

BONDING POWER OF ELECTRONS AND THEORY OF VALENCE¹

ROBERT S. MULLIKEN

Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

Received October 5, 1931

I. INTRODUCTION

Valence is commonly classified under the headings of polar and non-polar valence, and of primary and secondary valence. It has, however, long been evident that no sharp lines can be drawn in general between these various kinds of valence. In fact, the concept of valence itself is one which should not be held too sacred.

This paper will have to do principally with non-polar valence. Before trying to investigate the nature of this, it may be well to analyze the meaning of such a statement as "the valence of carbon is four." This meaning can be well illustrated by considering the series of conceivable compounds CH , CH_2 , CH_3 , CH_4 , CH_5 , CH_6 , and so on. Of these, only CH_4 is stable in the ordinary chemical sense. In this compound, the carbon atom exhibits a valence of four, if unit valence is attributed to each hydrogen atom. In nearly all of its stable chemical compounds, in fact, carbon is attached to four univalent atoms or the equivalent.

¹ Presented at the eighty-first meeting of the American Chemical Society held at Indianapolis, Indiana, March 31, 1931, and since then somewhat revised and considerably enlarged. This paper is partly a review, partly a presentation of more or less new material. In a paper just published (in "Molekülstruktur," Leipzig Vorträge, 1931, p. 167. S. Hirzel, Leipzig), Herzberg has arrived independently at conclusions many of which are practically identical with those given here. The author is indebted to him for the opportunity of seeing the manuscript of his paper. A few points taken therefrom and not included in the original draft of the present paper but incorporated in the process of revision are so indicated in the text. In a paper also presented at the Indianapolis meeting, Urey (*J. Chem. Education* **8**, 1114-32 (1931)) has discussed some of the points treated here, and partly in more detail.

What is wrong with the chemically unstable² molecules CH, CH₂, CH₃, CH₅, CH₆? There is really an essential difference between the cases of CH, CH₂, CH₃, and those of CH₅, CH₆, and so forth. An individual molecule of the first group is stable in the sense that a fairly large energy would be required to pull off a hydrogen atom ("physical stability²"), while CH₅ and CH₆ are presumably unstable even in this sense, just as a molecule composed of two helium atoms is unstable. The chemical instability of such a molecule as CH is, however, of an entirely different character from that of CH₅. The trouble with CH is not that the carbon and hydrogen atoms will not remain together, but that they can not keep other atoms away. Nevertheless the CH molecule is well known from the spectra of flames and of electric discharges, where artificial means are used to tear off the other atoms with which the CH normally unites.

This example illustrates two principal functions of valence theory, namely, to account for the existence of chemical binding, and to account for the phenomenon of saturation of valences.

II. THEORIES OF VALENCE

The Lewis theory

In the valence theory developed by Lewis and extended by Langmuir and others, atoms are supposed to be held together practically always by pairs of electrons, one electron usually coming from each atom. According to this theory, the electrons in each molecule seem tacitly to be considered as divided into two classes—the bonding electrons, nearly always in pairs, which actively hold the molecule together, and the remaining electrons, which may be called non-bonding electrons, since they are supposed to play an inert, or at least a minor, rôle in binding the atoms.

² The term "molecular stability" as contrasted with "chemical stability" was used by Mulliken: *Phys. Rev.* **32**, 189 (1928). Herzberg in his new paper (cf. footnote 1) uses the term "physical stability" instead.

The theory of bonding and anti-bonding electrons and of bonding power

Another conception, which seems to correspond in a more natural way to our knowledge of the structure of diatomic molecules based on the interpretation of their spectra, is that we must assume not only bonding and non-bonding electrons, but also anti-bonding electrons, i.e., electrons which actively oppose a union of the atoms (1). More generally still, one may assign to each type of electron in a molecule a "bonding power," which may have any value, positive, negative, or zero, within a certain range (1). These conceptions first grew out of a development of the fundamental work of Hund (2) on the formation of diatomic molecules from atoms. Later on, examples will be given of the action of bonding and anti-bonding electrons in such molecules as NO, O₂, and F₂.

But the empirical rules of non-polar valence, which of course summarize the usual facts of combining ratios in stable non-polar compounds, suggest that the electrons in polyatomic molecules usually act in a more standardized way, classifying themselves quite definitely under the two headings "bonding" and "non-bonding." Herzberg (3) has, however, suggested that these rules of valence can be accounted for equally well in terms of bonding and anti-bonding³ electrons. He points out that if each anti-bonding electron or electron-pair more or less exactly counterbalances a bonding electron or electron-pair, then the molecule behaves just as if the number of bonding pairs, i.e., the number of chemical bonds, were equal to the difference in the numbers of bonding and anti-bonding pairs.

If the numbers of bonding and anti-bonding electrons are equal, then zero valence bonds are present. This is the case when the attempt is made to bring together two atoms of a rare gas. The fact that two such atoms vigorously resist being brought together indicates that, although the bonding and anti-bonding electrons have been spoken of as more or less equal

³ Hund (3) uses the expressive term "loosening" (lockernde) electrons for what are here called anti-bonding electrons.

although opposite in effect, the anti-bonding electrons are really decidedly more powerful than the bonding ones.

Quantum theory and molecule formation

The rules of valence are really concerned with the question of what particular molecular forms are chemically the most stable. Although quantum mechanics has not yet reached the point of accounting in detail for all the facts of valence, it does very definitely give the solution of the more general problem of why it is that atoms are capable of forming molecules at all. Quantum theory, following experiment, demands the existence of discrete stationary states of energy, for molecules as well as for atoms. It shows further that in each such stationary state the electrons may be thought of as moving in what used to and may still with reservations, be called orbits. And finally it shows, in outline at least, how when two or more atoms come together, the orbits of their electrons can be altered in a perfectly continuous manner to give the appropriate electron orbits of the molecule (Hund (2)). In the case of diatomic molecules, as well as that of polyatomic molecules in which all the nuclei are on a straight line, the electron orbits can often be classified under such names as $1s\sigma$, $2p\sigma$, $3d\pi$, or $\sigma 1s$, σ^*1s , $\sigma 2s$, and so on, much the same as the electron orbits in atoms can be classified as $1s$, $2s$, $2p$, and so on.⁴

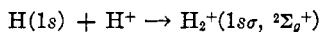
Formation of H_2^+ and H_2 molecules

Examples of bonding and anti-bonding electrons

The problem of valence is really one of energy relations. If there were rules for determining the energies of all the different kinds of possible electron orbits in molecules, and comparing

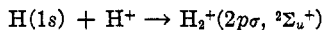
⁴ For a brief discussion of the meaning of σ and π orbits, see Mulliken, R. S.: Chem. Reviews **6**, 532 (1929). For a more detailed discussion, cf. reference 4. The present discussion of London and Heitler's valence theory should be taken as superseding that given in this earlier review. The $U(r)$ curves and dissociation products of the CN and N_2^+ molecules are also, according to the present belief, of the author, different from those given in figure 6 of this earlier review. For revised $U(r)$ curves see reference 4.

them with those in atoms, the rules of valence should follow more or less automatically. Suppose for instance an ordinary hydrogen atom and a hydrogen ion be allowed to come together. (In emphasizing H_2^+ , the author is in part following Herzberg's new paper.) It is known, from quantum theory and experiment, just how firmly the hydrogen atom electron, which is of the $1s$ type, is bound. It is also known from quantum theory that when the atom and ion approach in the right way, the electron orbit tends to reach out and surround both nuclei, thereby becoming more firmly bound because it is now attracted by two nuclei instead of one. This goes on until the resulting attractive forces are balanced by the repulsion between the two nuclei. This is the simplest case of an electron acting as a bonding electron. The shape of the orbit is greatly changed when the atom and ion come together, but it can still be classified as of the $1s$ type. It is usually called $1s\sigma$, although in the simple case of $1s$ electrons, the " σ " really adds nothing to the meaning. For the change which occurs when the H_2^+ molecule is formed we may write:



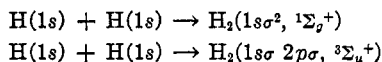
The changes in the electron orbits when molecules are formed are usually not so simple as in this case. Even here, there is a second, more complicated way in which the atom and ion may approach each other. In this, the electron undergoes a gradual change, which will be referred to as a promotion, from its original 1-quantum orbit to a 2-quantum orbit; more specifically, to a $2p\sigma$ orbit.⁴ The change occurs gradually as the distance between the nuclei is decreased (4), and would not be complete until the nuclei were completely united ("united-atom"), which of course is in practice impossible because of their mutual repulsion. The change to a $2p\sigma$ orbit, if completed, would involve a very large increase in energy as compared with a $1s\sigma$ orbit, since in any atom the 2-quantum orbits are always much less firmly bound than the 1-quantum orbit. The net result is that when the atom and ion approach in such a way that the electron is promoted to $2p\sigma$, the energy of promotion, which increases gradually as the nuclei are brought together, together with the energy of repulsion

of the nuclei, causes the atom and ion continuously to repel each other, except at very large distances, so that no molecule is formed. The 1-quantum ($1s$) electron which would become $2p\sigma$ acts here as a typical anti-bonding electron. For the change which occurs when the atom and ion come together in this case we may write:



What happens to the original orbit as the atom and ion approach may be described in more detail approximately as follows. For $r = \infty$, the electron moves in 1-quantum orbit about one of the two nuclei. As r is decreased, the shape of the orbit is somewhat modified, in such a way that in the $1s\sigma$ case the electron spends more than half its time on the side of the original nucleus toward the other nucleus, or in the $2p\sigma$ case, on the side away from the other nucleus. Also, after going around the first nucleus a number of times, the electron jumps to the second nucleus; after usually about the same length of time, it jumps back to the first nucleus, and so on. As r is further diminished, the orbit becomes more and more deformed, and at the same time the jump frequency becomes larger and larger compared with the frequency of motion of the electron in its orbit around either nucleus. Finally when r is small enough—as is true in H_2^+ when r is equal to its equilibrium value—the two frequencies are of the same order of magnitude and the electron may best be thought of as moving in a single complicated orbit around both nuclei.

In the case of two neutral hydrogen atoms, just as in the case of $\text{H} + \text{H}^+$, there are two ways in which the atoms can approach each other. In the one mode of interaction, both electrons become $1s\sigma$ electrons and so act as bonding electrons, forming an ordinary stable H_2 molecule. In the other, one electron becomes $1s\sigma$ but the other is promoted to $2p\sigma$. The energy of promotion is so large in this case that it more than balances the energy gained by the increased firmness of binding of the $1s\sigma$ electron, and no stable molecule is formed. The changes which occur in the two cases when two hydrogen atoms come together may be written:



The heat of dissociation of the stable H_2^+ molecule held together by one $1s\sigma$ electron has been calculated with a fair degree of accuracy by quantum theory, and is about 61,000 calories per mole. This is approximately half as large as the heat of dissociation (103,000 calories) of H_2 , which is held together by two $1s\sigma$ electrons. This fact indicates that to a first approximation each $1s\sigma$ electron acts independently as a bonding electron in H_2 (cf. also the next section).

Calculation method of Heitler and London

It should be pointed out that the method used above, which really amounts to an interpolation between separated-atoms and united-atom, can not always be relied on to determine whether or not a stable molecular state can be formed from two atoms interacting in a given way, although in most cases it gives good results. In the above case of $H_2(1s\sigma 2p\sigma, {}^3\Sigma)$, for example, there might *conceivably* be a considerable attraction between the atoms at large distances, leading to the formation of a fairly stable molecule, in spite of the fact that at least at smaller distances the large promotion energy of $2p\sigma$ gives assurance of a strong repulsion. In other words, the process of promotion might conceivably at large distances not proceed fast enough to produce a repulsion.

But Heitler and London (5) have introduced a very valuable method of calculation, which shows definitely in the case of $H + H$ that for $(1s\sigma)^2$ there is attraction, for $(1s\sigma)(2p\sigma)^3\Sigma$ repulsion, at all distances,—except that there is a superposed small van der Waals' attraction at very large distances. A similar result is found for $1s\sigma$ and $2p\sigma$ in H_2^+ (6). The method of Heitler and London consists in the application of the perturbation theory of quantum mechanics to the problem of calculating the energies of interaction of atoms. This *method* of Heitler and London should be carefully distinguished from the *valence theory* of Heitler and London, which will be discussed below.

In this and other simple cases in diatomic molecules, the method of Heitler and London makes it possible to calculate approximate values of the heat of dissociation, equilibrium distance be-

tween the nuclei, and other constants of stable molecular states, and to predict which of the various states that can in general be formed from two normal atoms should be attractive and which repulsive. The necessary calculations promise, however, to be rather complicated in all but the simplest cases. The method also fails to give a detailed insight into the nature of the changes which take place in the electron orbits when atoms come together.

In the method which is emphasized in this review, quantitative information and predictions as to the energies of interaction of two atoms and as to molecular constants are based mainly on empirical spectroscopic data (atomic and molecular). With the help of quantum theory, there is obtained a rather intimate picture of the changes which occur in the electron orbits when atoms unite.

Application of Heitler and London method to H_2 and H_2^+

Lack of fundamentalness, for valence theory, of the establishment of symmetrical relations between electrons during molecule-formation

In order to dispel what, in the author's opinion, are some misconceptions that have arisen in connection with the work of Heitler and London on molecule-formation and valence theory, and for other reasons, it will be of value to consider in some detail certain features of the Heitler and London method as applied to H_2^+ and H_2 . (*This section can best be omitted, or at least postponed, by the casual reader.*)

For the energy change ΔW which occurs when an H atom and an H^+ ion come together, their method (6) gives the following expressions:

$$\Delta W = e^2/r - \frac{e^2 I_1}{1+S} - \frac{e^2 I_2}{1+S} \quad (\Delta W < 0 : 1s\sigma)$$

$$\Delta W = e^2/r - \frac{e^2 I_1}{1-S} + \frac{e^2 I_2}{1-S} \quad (\Delta W > 0 : 2p\sigma)$$

Here e^2/r is the energy of repulsion of the nuclei, while $e^2 I_1$ is the energy of attraction which the hydrogen ion would have for the

electron of the hydrogen atom, as calculated by quantum mechanics, if the electron orbit, or better, wave-function, were completely undeformed by the approach of the ion. The sum $e^2/r - e^2I_1$, commonly called the "Coulomb energy," gives at all values of r a repulsion, which is, however, slight except at small r values. The quantity S in the equations is small at large r values but approaches unity as $r \rightarrow 0$ (6).

The quantity e^2I_2 is the "exchange" (or "resonance") energy. The name "exchange energy" corresponds to the fact that the existence of this term is connected with the exchange or jumping back and forth of the electron between the two nuclei, described above. This exchange energy, modified by the factor $1/(1 \pm S)$, when *physically interpreted* is evidently essentially the energy required for the deformation of the $1s$ atomic orbit in $H + H^+$ either into $1s\sigma$ of H_2^+ (negative exchange energy and ΔW , increased firmness of binding) or into $2p\sigma$ of H_2^+ (positive exchange energy and ΔW , decreased firmness of binding).

In the case of two neutral hydrogen atoms, the results are similar, but are somewhat complicated by the presence of two electrons. The method of Heitler and London (6) gives the following:

$$\Delta W = e^2/r - \frac{e^2(2I_1 - I_4)}{1 + S^2} - \frac{e^2(2SI_2 - I_6)}{1 + S^2} \quad (\Delta W < 0 : 1s\sigma^2)$$

$$\Delta W = e^2/r - \frac{e^2(2I_1 - I_4)}{1 - S^2} + \frac{e^2(2SI_2 - I_6)}{1 - S^2} \quad (\Delta W > 0 : 1s\sigma 2p\sigma)$$

As compared with H_2^+ , the most important changes in the ΔW formulas, for values of r corresponding to equilibrium in the stable state $(1s\sigma)^2$, are (a) $2I_1$ and $2I_2$ appear in place of I_1 and I_2 because there are now two electrons, *each* of which is attracted by the other nucleus as well as by its own; (b) the new terms I_4 and I_6 , which represent energy of mutual repulsion of the two electrons, appear.

The Coulomb energy, given by $e^2/r - e^2(2I_1 - I_4)$, and corresponding to the net energy change which would result from the mere overlapping, if this were possible, of two undeformed hydrogen atoms, would give rise here to a mild attraction at moderate r values and to repulsion at small r values.

The exchange energy $e^2(2SI_2 - I_6)$ now consists of two parts. (1) The quantity $2e^2SI_2$ corresponds to the exchange or jumping of the electrons between the two nuclei, just like the analogous term in H_2^+ , except that now two electrons jump (simultaneously, as it happens). Modified by the factor $1/(1 \pm S^2)$, it gives essentially the direct energy changes resulting from the deformation of the atomic $1s$ orbits to become molecular $1s\sigma$ or $2p\sigma$ orbits. With a minus sign in the ΔW equation it gives increased binding energy ($1s\sigma^2$); with a plus sign it gives decreased binding energy ($1s\sigma 2p\sigma$). (2) The quantity e^2I_6 corresponds to an exchange of orbits between the two electrons. Modified by the factor $1/(1 \pm S^2)$, it gives mainly the changes in the energy of mutual repulsion of the two electrons which are incidental to the orbit-deformations just mentioned under (1). In the case of both the states $(1s\sigma)^2$, $^1\Sigma$ and $(1s\sigma)(2p\sigma)$, $^3\Sigma$, the terms $\pm e^2I_6$ oppose and partially cancel the terms $\mp 2e^2SI_2$.⁵

The physical reasons why the terms e^2I_6 appear in both the ΔW equations with opposite sign to the terms $2e^2SI_2$ are probably as follows. (1) In the $(1s\sigma)^2$ state, both orbits are relatively small, so that the mutual repulsion of the electrons is increased as compared with what one would get from the I_4 part of the Coulomb energy, which corresponds to the mutual repulsion energy of undeformed but overlapping atomic $1s$ orbits. In the $(1s\sigma)(2p\sigma)$, $^3\Sigma$ state, however, one orbit ($2p\sigma$) becomes relatively large, the other ($1s\sigma$) relatively small, so that the energy of repulsion of the electrons is decreased. (2) These effects, which are probably the main ones, are somewhat intensified by the fact that in every singlet state (resultant spin $S = 0$) of a two-electron system the electrons are symmetrically related or symmetrically "connected" (in the words of London, "symmetrisch verknüpft"), and in every triplet state ($S = 1$) they are antisymmetrically

⁵ A rough calculation shows that for $r = 1.5 a_0$, corresponding to the equilibrium separation in H_2 as calculated by the Heitler and London method, the electronic repulsion term $\frac{e^2I_6}{1 + S^2}$ is 5 volts, while the primary orbit-deformation term $\frac{2e^2SI_2}{1 + S^2}$ is 14 volts, for the $(1s\sigma)^2$, $^1\Sigma^+$ state.

related. (It should perhaps be pointed out that the letter S is here used with an entirely different meaning than in the last few paragraphs. It has still a third meaning in symbols such as 1S , 2S , 3S used elsewhere in this paper.)

Strictly speaking, one should not say here that the electrons are symmetrically or antisymmetrically related, but only that in respect to their position coördinates, such relations exist. Really, when their spins are included, electrons in atoms or molecules are always antisymmetrically related. But for the sake of simplicity, the word "electrons" will be used in this connection throughout this paper with the tacit understanding that it implies position coördinates only and neglects spins.

The effect of a symmetrical relation is to make the electrons keep on the average closer together than they otherwise would, while an antisymmetrical relation makes them keep farther apart. Hence, unless other indirect effects are important, a symmetrical relation increases the energy of repulsion of the electrons and so the total energy, while an antisymmetrical relation decreases it. It was so that Heisenberg first explained the fact that, for example, the energy of the $1s\ 2s$, 1S state of the helium atom (electrons symmetrically related, spin = 0) is higher than that of the $1s\ 2s$, 3S state (electrons antisymmetrically related, spin = 1).

Most writers on the subject, beginning with London and Heitler, have emphasized the fact that when a stable H_2 molecule ($1s\sigma^2$) is formed, a symmetrical relation is established between the two electrons of $H + H$. But from the preceding analysis of the meaning of the "exchange energy" in the formation of H_2^+ and H_2 , it seems clear that the establishment of a symmetrical relation between two electrons in H_2 when a valence bond is formed, is purely incidental.⁶ Indeed it seems evident that the

⁶ Two electrons need not necessarily go into the same kind of orbit in order to be symmetrically related. For example, in the 1S state of the helium atom with one $1s$ and one $2s$ electron ($1s\ 2s$, 1S), the two electrons are symmetrically related. When two like univalent atoms, e.g. two hydrogen atoms or two sodium atoms, unite to form a stable molecule, the two valence electrons become symmetrically related and are undoubtedly both in the same kind of orbit. But when two unequal atoms, e.g. sodium and hydrogen, unite, although their valence electrons become symmetrically related, it is open to some question whether they should be considered as being in the same kind of orbit (cf. discussion of heavier diatomic molecules on p. 379).

symmetrical relation *per se*, since it gives a positive contribution to the total energy, tends to weaken the binding of the two atoms.

. Two helium atoms

The case of two helium atoms is similar to that of two hydrogen atoms. In the latter case, however, there was a choice between the two molecular electron configurations $(1s\sigma)^2$, which is ordinary stable H_2 , and contains one valence bond according to usual valence theory, and $1s\sigma 2p\sigma$ where there is no valence bond. But in the helium case, there is no choice. Each helium atom has two $1s$ electrons to begin with, and if the atoms came together this would make four $1s$ electrons. But we know that no atom can have more than two $1s$ electrons, and this holds equally for a molecule. (This is an example of what is known as the Pauli exclusion principle.) Hence when the two helium atoms approach each other, two of the $1s$ electrons necessarily begin to be promoted to $2p\sigma$ electrons. From our empirical knowledge of the properties of helium gas, it is evident that these two anti-bonding electrons overpower the effect of the two bonding $1s\sigma$ electrons, causing the atoms to repel each other even at fairly large distances, so that no molecule is formed. Calculations by the method of Heitler and London give the same result (7).

London and Heitler's spin theory of valence

The principles that underlie these well-understood results for hydrogen and helium are presumably the same that must be used for explaining valence in general. London and Heitler tried to generalize the results of their calculations on these atoms in their well-known spin theory of valence (8). They noticed that in hydrogen a valence bond is formed when two originally unpaired electrons become paired and both go into the same kind of orbit, i.e., when they become symmetrically related.⁶ London and Heitler then *postulated* that this establishment of a symmetrical relation between two electrons originally belonging to two separate atoms is characteristic of valence bonds in general. Thus they had a quantum-mechanical theory closely paralleling the Lewis theory of bonding electron pairs (9), at least for the usual case where each atom contributes one member of the pair.

In their theory, the valency, V , of an atom is supposed to be equal to the number of unpaired electrons. Since each unpaired electron has a spin quantum number $\frac{1}{2}$, and since all these unpaired spins stand parallel to each other, they give a resultant spin quantum number S for the atom which is equal to $V/2$. Thus it happens that in Heitler and London's theory the spin S can be taken as a convenient indicator of the number of free valences: $V = 2S$. The resultant spin in turn is related to the "multiplicity" m : $m = 2S + 1$. It also happens, in consequence of the Pauli principle, that when unpaired electrons become paired, i.e., symmetrically related, in a molecule, their spins pair off too, the members of each pair being arranged with their axes opposite so as to make a zero contribution to the resultant spin. If two atoms, each having the same number n of unpaired electrons and a spin $S = n/2$, unite in such a way that all the electrons thereby become paired off, the molecule has a spin of zero, and, incidentally, is as a result diamagnetic in all ordinary cases. This corresponds, according to London and Heitler, to the formation of a multiple valence bond, e.g., if $n = 3$, a triple bond.

London and Heitler's theory is enticingly simple but, in the opinion of the author, really does not hit the nail on the head. For many types of atoms, to be sure, especially if at least one atom is in an S state, it gives nearly always the correct valence, although in some cases it is necessary to make use of atoms in somewhat excited states. In other cases, however, especially atoms in P , D , and other states, it does not work so well. Moreover, its emphasis on spins and the pairing of spins, or even on the pairing of electrons, i.e., the establishment of symmetrical relations between them, seems misleading to the author, for reasons that have been outlined in a preceding section entitled "Application of Heitler and London method. . . ." ⁷ The presence of unpaired electrons and their spins, and their pairing in molecules, undoubtedly act usually as convenient indicators

⁷ Kemble and Zener (Phys. Rev. **33**, 512 (1929)) and Urey (Ruark and Urey: Atoms, Molecules, and Quanta, p. 687. McGraw-Hill Book Company, New York (1930)) also conclude that the symmetric relation of the electrons *per se* is relatively unimportant for molecular stability. See also Herzberg (footnote 1) and others.

of valence and of the formation of valence bonds, respectively, but even then in the author's opinion, they conceal something which is more fundamental.

This something is clearly revealed even in the simple example of the formation of the hydrogen molecule. Here a stable molecule is formed simply because $1s$ orbits in hydrogen atoms are capable of being sufficiently more firmly bound when they have two hydrogen nuclei to run around than when each has only one. The fact that two electrons become paired, i.e., that one comes from each atom and that they then become symmetrically related, seems to be largely incidental, as does also the pairing of the spins. In H_2^+ , where there is only one electron, the case is even clearer, since here there is no possibility that pairing of electrons can be of importance for the result. What is fundamental here, it seems to the author, is that we have in the $1s$ orbit in hydrogen an orbit whose character permits it to become considerably more firmly bound when the hydrogen atom unites with another hydrogen atom, or in fact with any other kind of atom which can accept this electron without the necessity of an excessive promotion energy.

The molecules HeH, He₂⁺, CaH, and so on

In seeking further light on valence theory, one may ask, why should not a helium atom, with two $1s$ electrons, be able to unite with a hydrogen atom to form a stable molecule? Calculations by the method of Heitler and London show that these two atoms do *not* form a stable molecule (10). The question is one that the valence theory of London and Heitler accounts for very promptly by saying that the two $1s$ electrons in helium are already paired, their valences being mutually satisfied inside the helium atom, so that the latter is incapable of forming a compound with any other atom. From the present point of view, however, the explanation is different. It is known from the Pauli principle that no atom or molecule can contain more than two $1s$ electrons, at least not if these $1s$ orbits get near one another. Hence the $1s$ electron of the hydrogen atom, when it comes into contact with a

helium atom containing two $1s$ electrons, is promoted to a $2p\sigma$ orbit. It is easy to understand that this can take so much energy that the two atoms repel each other.

But in other analogous cases, it is known from spectroscopic evidence that a physically stable molecule is formed. Thus a helium atom (two $1s$ electrons) and a helium ion (one $1s$ electron) unite to form a fairly stable molecule $\text{He}_2^+(1s\sigma^2 2p\sigma)$. Here the two bonding electrons $1s\sigma$ evidently outweigh the one anti-bonding electron (this idea is taken from Herzberg's paper (see footnote 1)).

There seems to be no good reason to suppose that the difference in behavior of $\text{He} + \text{H}$ and $\text{He} + \text{He}^+$ is other than a quantitative one. Possibly, to be sure, the fact that one of the particles which unite to form He_2^+ is an ion is partly responsible for the difference. But it is known from band spectrum evidence that such neutral molecules as MgH and CaH are formed with heats of dissociation of 30,000 calories or more, from unexcited magnesium or calcium atoms, whose electrons are all paired like the electrons in helium. Other examples can also be cited in which atoms with $S = 0$, hence $V = 0$ according to London and Heitler, form stable molecules. Secondary valence compounds, such as for example the $\text{Cu}(\text{NH}_3)_4^{++}$ ion, which are ascribed by Lewis and others to the bonding action of already formed electron pairs in the NH_3 molecules (9), also fail to come within the theory of Heitler and London.

Orbital valence

Heitler has sought to supplement the theory of spin valence by introducing the concept of "orbital valence." The idea is that in the case of atoms in P, D, \dots states, certain changes occur in the electron orbits (more precisely, in the "coupling of the l vectors"), giving rise to valence bonds (8). This idea when applied seems, however, to involve nothing different than is obtained by considering the effects of the molecular electric axis or axes in removing the degeneracy of the molecular electron orbits with $l > 0$ (p, d, \dots orbits) (11). Pauling and Slater have shown with striking success how such effects may suffice to

account for a great many of the directional and other related properties of chemical bonds (12).

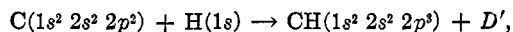
Perhaps it will be best at this point to leave the perplexing problem of trying to find a general quantum-mechanical theory of non-polar valence. The author hopes to take up the discussion of this problem again in a later paper.

III. VALENCE IN SIMPLE HYDRIDE MOLECULES

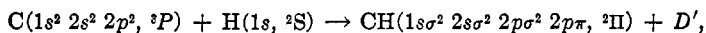
Carbon-hydrogen compounds

Meantime it may be profitable, in the present review, to try to understand, by a somewhat detailed consideration of electron orbits, the relations between a number of typical molecules and their atoms. The examples already considered, in particular the diatomic molecules of hydrogen and helium, have yielded the concepts of bonding and anti-bonding electrons, of promotion, and of the effect of the Pauli principle in requiring promotion of any electron which would otherwise be in an orbit occupied by two other electrons. The importance of all these concepts becomes increasingly evident in a study of more complicated molecules.

First let us consider the step-by-step building-up of a methane molecule from a carbon atom and four hydrogen atoms. An equation for the formation of a CH molecule can be written as follows:



or, more accurately,



Here D' stands for the heat of dissociation of CH into C + H. The symbols in parentheses describe the electron configurations and electron states of the atoms and molecule. Thus the symbols for the carbon atom mean that it contains two 1s, two 2s, and two 2p electrons (this is its electron configuration) and, less

important, that the atom as a whole is in what is called a 3P (triplet P) state. The hydrogen atom contains one $1s$ electron, and is in a 2S state. In the carbon atom, there are only two of the very firmly bound $1s$ electrons, because according to the Pauli exclusion principle, more than two are not allowed in one atom. The $1s$ electrons here are very much more firmly bound than the $1s$ electron of the hydrogen atom, because of the much greater charge on the carbon nucleus. As with the $1s$, there are only two of the next most firmly bound kind of electrons, namely $2s$. The groups $1s^2$ and $2s^2$ can be called closed groups or closed shells, since no more electrons can be admitted. The last two electrons are $2p$, which comes next in order of binding.

In the symbols describing the CH molecule, there are again only two $1s$ and two $2s$ electrons (denoted above by $1s\sigma^2$ and $2s\sigma^2$), in accordance with the Pauli principle. There are, however, three $2p$ electrons. This is not in conflict with the Pauli principle, because p electrons, unlike s electrons, can appear in more than one form. So long as not more than two orbits of the same form are present, the Pauli principle is satisfied. In the example of CH , two of the $2p$ electrons are in the form $2p\sigma$, giving a closed shell, and one is in the form $2p\pi$.⁴ On looking into what has happened in the formation of the molecule, it appears that one of the $2p\sigma$ electrons in CH is nothing other than the $1s$ hydrogen electron, promoted, while the other $2p\sigma$ and the $2p\pi$ electron are nothing other than the two $2p$ electrons of the carbon atom (4).

In the case of a single atom, the distinction between $2p\sigma$ and $2p\pi$ electrons is not made. It comes into existence only when an axis of electrical (or magnetic) force is set up, such as is produced here by the charge of the hydrogen nucleus.

In the formation of the CH molecule, the most obvious change in the electron orbits of the atoms is that the $1s$ electron of the hydrogen has been promoted to $2p\sigma$ and has joined the ranks of the carbon electrons. In a previous example, that of two hydrogen or two helium atoms, promotion of a $1s$ electron to $2p\sigma$ caused the atoms to repel each other. In the present case, however, it does not prevent the atoms from attracting each other

strongly, giving a stable molecule with a heat of dissociation of the order of 90,000 calories, according to band spectrum data. Why is this? It is essentially because in spite of the promotion from $1s$ in hydrogen to $2p\sigma$ in CH, the firmness of binding of the electron is not decreased, because of the relatively high effective charge of the carbon nucleus. In general, the energy of binding of an orbit of given type varies as the square of the effective nuclear charge. We may assume as a reasonable guess that the promoted $1s$ electron is just as firmly bound in CH as in H. This alone, to be sure, would not suffice to give a stable CH molecule. But there can be little doubt that the electrons originally on the carbon atom become on the whole more firmly bound in the presence of the hydrogen nucleus, and that the sum total of energy changes suffices to account for the stability of the molecule. The increases in binding energy of the carbon electrons may be thought of as resulting from polarization of their orbits by the hydrogen nucleus.

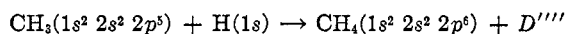
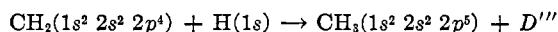
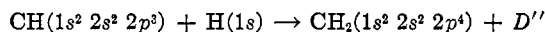
In discussing the formation of a CH molecule, it has been assumed that the molecule is in its most stable, or normal, state. There are really four ways in which a carbon and a hydrogen atom could come together, one leading to repulsion, as in the case of the second mode of interaction of two hydrogen atoms considered above (12a). But here and in what follows we are interested only in the most stable molecular state which can be obtained from two given atoms, and from now on only this will be dealt with, although in most cases there are also other modes of interaction, which are important in spectroscopic and other problems.

The CH molecule has the same number of electrons as the nitrogen atom, and is indeed identical in its electron configuration with what would be obtained if one could detach a proton from a nitrogen nucleus in a nitrogen atom⁸ and let the system come to equilibrium with a minimum of disturbance. This close relationship to the nitrogen atom will be made use of later.

Meantime let us consider the series of molecules CH_2 , CH_3 ,

⁸ Strictly speaking, one must start with a slightly excited (2D) nitrogen atom.

CH₄. Without going into details as to the subdivision of the *p* orbits into different forms,⁹ we can write



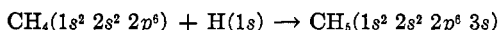
The molecules CH₂, CH₃, and CH₄ have respectively the same electron configurations as the oxygen, fluorine and neon atoms. Of course all the orbits are more or less deformed, and the *p* orbits become differentiated into not more than three sub-forms, as a result of the fact that parts of the positive charge are located in the protons instead of being concentrated in the central nucleus. Or probably, as Pauling and Slater have shown (12), all the outer orbits are so much modified that we no longer should distinguish 2*s* and 2*p* orbits, but may better think, in CH₄, in terms of four new 2-quantum orbit-types, each a sort of hybrid of 2*s* and 2*p*, with 2*p* predominating in the mixture. These new orbit-types are adapted to the probable tetrahedral symmetry of the molecule. In CH₄ and other polyatomic molecules, a considerable part of the energy of formation probably results from the possibility for the geometrical configuration of the nuclei and the orbits of the valence electrons to adjust themselves mutually to give minimum energy.

As each hydrogen atom is added, its 1*s* electron is promoted to a 2-quantum orbit. This goes on, giving a stable molecule at each step, so long as the maximum number of 2-quantum orbits allowed by the Pauli exclusion principle, namely eight (two 2*s* and six 2*p*, or eight tetrahedral-type), is not exceeded. When this maximum number is reached, as in methane, the molecule strongly resembles the isoelectronic atom neon in having a very low boiling point and in refusing to combine stably with other atoms or

⁹ In molecules composed of more than two atoms, the nature of these orbit-types is usually different from that of those in diatomic molecules, and less easy to explain. It is still true, however, that *s* electrons give only one type; *p* electrons give not more than three types. Or, if the molecule is sufficiently stable, a hybridization of *s* and *p* electrons may occur. The total number of orbit-types derived from *s* and *p* together is not more than four in any case.

molecules. Methane is physically less inert than neon because parts of its positive charge, namely the four protons, are near the surface. Chemically also it is less inert, because it is not very difficult to remove one or more of these protons (together with an equal number of electrons), whereas in neon it would be very difficult to remove a proton from the nucleus.

Why is methane as inert as it is, and why does it not take on more hydrogen atoms to form CH_5 , CH_6 , and so on? The interpretation in terms of the principles here used seems to be clear. If one should bring a CH_4 molecule and a hydrogen atom together, the hydrogen $1s$ electron could no longer be promoted merely to a 2-quantum orbit but would have to go up to at least the next higher stage of promotion, which is a $3s$ orbit. Now from our knowledge of the spectra of the neon and sodium atoms, we know that a $3s$ orbit in sodium is bound only about one-fourth as firmly as the last $2p$ orbit in neon. Roughly the same relation probably would hold between a $3s$ and the last 2-quantum orbit in CH_5 if this molecule were stable. Hence although we may write



we cannot expect CH_5 to be even a physically stable molecule. Possibly it has a slight physical stability, but it is certainly not chemically stable. The energy required to promote the hydrogen $1s$ electron to $3s$ is so large that the hydrogen atom is probably repelled by the CH_4 molecule, except perhaps at large distances. The $3s$ orbit thus acts as an anti-bonding one. The same difficulties would be met in trying to form a molecule, e.g., CH_6 , with more hydrogen atoms. Urey¹ has also explained the non-existence of molecules like CH_5 in the same way as that given here.

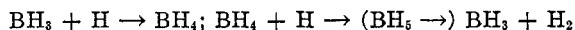
We must next explain why the molecules CH , CH_2 , CH_3 , although stable as individuals, are not chemically stable. A sufficient explanation follows from the fact, already noted, that these molecules have essentially the same electron configurations as the atoms nitrogen, oxygen, and fluorine. According to the quantum theory, the behavior of two neutral atoms on coming together depends primarily on the nature and number of their electron

orbits. The same should be true of radicals such as CH , CH_2 , and CH_3 . We may therefore say that if we can explain why nitrogen, oxygen, and fluorine form stable molecules N_2 , O_2 , F_2 , then we understand why C_2H_2 , C_2H_4 , and C_2H_6 are stable. N_2 , O_2 , F_2 , and C_2H_4 will be considered a little later.

Boron-hydrogen compounds

The same methods that have just been applied to the compounds of carbon with hydrogen can also be applied to other hydrides. In the case of boron, for example, we might expect BH , BH_2 , BH_3 , BH_4 , BH_5 all to be capable of stable existence as individual molecules. We know from spectroscopic work that this is true of BH . The fact that BH , BH_2 , and BH_3 are not found as chemically stable individuals is not surprising, since their electron configurations must be the same as those of the atoms carbon, nitrogen, and oxygen. The existence of B_2H_6 , for example, although contrary to ordinary valence theory, is explained in the same way as that of O_2 . (See p. 381 for further details.) This idea is not a new one, but it is worthy of note that the present method gives it a very simple and obvious justification.¹⁰

But what about BH_5 , whose existence as a gas resembling CH_4 seems to be predicted by the present method? Its absence can very likely be explained by the following equations:

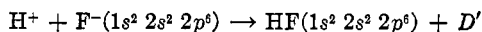
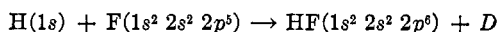


In other words, although BH_4 , as well as BH_3 , is doubtless capable of attracting another hydrogen atom rather strongly, the resulting molecule has probably a higher energy content than the system which results when a hydrogen molecule is split off. One of the main reasons why BH_5 should be less stable in this respect than CH_4 is that because of the smaller nuclear charge of the boron atom, the 2-quantum electrons in BH_5 are all decidedly less firmly bound than in CH_4 .

¹⁰ Herzberg in his new paper has independently given the same explanation of B_2H_6 (footnote 1). It seems to the author that this is far simpler than one recently given by Pauling (14).

Polar molecules

It will be instructive at this point to consider the HF molecule as an illustration of the impossibility of drawing a sharp line between the polar and the non-polar bond. So far as the general principles of the quantum theory are concerned, either of the two following reactions might lead to identically the same result.



Whichever is correct, we may be sure that the HF molecule has the same electron configuration as the neon atom, although it is much less inert than the latter because of the fact that its positive charge is divided into two parts. It is not definitely known which of the above equations is the correct one. Very likely HF is formed from $\text{H}^+ + \text{F}^-$, while HCl is formed from $\text{H} + \text{Cl}$. But the properties of the finished molecule depend very little on the starting point and much more on the resulting electron configuration. A molecule having very little polarity could conceivably, according to the quantum theory, be formed from two ions, and a highly polar molecule conceivably from two neutral atoms. The HF molecule does indeed act like a dipole, because there is a slight excess of negative charge around the fluorine nucleus, although nothing like the excess of one whole electron which such a symbol as H^+F^- would suggest. Only in extreme cases, e.g., perhaps Cs^+F^- , is it really justifiable to think of a diatomic vapor molecule as actually even approximately *consisting of* two ions. A molecule like HF or HCl may correctly be said to be *formed from* two ions, or from two atoms, as the case may be, but what it really consists of may better be thought of as a unitary electron configuration whose outer shell surrounds both nuclei. The inner electrons, of course, remain close to the fluorine or chlorine nucleus.

Similar considerations apply to polyatomic molecules. For example, H_2O might conceivably be formed from $\text{O} + \text{H} + \text{H}$, or from $\text{O}^- + \text{H}^+ + \text{H}$, or from $\text{O}^- + \text{H}^+ + \text{H}^+$, but in any case the finished molecule would be essentially an electron configura-

tion $2s^2 2p^6$ surrounding the two hydrogen nuclei and the oxygen nucleus with its two $1s$ electrons. Actually, the stable (normal) state of H_2O , although strongly polar like HF , is probably formed from neutral atoms $O + H + H$. Again, CH_4 might conceivably be reached by the route $C^{\equiv} + 4H^+$, or from $C + 4H$ as we have assumed, or in other ways, but our understanding of the nature of the CH_4 molecule does not depend on a knowledge of how it might be formed from atoms or ions.

Superfluity of the concept of valence bonds in the "molecular" point of view

In the "molecular" point of view advanced here, the existence of the molecule as a distinct individual built up of nuclei and electrons is emphasized, whereas according to the usual atomic point of view the molecule is regarded as composed of atoms or of ions held together by valence bonds. From the molecular point of view, it is a matter of secondary importance to determine through what intermediate mechanism (union of atoms or ions) the finished molecule is most conveniently reached. It is really not necessary to think of valence bonds as existing in the molecule. In hydrides, it is perhaps better not to think in terms of valence bonds between the hydrogen and other atoms, although in the case of heavier atoms, it is usually more convenient to assume valence bonds between them. (For an instructive example involving both cases, compare the discussion of B_2H_6 and C_2H_4 at the end of the section on "Polyatomic hydrides with two heavy atoms," on p. 380.) But whenever one is in doubt as to what kind of binding is present, e.g., polar or non-polar, the molecular point of view serves as the natural means to reconciliation.

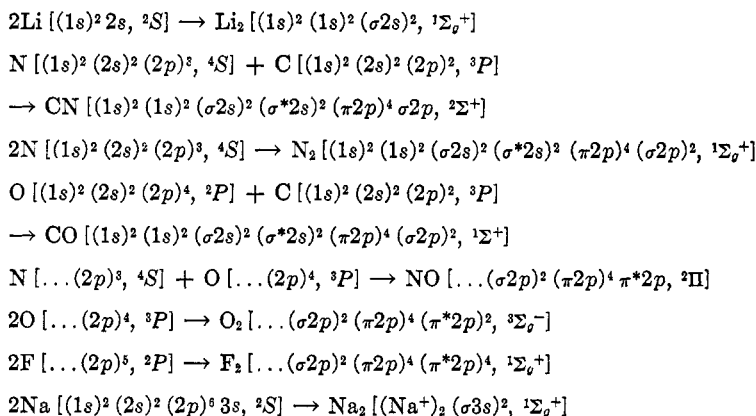
IV. VALENCE IN COMPOUNDS CONTAINING TWO MANY-ELECTRON ATOMS

In the most stable molecules formed from two atoms, each containing several or many electrons (e.g., N_2 , CO), the outer shells are often rather thoroughly shared, and are properly thought of for many purposes as forming a single unit. In less stable molecules, e.g., the halogens, the outer shells are only incompletely

shared, and the molecule may often be thought of as consisting of two atoms. Just what these statements mean can best be seen by considering again a series of examples.

Electron configurations of atoms and molecules

The results will be given first and the explanation afterwards. The electron states and probable electron configurations of several diatomic molecules formed from such atoms as lithium, nitrogen, oxygen, and fluorine are essentially as given in the following:



Nomenclature and bonding properties of orbit-types

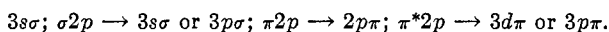
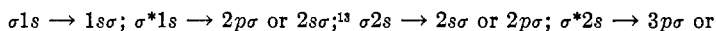
The designations $\sigma 2s$, $\sigma^* 2s$ indicate σ electrons derived from atomic $2s$ electrons. Similarly $\sigma 2p$, $\pi 2p$, $\pi^* 2p$ indicate σ or π electrons derived from $2p$ atomic electrons.⁴ Designations of this sort, first used by Lennard-Jones (who, however, used the symbols $2s\sigma$, $2s\sigma'$, $2p\sigma$, and so on for this purpose) are more appropriate for most molecules, except hydrides, than designations like $2s\sigma$, $2p\sigma$ so far used in this review.¹¹ The latter sym-

¹¹ Instead of $\sigma 2s$, $\sigma^* 2s$, $\sigma 2p$ it would be more accurate in some cases to use designations such as $\alpha\sigma$, $\gamma\sigma$, $x\sigma$ which do not imply definite relationships to $2s$ and $2p$ atomic orbits (see reference 4 for details). This is because in some of the molecules here under consideration there must be a partial breakdown of the s - p distinction, such as Slater and Pauling (12) assume.

Pauling in his discussion of the molecules CO, CN, N₂, and NO (reference 12, pp. 1383-5), uses the symbols σ_0 and σ_s , the first corresponding to $\sigma 2s$ and $\sigma^* 2s$ (or

bols are based on a consideration of what the orbits designated would become if the distance between the nuclei could be steadily decreased to zero, giving the "united-atom." Except in hydrides, however, the electron orbits are much more closely related to those of the separate atoms to which they originally belonged.¹²

It is not possible to give a completely unambiguous set of correlations between the separated-atoms and the united-atom designations for molecular orbits. The following, however, are the usual correlations:



It will be seen that with the exception of $\sigma 1s$, $\sigma 2s$, and $\pi 2p$, all the orbits named become promoted orbits in the united-atom. For the most part, outer-shell electrons in unpromoted orbits are bonding, while those in promoted orbits are anti-bonding (13), especially in molecules whose atoms are in the same or in not far distant columns of the periodic system. Exceptions will be discussed shortly. More accurately—as it *happens* (?)—, the unstarred orbit-types always correspond to bonding, the starred types (e.g., $\sigma^* 2s$, $\pi^* 2p$) to anti-bonding electrons, in molecules composed of like or not too unlike atoms.

Li₂ molecule: non-bonding inner electrons

The relations between atomic and molecular electron configurations given above can be interpreted in terms of bonding and

$z\sigma$ and $y\sigma$) and the second to $\sigma 2p$ (or $x\sigma$). The author finds himself to a considerable extent unable to agree with Pauling's treatment of these molecules, which he thinks suffers from the failure to distinguish between $\sigma 2s$ and $\sigma^* 2s$ and between $\pi 2p$ and $\pi^* 2p$ orbit-types, and also from the assumption that the pairing of two originally unpaired electrons is usually necessary for the formation of a valence bond. Pauling considers O₂, however, and in a later paper (14) also NO, to be partial exceptions to this pairing rule.

¹² In a previous article (Chem. Reviews **6**, 532 (1929)) these united-atom designations have been used throughout.

¹³ The first four electrons in the electron configuration of each of the molecules given above might have been designated $(\sigma 1s)^2(\sigma^* 1s)^2$, but for reasons to be given shortly, the simpler symbols $(1s)^2(1s)^2$ have been used.

anti-bonding electrons, etc., as follows. When two lithium atoms approach, their 2s electrons become more firmly bound and move in the field of both nuclei, just as the 1s electrons of two hydrogen atoms do in the formation of the hydrogen molecule. The two $\sigma 2s$ electrons in Li_2 can be called bonding electrons, and they may be said to form a valence bond. The energy of formation of Li_2 is, however, much less than that of H_2 , mainly because the 2s electrons are much less firmly bound in Li and in Li_2 than are the 1s electrons in H and H_2 .¹⁴ Since the total binding energy is so much less, the change in binding energy when the molecule is formed is naturally also less, in somewhat the same proportion.

The two $1s^2$ shells of the two atoms tend to cause the latter to repel each other and, technically, two of the 1s electrons begin to be promoted to σ^*1s orbits, just as when two helium atoms approach. But the distance between the nuclei in Li_2 is so large, namely 2.67×10^{-8} cm., when equilibrium is reached under the bonding action of the two $\sigma 2s$ electrons, that the promotion energy of the two $1s^2$ shells is negligible. This is because the $1s^2$ shells in the lithium atoms are only about 0.2×10^{-8} cm. in radius, and because the "exchange" forces between two such groups of electrons are not large if the distance between them much exceeds their own dimensions. The 1s electrons in Li_2 may evidently appropriately be called non-bonding electrons. This is indicated in the configuration formula given for Li_2 by the use of the simple designations $(1s)^2 (1s)^2$. The same is true of the 1s electrons in all molecules composed of atoms each containing several electrons. In fact, in the case of molecules composed of atoms containing many electrons, all inner closed shells of the atoms act, like the 1s electrons in Li_2 and for the same reasons, as non-bonding electrons (cf. the inner electrons in Na_2). Only outer electrons take an active part in the formation of molecules.

¹⁴ The values of the energy of formation of Li_2 and of Na_2 have been calculated by the Heitler and London method. The results agree very well with the observed values. For Li_2 see DELBRÜCK, M.: *Ann. der Physik* [5] **5**, 36 (1930) and BARTLETT, J. H., JR. AND FURRY, W. H.: *Phys. Rev.* **37**, 1712 (1931). For Na_2 see ROSEN, N.: *Phys. Rev.* **38**, 274 (1931).

Nitrogen molecule (also CO, CN)

In the case of the nitrogen molecule, there are five outer electrons in each of the atoms from which it is formed. Of the four $2s$ electrons in the two atoms, two become $\sigma 2s$ electrons (unpromoted type) while two become $\sigma^* 2s$ (promoted type). The spectroscopic facts about the N_2 molecule indicate (cf. table 1) that there is a relatively very large decrease (perhaps 150,000 calories per electron) in firmness of binding of the atomic $2s$ electrons when they become molecular $\sigma^* 2s$ electrons. But the anti-bonding action indicated by this is presumably approximately balanced, although we have no spectroscopic evidence thereof, by a strong bonding action on the part of the $\sigma 2s$ electrons, so that the group $(\sigma 2s)^2(\sigma^* 2s)^2$ as a whole has very likely nearly a non-bonding action, or a mild anti-bonding action.

Next come four $\pi 2p$ and two $\sigma 2p$ electrons, all bound with about equal firmness in the molecule, as is shown by the band spectra of nitrogen. These electrons are all considerably more firmly bound in the molecule than in the atoms, as is shown by spectroscopic facts (see table 1) and must therefore all be classed as bonding electrons. If we now count up all the electrons in the molecule, there are two pairs of non-bonding electrons $(1s)^2(1s)^2$, four pairs of bonding electrons $(\sigma 2s)^2$, $(\pi 2p)^4$, $(\sigma 2p)^2$, and one pair of anti-bonding electrons $(\sigma^* 2s)^2$. The practical result is about the same as if there were just three bonding pairs $(\pi 2p)^4$, $(\sigma 2p)^2$ with all the other electrons acting as non-bonding, and in this sense we may say that there are three valence bonds between the atoms. The discussion which has just been given shows, however, that the real state of affairs is less simple in that the $\sigma 2s$ and $\sigma^* 2s$ electrons are really far from being unshared and non-bonding as the $1s$ electrons are.

The $\sigma 2p$ orbit-type is of special interest in that it acts as a bonding type in spite of its promoted character ($\sigma 2p \rightarrow 3s\sigma$ or $3p\sigma$ in the united-atom). According to Pauling (14), $\sigma 2p$ should give a stronger bond than $\pi 2p$. Actually, however, the bonding powers of $\sigma 2p$ and $\pi 2p$ are about equal in N_2 , while in CN and CO the bonding power of $\sigma 2p$ appears to be less than that of

TABLE I
Ionizing potentials of molecules

MOLECULE	STATE	ELECTRON IONIZED	STATE OF ION	IONIZATION POTENTIAL ¹	IONIZATION POTENTIAL CORRECTED ² FOR r	ATOMIC IONIZATION POTENTIAL CORRECTED ³
H ₂	$(1s\sigma)^2, {}^1\Sigma_g^+$	$1s\sigma$	$2\Sigma_g^+$	15.4	15.9	13.54 (uncorrected)
CO.....	$(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p)^2, {}^1\Sigma^+$	$\sigma 2p$ $\pi 2p$ $\sigma^* 2s$ $\sigma 2p$ $\pi 2p$ $\sigma^* 2s$	$2\Sigma^+$ 2π $2\Sigma^+$ $2\Sigma_g^+$ 2π $2\Sigma_u^+$	14.2 16.7 19.8 16 (?) 19	14.2 17.3 19.8 16.5 (?) 19	10 (C) 14 (O) 20 (C) 12 12
N ₂	$(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p)^2, {}^1\Sigma_g^+$	$\sigma 2p$ $\pi 2p$ $\sigma^* 2s$	$2\Sigma_g^+$ 2π $2\Sigma_u^+$	16 (?) 19	16.5 (?) 19	12 12 24
NO.....	$(\sigma 2p)^2(\pi 2p)^4(\pi^* 2p), {}^2\Pi$	$\pi^* 2p$	$1\Sigma^+$	9.4	9.9	14 (N)
O ₂	$(\sigma 2p)^2(\pi 2p)^4(\pi^* 2p)^2, {}^3\Sigma_g^-$	$\pi^* 2p$ $\pi 2p$	$2\pi_g$ $2\pi_u$	12.5 17.2	12.5 17.8	17 17
HCl.....	$(3p\sigma)^2(3p\pi)^4, {}^1\Sigma^+$	$3p\pi$	2π	13.8	13.8	13 (Cl)

¹ The molecular ionization potentials given here represent the minimum values theoretically capable of producing ionization. Cf. H. D. Smyth, *Rev. Modern Physics*, **3**, 347 (1931), and R. S. Mulliken, *Phys. Rev.* **32**, 186 (1928), for data.

² The "corrected" molecular ionization potentials correspond to ionization of the molecule without change in the distance r between the nuclei.

³ The atomic ionization potentials given here for comparison have been corrected to make a rough allowance for the change in multiplicity in the process of ionization. If, for instance, when the N₂ molecule is ionized a ${}^1\Sigma$ gives a ${}^2\Sigma$ state, so that the multiplicity is increased from singlet to doublet, it is fairer to compare this with an atomic ionization process in which the multiplicity increases (e.g., ${}^2D \rightarrow {}^3P$ in the nitrogen atom) than with one in which it decreases (e.g., ${}^4S \rightarrow {}^3P$). But there seems to be no way of making accurate corrections so as to make these comparisons quantitative. In fact the significance of such comparisons is in general decidedly dubious from a theoretical standpoint, and their use for distinguishing bonding from antibonding electrons should be considered more or less empirical. The "corrected atomic ionization potentials" are based on a careful study of existing spectroscopic data. A long table of such data was at first included, but for the present purpose it did not seem worth the space required. See A. A. Noyes and A. O. Beckman, *Chem. Reviews* **5**, 85 (1928), for a condensed table, which, however, does not consider the various atomic states of different multiplicity which might be used in getting ionization potentials.

$\pi 2p$. These statements are based on the relative ionization potentials of $\sigma 2p$ and $\pi 2p$ in CO and N_2 (cf. table 1).

It seems probable that in less stable molecules, where the distance r between the nuclei is larger, $\sigma 2p$ really has greater bonding power than $\pi 2p$, in agreement with Pauling. There is a little spectroscopic evidence for this (4). A reasonable explanation is the following. When r is large the $\sigma 2p$ and $\pi 2p$ orbits are essentially orbits of the original atom, modified by the electric field of the second atom. Because of the orientation of $\sigma 2p$ with reference to the electric axis, or better, because of the form of its wave-function, it is more strongly influenced than $\pi 2p$ by the second atom and so is more firmly bound. But when r is smaller, as in N_2 or CO at equilibrium, the effect of the promotion which must occur as $r \rightarrow 0$ causes the binding of $\sigma 2p$ to be decreased relative to $\pi 2p$, with the observed results. Both $\sigma 2p$ and $\pi 2p$ electrons, however, have high bonding power in N_2 .

Molecules NO, O₂, F₂: anti-bonding $\pi^ 2p$ electrons*

In the molecules NO, O₂ and F₂ the distance between the nuclei is greater than in N_2 and at the same time the $\sigma 2p$ orbits are smaller, since the $2p$ orbits of oxygen and fluorine are smaller than those of nitrogen. They should therefore be more firmly bound than the $\pi 2p$, and this has been assumed in writing the electron configurations of these molecules.

In the molecules NO, O₂, and F₂, we note a steady decrease in the heat of dissociation (cf. table 2), paralleling a steady increase in the number of $\pi^* 2p$ electrons assigned to their electron configurations. These $\pi^* 2p$ electrons are promoted electrons ($3d\pi$ or $3p\pi$ in the united-atom). They act strongly as anti-bonding electrons. This can be seen very clearly in a comparison of NO with N_2 . In $N + N$, the lowest ionizing potential, corresponding to a removal of a $2p$ electron, is 14.5 volts. For removal of a $\sigma 2p$ or $\pi 2p$ electron from N_2 , about 16 volts is required, indicating that these electrons are more firmly bound in N_2 than in $N + N$.¹⁵

¹⁵ One should not overemphasize the quantitative significance of such comparisons (cf. table 1, notes), but qualitatively they distinguish rather clearly between bonding and anti-bonding electrons.

For removal of a π^*2p electron from NO, only 9.4 volts are required, as compared with 14.5 volts for the corresponding $2p$ electron in the nitrogen atom of $N + O$, or of 13.6 volts if the

TABLE 2
Heats of dissociation (D) of some diatomic molecules†

MOLECULE	D	NUMBER OF BONDS (N)	D/N	MOLECULE	D	NUMBER OF BONDS (N)	D/N
	<i>kg-cal.</i>				<i>kg-cal.</i>		
H ₂ ⁺	60.9	$\frac{1}{2}$	122	C ₂	[126]	2	[63]
H ₂	103	1	103	BO.....	[152]	$2\frac{1}{2}$	[61]
He ₂ ⁺	[60]	$\frac{1}{2}$	[120]	CN.....	[164]	$2\frac{1}{2}$	[66]
HeH.....	0	$\frac{1}{2}$? or 0	—	N ₂ ⁺	[157]	$2\frac{1}{2}$	[63]
HgH.....	8.5	$\frac{1}{2}$?	17?	CO ⁺	(164)	$2\frac{1}{2}$	(66)
CaH.....	[35]	$\frac{1}{2}$? or 1?	[70?]	CO.....	(231)	3	(77)
LiH.....	57	1		N ₂	[210]	3	[70]
CH.....	(92)	1		NO ⁺	(238)	3	(79)
HF.....	148	1	57	NO.....	(142)	$2\frac{1}{2}$	(57)
HCl.....	102	1	(92)	O ₂ ⁺	(143)	$2\frac{1}{2}$	(57)
Li ₂	26	1	148	O ₂	117	2	59
Na ₂	18	1	102	S ₂	102	2	51
			26	F ₂	(66)	1	(66)
			18	Cl ₂	57.0	1	57

† (1) The D values are all measured from the lowest energy level of the molecule, i.e., they are corrected to 0 K . (2) The values for H₂, Li₂, Na₂, O₂, Cl₂ are reliable values (probable error 0 to 2 kg-cal.) from band spectrum data, those for LiH, S₂, O₂⁺ are somewhat less reliable values from the same source. The value for HCl is based on reliable chemical data. Values for F₂ and CH are estimates which are probably rather accurate, that for He₂⁺ is an estimate of low reliability. Values for C₂, BO, CN, N₂⁺, N₂, are relatively unreliable values based on spectroscopic data or estimates from these. Values for CO, CO⁺, NO, NO⁺ are based on spectroscopic and chemical data combined. The value for H₂⁺ is based upon accurate quantum-mechanical calculations by Burrau and Hylleraas. Values in brackets are the least reliable, those in parentheses also not very reliable (probable error 5 to 15 kg-cal.); other values are rather reliable. All the values have been more or less critically considered, and some have been estimated or revised, by the author. (3) The number of bonds (N) is taken equal to half the difference between the numbers of bonding and anti-bonding electrons.

electron is derived from a $2p$ of the oxygen atom.¹⁵ Clearly the π^*2p electron is much less firmly bound in NO than in $N + O$, and the corresponding strong anti-bonding action is responsible for the large decrease in heat of dissociation from N₂ to NO. As

we go to O_2 and F_2 , each additional π^*2p electron causes a further decrease in the heat of dissociation, and in O_2 as in NO (no data are available for F_2) the ionizing potential of the molecule is considerably less than that of the atoms (table 1).

Transformation of bonding and anti-bonding electrons into non-bonding electrons with increasing atomic number and with decreasing valence

The reasons why two neon atoms refuse to form a molecule can now be at least qualitatively understood. But first it will be helpful to point out that in the series N_2 , O_2 , F_2 we not only have an increasing number of π^*2p electrons and a decreasing dissociation energy, but also a resulting increase in the equilibrium distance r_e between the nuclei. This has the values, 1.1, 1.2 and about 1.5, each times 10^{-8} cm., in N_2 , O_2 , and F_2 . As a result of this increase in r_e , and of the concomitant decrease in size of the $2s$ and $2p$ orbits (due to increase in nuclear charge) in going from nitrogen to fluorine, the condition of the $\sigma 2s$, σ^*2s , $\pi 2p$ and $\sigma 2p$ electrons must be very different in F_2 than in N_2 . Probably in F_2 the strong bonding and antibonding effects which exist for the $\sigma 2s$ and σ^*2s electrons in N_2 are very nearly gone, so that these electrons are in truth practically non-bonding electrons (15).

Roughly speaking, each $\sigma 2s$ and σ^*2s electron in N_2 may be considered to belong almost equally to both nuclei, while in F_2 one electron of each kind probably belongs pretty definitely to each nucleus. More precisely (cf. discussion on p. 352), this means that in N_2 , each $\sigma 2s$ and σ^*2s electron moves back and forth from the vicinity of one nucleus to that of the other with about the same frequency as that of the orbital motion which the $2s$ electron in the nitrogen atom would have according to the Bohr theory, while in F_2 each $\sigma 2s$ and σ^*2s electron moves very nearly as it would in a $2s$ orbit in a fluorine atom, and only occasionally, with a frequency very much less than that of the orbital motion, jumps from the neighborhood of one nucleus to that of the other, usually almost simultaneously with the transfer of another $2s$ electron in the opposite direction.

Now as for the $2p$ electrons of $F + F$ or $N + N$, it is clear that they also must be much more nearly like atomic electrons in F_2 than in N_2 . The differences, whether positive or negative, in firmness of binding in the molecule as compared with the atoms, must therefore be much less in F_2 than in N_2 , for all the orbit-types derived from $2p$. The ionizing potential of F_2 , for example, should be rather close to that of the fluorine atom. Also, the differences in binding energy between $\pi 2p$ and $\pi^* 2p$ should be much less in F_2 than in NO or N_2 . Probably each of the $\pi 2p$ and of the $\pi^* 2p$ electrons in F_2 is more or less definitely attached to one nucleus, in the sense above described. Very likely the $\sigma 2p$ electrons, however, because of the form of their orbits and the probable firmness of their binding, are still pretty well shared by the nuclei. Probably one may with a considerable degree of truth think of the two $\sigma 2p$ electrons in F_2 as bonding electrons which constitute the single valence bond demanded by the ordinary rules of valence, and of all other electrons as non-bonding electrons. There cannot be much doubt, however, that in reality the $\pi 2p$ and $\pi^* 2p$ electrons are still acting, even though perhaps only rather weakly, as bonding and anti-bonding electrons respectively (15). It seems likely that in polyatomic molecules the situation commonly resembles that here described for F_2 .

Two neon atoms

In $Ne + Ne$, we have two more $2p$ electrons than in $F + F$. Since F_2 contains four $\pi^* 2p$ electrons, which is the maximum number allowed by the Pauli principle, the two new $2p$ electrons must be promoted to some other kind of orbit. Moreover they must be even more loosely bound in this new kind of promoted orbit than are the $\pi^* 2p$ electrons, and must therefore exert an even stronger anti-bonding action. This we can be fairly sure of from the fact that the four least firmly bound electrons in ordinary F_2 are all $\pi^* 2p$. If any other *more* firmly bound orbit were available, some of the electrons would go into it.

On extrapolating from the heats of dissociation of N_2 , O_2 , and F_2 , we see that the incorporation of two more strongly anti-bonding electrons, which we have just seen to be necessary in Ne_2 ,

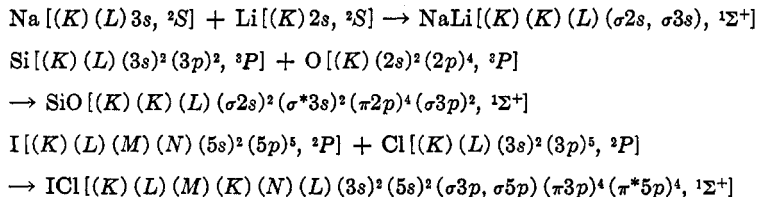
must reduce the heat of dissociation to about zero. Thus we can understand why two neon atoms do not form a stable molecule. This understanding is of course semi-empirical in that it is partly based on a study of spectroscopic data.

On theoretical grounds and from the spectra of the halogen molecules, the last two electrons in Ne_2 are σ^*2p electrons, although it is not obvious just why this kind of orbit should have such a strong anti-bonding action. As in the case of He_2 (and of Be_2), the number of anti-bonding electrons is equal to the number of bonding electrons in Ne_2 . Or, since the two neon atoms never come near enough together to get either strong bonding or strong anti-bonding reactions, we see that in Ne_2 all the electrons are non-bonding in fact. The same relations are true for any pair of (unexcited) atoms both composed only of closed shells. Such relations correspond to zero valence bonds.

Heavier diatomic molecules

Going on to $\text{Na} + \text{Na}$, we have a case very similar to that of $\text{Li} + \text{Li}$. The two $3s$ electrons of Na produce a weak binding of the two atoms which leads to equilibrium at such a large r_e that the repulsive "exchange" forces between the two neon-like inner shells are negligibly small.¹⁴ In other words, we have again a clear-cut case of a pair of outer electrons forming a valence bond, while the inner electrons all act merely as non-bonding electrons.

The formation of molecules like SiO , ICl , LiNa can also be understood by this method. The reactions can be written with approximate correctness as follows (4):



Here K , L , M , N stand for complete 1-, 2-, 3-, and 4-quantum shells. Pairs of symmetrically connected electrons like $(\sigma 3p, \sigma 5p)$ in ICl function as equivalent electrons in the molecule. If

one thinks in terms of separated-atom orbits, each electron must be considered to jump frequently from the I ($5p\sigma$) to the Cl ($3p\sigma$) orbit or vice versa. If one considers what happens as $r \rightarrow 0$ (united-atom), one concludes (probably) that the orbits of the two electrons become identical. When the electron configuration symbols are written as here, it is evident why molecules composed of atoms in the same columns of the periodic system (e.g., I_2 , ICl , Cl_2 , or CO , SiO , CS) are similar. Quantitative differences between similar molecules are, however, to be expected, since such differences exist in the atoms themselves.

The present method seems to offer a possibility of understanding such facts as that the resemblance between F_2 and Cl_2 is much closer than between N_2 and P_2 . In the halogens, with their rather small heats of dissociation, the molecule is not much different from two atoms, so that the close resemblances between the atoms suffice to account for those between the molecules. In N_2 , however, the electron orbits are so greatly modified by the strong bonding that the molecule has an individuality very distinct from that of its component atoms. P_2 , on the other hand, has a different distinct individuality, or more probably it, as well as As_2 , Sb_2 , and Bi_2 , acts more like a mere pair of atoms. In either case, its lack of close resemblance to N_2 is explained.

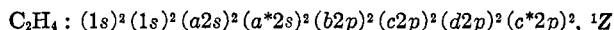
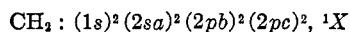
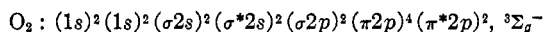
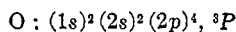
Polyatomic hydrides with two heavy atoms

As has been pointed out earlier, the formation of stable molecules C_2H_6 , B_2H_6 and C_2H_4 , C_2H_2 from the radicals CH_3 , BH_3 and CH_2 , and CH can be explained in the same way as the formation of F_2 , O_2 , and N_2 from fluorine, oxygen, and nitrogen atoms. Many other molecules, e.g., $HCHO$ and N_2H_4 , can be accounted for in a similar way.

The electron configuration of C_2H_2 , as Herzberg has pointed out,¹ can be described in exactly the same way as that of N_2 . Being a linear molecule, so that the field of force in which its electrons move is symmetrical with reference to an axis, as in a diatomic molecule, its electrons can all be classified under the headings σ , π , . . . just as in a diatomic molecule.

In a molecule like C_2H_4 the situation is somewhat altered.

Because the field of force in which the electrons move is no longer symmetrical around the line joining the carbon atoms, the orbit-types are now somewhat different. It is, however, not unreasonable to expect that the electron configuration of C_2H_4 is closely related to that of O_2 , from which an isotope of C_2H_4 might be obtained by splitting off two hydrogen nuclei from each oxygen nucleus. Assuming the closest possible analogy, we have (cf. pp. 365, 370):



As was noted earlier (4), atomic p electrons split into two types σ and π in diatomic molecules (e.g., $2p\sigma$ and $2p\pi$ in CH), but in general in polyatomic molecules into three types. Of each of these, as of σ electrons in the diatomic case, it takes only two to make a closed shell. If the total number of electrons is even, and if all are in closed shells, as is probable for the stablest state, the molecule is necessarily in a singlet state ($S = 0$). In the case of the π electrons of a diatomic or linear polyatomic molecule, it takes four to make a closed shell. Two π electrons, plus any number of closed shells, give ${}^3\Sigma^-$ as the stablest state, as in O_2 . The two bonding electron types $\sigma 2p$ and $\pi 2p$ of O_2 must probably be replaced in C_2H_4 by three which the author has called $b2p$, $c2p$, and $d2p$, while the anti-bonding types $\sigma^* 2p$ and $\pi^* 2p$ must probably also be replaced by three which may be called $b^* 2p$, $c^* 2p$, and $d^* 2p$. It is assumed that $c^* 2p$ is the most firmly bound of these last and is therefore present in the normal state of C_2H_4 . Two $c^* 2p$ electrons completing the electron configuration of C_2H_4 give a singlet state (which has been called 1Z), in contrast to the ${}^3\Sigma^-$ normal state resulting from the two π^* electrons in O_2 . This difference explains the fact that ethylene is diamagnetic while oxygen is paramagnetic.

A similar explanation of the electron configuration and diamagnetism of C_2H_4 has been given by Hückel (16), who, however,

has not considered carefully the existence of π^* as well as π (or c^* as well as c) electrons. Slater and Pauling (12) have given what at first sight seems an entirely different interpretation of the electronic structure of C_2H_4 , in terms of atoms joined by valence bonds.

The present explanation of the electronic structures of C_2H_4 , B_2H_6 , and the like completely dispenses with the idea of valence bonds between hydrogen atoms and boron or carbon atoms (cf. "Superfluity of the concept of valence bonds" on p. 369). It regards the electrons originally belonging to the hydrogen atoms as having become integral parts of the electron systems of radicals such as CH_2 or BH_3 which then function much like ordinary atoms. The original hydrogen atoms are thought of as having each been resolved into an electron which behaves as just stated and a proton which finds an equilibrium position in the radical. When two radicals like CH_2 or BH_3 unite, their outer electrons, without distinction as to whether or not they originally belonged to hydrogen atoms, are assumed to act as bonding or anti-bonding electrons for the union of the two radicals. One can then, if one wishes, define the number of valence bonds between the two radicals as equal to half the difference between the numbers of bonding and anti-bonding electrons.

The truth probably lies somewhere between the present point of view which assumes complete loss of individuality of the hydrogen atoms in molecules, and that of ordinary valence theory as used by Slater and Pauling, which assumes a preservation of the individuality of each atom, including hydrogen atoms, in the molecule. The case here is similar to the fact that in most molecules the truth lies between the two extremes polar and non-polar. That hydrogen atoms may usually largely lose their identity in molecules while other atoms usually largely preserve theirs is not unreasonable, since the H^+ ion is uniquely small as compared with the ions of other atoms.

The success of the present method in accounting for the molecule B_2H_6 suggests that the present explanation of B_2H_6 , and quite possibly also of C_2H_4 , C_2H_2 , and so on, is more nearly correct than are attempted explanations using ordinary valence

concepts. The author hopes to discuss these questions more fully elsewhere.

V. THE CHEMICAL BOND

Bonding energies in diatomic molecules

What is the unit chemical bond?

If with Herzberg (3) one defines the number of valence bonds as equal to the number of pairs of bonding electrons minus the number of pairs of anti-bonding electrons, then Li_2 , C_2 , CN , N_2 , CO , NO , O_2 , and F_2 have respectively 1, 2, $2\frac{1}{2}$, 3, 3, $2\frac{1}{2}$, 2, and 1 valence bonds, in agreement, except for CN , CO , and NO , with ordinary valence theory. Using the same method of definition, the molecules H_2^+ and He_2^+ have each $\frac{1}{2}$ valence bond. Table 2 shows that when the number of bonds N is defined in this way, the heat of dissociation varies very little from a characteristic mean value for each value of N , in the molecules from C_2 to F_2 . Further, the heat of dissociation per bond (D/N) is nearly constant. These relations would not be true if the number of bonds demanded by ordinary valence theory (3 in CN , 2 in CO , 2 in NO) were assumed;¹⁶ matters would be still worse if in O_2 only 1 bond were assumed, in accordance with the spin theory of valence.

The facts just brought forward strongly suggest that instead of treating the electron pair as a unit bond, we should regard a *single bonding electron as the natural unit bond*, and an anti-bonding electron as a negative unit. Although it is customary to treat the electron pair as the normal unit bond, the idea that a special kind of bond known as the "one-electron bond" occurs in some molecules has also been in use. Pauling has recently discussed this (14), using especially H_2^+ as an example, and has also introduced the concept of a "three-electron bond" in certain molecules (in particular He_2^+ , NO and O_2). But it seems probable that all such special concepts can better be reduced to terms of bonding and anti-bonding electrons. The one-electron bond is a

¹⁶ The existence of three valence bonds in CO has, however, often been assumed, first by Langmuir (*J. Am. Chem. Soc.* **41**, 1543 (1919)). Herzberg (3) first pointed out that it is given also by the present method.

single bonding electron, the electron-pair bond is two bonding electrons symmetrically related, while the three-electron bond consists of a pair of bonding electrons plus one anti-bonding electron.

In NO Pauling assumes one three-electron bond and two electron-pair bonds. The author believes it would be more nearly correct to speak of three electron-pair bonds and one negative one-electron bond, or in other words of six bonding electrons and one anti-bonding electron. More accurately still, there are eight bonding electrons and three anti-bonding electrons. The three-electron bond does not appear to be a natural *unit*. In O₂ Pauling assumes one electron-pair bond and two three-electron bonds. It seems to the author that it would be better to speak of three electron-pair bonds (one $\sigma 2p$ and two $\pi 2p$), or six bonding electrons, plus two anti-bonding electrons ($\pi^* 2p$).

In F₂, already discussed, there is one strong electron-pair bond, but there are also two rather weak electron-pair bonds and two equally weak pairs of anti-bonding electrons. Here the anti-bonding as well as the bonding electrons are symmetrically related in pairs.

That bonding electrons nearly always are found in symmetrically related pairs in chemical molecules can be explained on grounds of maximum stability (cf. Summary) without adopting the assumption that such pairing is a really fundamental characteristic of chemical bonding—still less that one member of each pair must be contributed by each atom, as London and Heitler's spin theory requires. An analysis indicating that the establishment of a symmetrical relation between two electrons is only incidental in the formation of an electron-pair bond, has already been given at the end of the section entitled "Application of Heitler and London method to H₂ and H₂⁺. . . ."

Arbitrariness of the concepts of valence and of bonding electrons

The molecules HeH, HgH, CaH and He₂⁺ illustrate well the essential arbitrariness of the concept of valence and the impossibility of accepting it as corresponding to an always sharply de-

finable, whole number property of atoms. Likewise they indicate that, while it is usually convenient to think in terms of definite numbers of electrons of the three classes bonding, anti-bonding, and non-bonding, or of the two classes bonding and non-bonding, the concept of bonding power as a continuous variable is more fundamental. The discussion given earlier (p. 377) of the $\sigma 2s$, $\sigma^* 2s$, $\pi 2p$, and $\pi^* 2p$ electrons in F_2 also points to the same conclusion. An even more fundamental viewpoint is that indicated in the section entitled "Superfluity of the concept of valence bonds," on p. 369.

We may interpret the instability of HeH by saying that its two $1s$ electrons are non-bonding at moderate r values—since being so firmly bound by the He atom (ionization potential 25 volts), they have very little tendency to enlarge their orbits so as to go around the hydrogen nucleus—and that the $1s$ electron of the hydrogen atom is anti-bonding at moderate r values, because it must be promoted to $2p\sigma$ as $r \rightarrow 0$, a process which would require much energy.

The small but not inappreciable D of HgH may be explained as follows. The two $6s$ electrons of the mercury atom (ionization potential 10.4 volts) here show a rather small positive bonding power, since they are decidedly attracted by the H^+ nucleus. The hydrogen $1s$ electron acts as an anti-bonding electron, being promoted to a $6p\sigma$ orbit, which is considerably less firmly bound in HgH than the $1s$ orbit in H , as is shown by spectroscopic data. The net effect is a very weak bonding.

In CaH the relations are qualitatively similar to those in HgH , but the two $4s$ electrons of calcium (ionization potential 6.1 volts), being less firmly bound in the atom than are the $6s$ electrons in mercury, are more strongly attracted by the hydrogen nucleus, and may perhaps be called bonding electrons. At the same time the hydrogen electron, in this case promoted probably to $3d\sigma$, acts as an anti-bonding electron as before.

In He_2^+ the two $\sigma 1s$ electrons are shared by the two nuclei, which approach to 1.06×10^{-8} cm. when the molecule is in equilibrium, and act definitely as bonding electrons, while the $\sigma^* 1s$ electron, being vigorously promoted, has a strong anti-bonding action.

VI. SUMMARY

From the foregoing one can see that the facts described by the rules of valence, as well as some of the exceptions to these rules, can be understood very clearly in terms of the electron configurations¹⁷ of the molecules and their atoms, at least for simple diatomic molecules and for some of the simpler polyatomic hydrides. The method is so far a semi-empirical one in that it very often makes use of spectroscopic and chemical data in determining the energies of binding of the various types of orbits.

London and Heitler's spin valence theory, when applicable, usually gives, somewhat fortuitously *in the author's* opinion, the same results as the present method. The latter gives, however, a detailed insight into what is going on in the formation of the molecule. It is also useful for excited states, while the spin theory fails. In those cases where the present method has to be guided by numerical calculations, as for $2\text{H}(1s) \rightarrow \text{H}_2(1s\sigma 2p\sigma, {}^3\Sigma)$, or by empirical data, as it does in concluding that two neon atoms repel each other, the same is true of Heitler and London's valence theory. In cases such as those of $\text{O} + \text{O}$, $\text{F} + \text{F}$, or $\text{Ca} + \text{H}$, where Heitler and London's theory is unsatisfactory, as well as in certain cases where ordinary valence theory fails (e.g., B_2H_6), the present method gives a clear understanding.

It is emphasized that the concept of a discrete, whole number property of atoms called valence, is less fundamental from the point of view of quantum theory than a continuous conception of chemical binding; likewise that the idea of a definite integral number of bonding electrons is not so fundamental as the idea that every outer electron has a certain bonding power (B.P.), positive or negative. More fundamentally still, one must recognize that it is not strictly possible to divide the energy of formation of the molecule into parts assignable to the separate electrons.

Nevertheless for practical purposes most electrons in most molecules can be definitely classified as bonding (large positive B.P.), *anti-bonding* (large negative B.P.), or *non-bonding* (very

¹⁷ For a detailed discussion of electron configurations in diatomic molecules, the reader is referred to an article (reference 4) in the January, 1932, number of *Reviews of Modern Physics*.

small B.P.). In agreement with Herzberg, it is concluded that the number of valence bonds according to ordinary valence theory is usually equal, at least in diatomic molecules, to half the difference between the numbers of bonding and of anti-bonding electrons. Probably in polyatomic molecules, however, anti-bonding electrons are less prominent than in diatomic molecules. Probably usually they are weaker in their action and approximately balanced by an equal number of weak bonding electrons, giving as net result a merely non-bonding effect.

It is argued that the primary unit in valence is a single bonding electron, with an anti-bonding electron as a negative unit, and with the symmetrically related electron pair as a very common secondary unit. The fact that valence electrons almost always occur in pairs in saturated molecules appears to have after all no fundamental connection with the existence of chemical binding. It can be adequately explained on the basis of the fact that, because of the Pauli principle and the properties of electron spin, each type of molecular orbit can be occupied by just two electrons. For example, if the orbit in question is of a bonding type, then naturally the stability of the molecule is greater when this orbit is occupied, if they are available, by two electrons than if it is occupied by only one while the second goes into an orbit of lower bonding power.

A clearer understanding of molecular structure, especially in hydrides, can often be obtained by dropping altogether the idea of atoms or ions held together by valence forces, and adopting the molecular point of view, which regards each molecule as a distinct individual built up of nuclei and electrons.

REFERENCES

- (1) MULLIKEN, R. S.: *Phys. Rev.* **32**, 196 (1928). On the subject of the relation of molecular electron configurations to chemical binding, see also HUND, F.: *Z. Physik* **51**, 788, 793 (1928) and elsewhere; also reference 3.
- (2) HUND, F.: *Z. Physik*. **40**, 743; **42**, 93 (1927), and later papers.
- (3) HERZBERG, G.: *Z. Physik* **57**, 616 (1929). Also HUND, F.: *Z. Physik* **63**, 731 (1930).
- (4) For further details about these matters reference may be made to the review by R. S. Mulliken in the forthcoming January, 1932, number of *Reviews of Modern Physics*.

- (5) HEITLER, W. AND LONDON, F.: *Z. Physik* **44**, 455 (1927). For a review of work using this method, see reference (8), also references 7 and 12 and footnote 14.
- (6) See the excellent discussion of the application of the method of Heitler and London to H_2^+ and H_2 given by L. Pauling in *Chem. Reviews* **5**, 173 (1928).
- (7) SLATER, J. C.: *Phys. Rev.* **32**, 349 (1928).
GENTILE, G.: *Z. Physik* **63**, 795 (1930).
ROSEN, N.: *Phys. Rev.* **38**, 275 (1931).
- (8) For a review of the work up to 1930 see HEITLER, W.: *Z. Physik* **31**, 185-204 (1930).
- (9) LEWIS, G. N.: *Valence and the Structure of Atoms and Molecules*. The Chemical Catalog Company, New York (1923).
- (10) GENTILE, G.: *Z. Physik* **63**, 795 (1930).
- (11) BARTLETT, J. H., JR.: *Phys. Rev.* **37**, 531 (1931).
- (12) SLATER, J. C.: *Phys. Rev.* **37**, 481; **38**, 325, 1109 (1931).
PAULING, L.: *J. Am. Chem. Soc.* **53**, 1367 (1931).
- (12a) Compare figure 36 of reference 4.
- (13) MULLIKEN, R. S.: *Phys. Rev.* **32**, 186, 202 (1928).
- (14) PAULING, L.: *J. Am. Chem. Soc.* **53**, 3225 (1931).
- (15) See reference 4, figure 43.
- (16) HÜCKEL, E.: *Z. Physik* **60**, 423 (1930).