl} : \text{Br} : \\ \cdot\cdot \end{array}$ we may say that there are three pairs of non-bonding Cl-electrons, three pairs of non-bonding Br-electrons, and also one pair of bonding ClBr-electrons. If now we are discussing another molecule

$\begin{array}{c} \cdot\cdot \\ \text{Cl} : \text{I} : \\ \cdot\cdot \end{array}$ with the same electronic structure, we must consistently bear in mind that there are large differences possible within this same structure, so that these two molecules may differ greatly in energy, in the distance apart of the atoms, and in electric moment, but these are differences within the same articulated structure and represent no change in articulation.

It is to be noted that when we assign the several occupied orbits to the individual atoms, or to pairs of bonded atoms, it makes no difference whether these atoms are unlike or identical, for we must remember that when the rotational and vibrational quantum numbers of the molecule are fixed, every atom in the molecule is thereby distinguished from every other atom, even though some of the atoms be identical.

In discussing a bond we must avoid saying that one electron of the bond comes from one atom and that the other comes from the other atom. We are not interested in the history of the particles that enter into our system. It is often of value in approximate applications of our mathematical methods to consider a hydrogen ion and a chloride ion coming from an infinite distance to form the molecule HCl, or again to consider a hydrogen atom and a chlorine atom uniting to form the same molecule. In the first case the chloride ion might be said to have furnished both electrons of the bond, while in the second case one would be said to come from the hydrogen atom and one from the chlorine atom. In both cases the same bond is produced, and in that bond the two occupied electronic orbits

must be regarded as welded into a single entity.

If we ignore spin, any non-bonding pair requires three quantum specifications in addition to the designation of the atom to which it is attached. Now it is also true that a bonding pair is fully described when we state which two atoms it binds, together with three, and never more than three, further quantum specifications. This is a point of so much significance that it requires some amplification. Let us consider the simplest of all bonded systems, the hydrogen molecule ion. Here we have a system of two protons and one electron. Making use of the universal rule that each particle contributes three degrees of freedom to the system (again ignoring all spins), we have a total of nine degrees of freedom. This is another way of saying that the quantum state of the system can be fully described by nine quantum specifications. Three of these degrees of freedom are assigned to the translation of the molecule as a whole, two to rotation of the molecule, and one to its vibration. This leaves only three degrees of freedom for the representation of the electronic states, which is the same number that we would have for an electron attached to a single atom.

It would therefore seem, on hasty inspection, as though it would be incorrect to say that a bonding pair has one principal quantum number with respect to one atom and another with respect to the other, but this conclusion is not valid. The principal quantum number of an electron with respect to either atom is associated with the average distance from electron to atom. Likewise the vibrational quantum number is associated with the distance between the two atoms. Now if two of these distances are given, the third is determined. We shall, therefore, find it useful to speak of the principle quantum number of a bonding pair with respect to each of the atoms to which it is attached. So in methane we have assumed that each electron pair is in the second shell of carbon and the first shell of hydrogen; and this is presumably true of every bond between carbon and hydrogen.

In speaking of the electronic structure in the series CH_4 to HF , I stated that this was the same electronic structure with respect to the central atom. It seems not to be the same with respect to the hydrogen atom. While methane

is the type of a saturated molecule; water, ammonia, and hydrofluoric acid behave very differently. Their strong tendency to form complex molecules cannot, I believe, be explained except by assuming the hydrogen bond of Latimer and Rodebush. According to this assumption a hydrogen atom may be bonded to two other atoms. Now it would be impossible for both the two bonded pairs to be in the first shell of hydrogen. We must assume, therefore, that in these substances and probably in all others from which hydrogen can be easily removed as hydrogen ion, the bonding pair is not in the first shell of the hydrogen. This is essentially the view that I put forward in my book on Valence, where I wrote, "Hydrogen when attached firmly to a pair of electrons, as in the hydrogen-hydrogen or hydrogen-carbon bond, shows no tendency whatsoever to become bivalent, or in other words, to form a hydrogen bond. On the other hand, when combined with an extremely negative element like nitrogen, oxygen or fluorine, toward which the electron pairs are very tightly drawn, the bonding pair may be drawn out of the first valence shell of hydrogen into a secondary shell, and it is apparently under some such circumstances that the hydrogen atom can form a loose attachment to another pair of electrons, thus forming the hydrogen bond."

When a molecule like HF is excited to higher vibrational states, it is probable that in most of the new quantum states the bonding pair changes to higher principle quantum states with respect to the proton, until finally the molecule is broken into fluoride ion and hydrogen ion. Up to this point the bond exists, and to call it a "polar bond" at one stage or another of this process seems to contribute nothing to the subject. When I originally proposed the new theory of valence one of my chief hopes was that it might lead toward a simpler and more consistent nomenclature. It is with some sense of discouragement that I have seen the modern terminology developing. We have polar bonds and non-polar bonds, heteropolar and homopolar bonds, covalence bonds and semipolar double bonds.

No one who has accepted the electronic structure as the primary basis of chemical classification can possibly need these various kinds of bonds. Let us consider a molecule such as hy-

droxylamine which has the primary structure
 $\begin{array}{c} \cdot\cdot \\ \cdot\cdot \\ :\text{N}:\text{O}: \\ \cdot\cdot \\ \cdot\cdot \end{array}$, with three protons attached to three of the electron pairs. They are loosely attached in the sense that even in the lowest energy state of the molecule the bonding pairs are presumably not in the first principle quantum state with respect to the protons. These protons move about from one electron pair to another with the greatest ease. Now if two of the protons are attached to nitrogen and one to oxygen, then the bond between nitrogen and oxygen is called a "covalent bond," if all three protons are attached to nitrogen, then the bond between nitrogen and oxygen is called a "semipolar double bond," but if in a case like this we cannot assume a permanence of the electronic structure with respect to nitrogen and oxygen, then we might as well abandon our system altogether. The bond between nitrogen and oxygen is the same wherever the protons are, or even if some of them leave altogether as ions.

It is true that there are other things to talk about in the molecule besides the electronic structure. Thus it is useful at times to speak of the *formal* electric charge on each atom, which is obtained by subtracting from the number of positive charges on the kernel, the number of non-bonding electrons and half the number of bonding electrons which are attached to that kernel. This procedure will usually enable us to predict whether or not a molecule has a high dipole moment. However, all such properties are to be ascribed to the molecule as a whole, and not to some one bond in the molecule.

Whenever we have a free molecule, as in the gaseous state, I see no evidence for the existence of any other kind of bond than the one which we have been discussing under the name of the chemical bond. It is true that in the vapor of sodium chloride this bond may be easily broken. When chloride ion combines with sodium ion the pair of bonding electrons must start a new incomplete shell in the sodium atom. Moreover, this pair may possibly not be in the third principal quantum state with respect to the sodium, even in the state of lowest energy. If the molecule is activated, certainly some, and probably the most important, of the quantum states are those in which the bonding pair has a high principal

quantum number with respect to the sodium. However, the bond persists until the molecule finally dissociates, and then there is no longer a bond.

MOLECULES WITH INCOMPLETE SHELLS

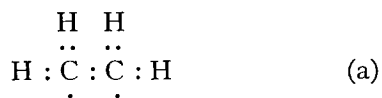
The molecules with completed shells are of extraordinary interest because of the simplicity with which they can be catalogued, and because the normal states of an enormous number of chemical substances are of this type. When we are considering the physical properties of saturated substances at ordinary temperatures, it is the electronic structure of completed shells that must be our guide. On the other hand, it is the excited states of the molecule which are of interest to the spectroscopist. These excited states must in the future be of equal interest to the chemist, because it is ordinarily through the intervention of such states that a chemical reaction occurs. However, the study of molecules with incomplete shells presents enormous difficulties and many of the rules which we have laid down for the saturated molecule can be used only as rough guides in an approach to an understanding of the unsaturated molecule.

Let us examine for a moment the organic chemist's use of the term "saturated." The hexamethylene molecule, C_6H_{12} , is called a saturated molecule, and is one in every respect, although if the ring were broken, it would not have enough electrons to fill all the valence shells. Now it was pointed out by Baeyer that as the number of methylene groups in the ring diminishes, there is an increasing strain, or instability, which becomes very evident in the trimethylene ring. According to Baeyer's theory, the series does not end with trimethylene, but with the two-membered ring ethylene, C_2H_4 , only here the ring has become the double bond. Now in spite of this theory of Baeyer the organic chemist classifies this single member of the series, the ethylene molecule, as an unsaturated hydrocarbon. Here again his uncanny instinct proves to be sound.

We must not call a molecule unsaturated merely because it takes only a small amount of energy to change it to a new electronic structure. This, however, is true of the double bonds and we could arrange them more or less in the order

of increasing instability, $C=C$, $C=N$, $C=O$, $N=N$, $N=O$, $O=O$. In the case of molecular oxygen, one of the two bonds is definitely broken in the state of lowest energy. The unpaired electrons give rise to the pronounced paramagnetism of oxygen, and it is only among the excited states of oxygen that the spectroscopists have found the $^1\Sigma$ state in which we recognize the true double bond. So also the bond between nitrogen and oxygen in some nitroso compounds is broken, although we do not know in how many cases this is true. In the other cases, as far as is now known, the doubly bonded formula with completed shells represents the normal state of the molecule.

The mere fact that ethylene is near the breaking point would not justify us in calling it a truly unsaturated molecule. This is justified by another line of reasoning which indicates the difficulty of assigning definite formulae to unsaturated molecules. We have pointed out that it would not take much energy to break one of the ethylene bonds and thus produce a molecule of the oxygen type represented by

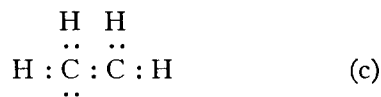


Now there is no way of compromising between this state and the normal state



One changes to the other in an abrupt transition which changes the whole character of the molecule. If we think of electronic orbits as tracks upon which the electrons can run, then we might say that in this transition the gauge of all these tracks is suddenly changed so that it would be impossible for an electron to run on both types of tracks simultaneously. On the other hand, there may be different formulae which represent the same essential electronic structure and these we must now examine.

We have said that a completed electronic structure will always give rise to a $^1\Sigma$ state of the molecule. The converse of this is by no means true. Thus if we should write for ethylene the formula



this also would presumably belong to the $^1\Sigma$ type and therefore would presumably be, if we may so speak, of the same gauge as the doubly bonded formula (b). Now if we have two formulae such as (b) and (c) which differ only in electronic arrangement and are of the same spectral type, or, as we have said, of the same gauge, then these two formulae cannot be regarded as two possible separate states of the molecule. They must rather be regarded as two different *representations* of a single structural state, which ordinarily has a lower energy than would be predicted if we should assume that there are two separate states and that some of the molecules are in one state and some in the other.

This is the phenomenon which has been called by Ingold the T-effect and which has been studied recently by Pauling under the name of resonance. We must not think that this phenomenon is due to the fact that we can write two or more different formulae to represent the same structure, but rather we must think that we can write two or more formulae because there has been a considerable loosening, without fracture, of the skeletal structure, so that within this skeletal structure there is far more freedom from the effects of quantum restrictions than in a saturated molecule such as ethane.

In the case of ethylene, formula (c), which is one of the ways of representing the compromise or resonance state, shows a structure of incomplete shells, and it is for this reason that we are justified in speaking of ethylene as an unsaturated molecule. On the other hand, in this particular case formula (c) represents an extreme displacement of electric charge from one side of the molecule to the other and presumably, therefore, plays only a minor part in determining the properties of the compromise state. This is no longer true in acetylene where the formulae $\text{H} : \text{C} :: \text{C} : \text{H}$ (a) and $\text{H} : \text{C} : \text{C} : \text{H}$ (b) might

seem equally reasonable. If these are two ways of expressing the same fundamental electronic structure, the properties of the system may perhaps be more nearly represented on the basis of the second rather than the first of the two. On

the other hand, if formula (b) represented the only possible form of the molecule, it would presumably not be stable, for by analogy to the results obtained from atomic spectra, we should expect this form alone to be unstable with respect to $\text{H} : \overset{\cdot}{\underset{\cdot}{\text{C}}} : \overset{\cdot}{\underset{\cdot}{\text{C}}} : \text{H}$ (c) which would represent an entirely different type of electronic structure. However, the compromise state, of which formulae (a) and (b) may be regarded as two reasonable representations, is stable with respect to any other different type of electronic structure such as is represented by formula (c).

It seems to be a rule that when two electrons are absent from a completed shell, the two empty orbits will not belong to the same pair, unless all the electrons present are employed in forming bonds, in which case the pairs are stabilized by acting as bonds. Thus there is a sharp contrast between the oxygen atom with its six electrons, two of which are unpaired, and the nitrate and carbonate ions in which there are six electrons on the central atom, which, however, are all employed in forming the bonds with oxygen. These ions therefore behave as though they were, and almost undoubtedly will be found to be, in the $^1\Sigma$ state.

I wish now to raise a question concerning the meaning of the dots in the formulae that we have been using. In the ordinary case of the saturated molecule we have said that these dots indicate occupied electronic orbits. Therefore, by counting the dots, we have the total number of valence electrons in the molecule. Now, however, that we are discussing incomplete shells, shall we adhere to this rule, or shall we let the dots represent orbits which are occupied, as one might say, a considerable part of the time? I am inclined to suggest the latter, and to write for the hydride of boron, B_2H_6 , the same formula that we have written for ethane, indicating in some way that two electrons are missing, so that on the average each bonding pair of orbits is occupied only six sevenths of the time. We shall then have a picture of a molecule in which all the electrons remain paired, but in which the orbits are not fully occupied. If we imagine the electrons in rapid motion throughout the several orbits, and in such phase relations as to preserve the pairs at

all times, we should presumably diminish the strength of the bonds without altogether destroying their stability. In fact, we know that the boron-boron bond is broken when the hydrogens are replaced by other radicals. If B_2H_6 proves as I suspect that it will, to be in the $^1\Sigma$ state, I think that this will be the best way to represent its structure.

When a molecule of completed shells becomes unsaturated, it may do so through a change which renders some of its existing shells incomplete, or by beginning new shells. Thus in a paraffin hydrocarbon the only way in which electrons can be added is through the occupation of orbits which are higher than the first shell for hydrogen, or than the second shell for carbon. Phenomena of this sort undoubtedly exist. Triphenylmethyl seems to form a compound with hexane. There is no possible way of explaining the interesting phenomenon known as the Walden inversion without assuming that for a brief moment, at least, the asymmetric carbon atom has become quinquivalent. In this case it is probable, however, that the fifth atom does not attach itself unless one of the other four atoms is already (either in the normal state or through excitation) in a high principle quantum state with respect to its bonding pair.

Whenever we have one more or one less electron than the number required to fill the shells, in some cases it may be easy to locate the particular atom on which the excess or deficiency occurs. In other cases, however, we may only indicate the group of atoms where this occurs, and in extreme cases it may only be possible to say that the molecule as a whole has an excess, or a deficiency, of one electron. Even in my first discussion of the problem of odd molecules of the inorganic type, I took pains not to indicate which atom possessed the odd electron. In such extreme cases the usefulness of structural formulae may nearly disappear, but this is no reason why in other cases we should not use the structural formulae as far as they will go.

In the study of atomic spectra an extraordinary similarity has been found between states which have an electron in excess of the completed shell, and those in which one electron is lacking. The only suggestion that I feel competent to

make regarding molecular spectra is that we should start, as a norm, with the molecule of completed shells, assigning each electron orbit to a given atom, or to a given bond between two atoms. From the norm we should proceed, symmetrically in both directions, to the discussion of cases where one electron is in excess or one electron is lacking, proceeding next to the case where two electrons are in excess, or two are

lacking. An attempt should be made to assign these electron excesses or deficiencies to individual atoms, although we know in advance that in some cases this attempt will fail.

I am afraid I have not contributed much to this difficult subject of the incomplete shells, but I believe that the study of such systems is the greatest field for the future development of chemistry and spectroscopy alike.