

Electronic Structures of Polyatomic Molecules and Valence. II. General Considerations

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A description of electronic structures of polyatomic molecules in terms of atomic and molecular orbitals (one-electron orbital wave functions) is suggested, as follows. Unshared electrons are considered as occupying atomic orbitals associated with the various nuclei to which the electrons belong. Shared electrons are described from several points of view, whose simultaneous consideration should give a better understanding of their condition and functions in the molecule. In the first place, they are described, in terms of atomic orbitals, from the point of view of *each nucleus* in the molecule. In the second place, they are described from a unitary molecular point of view, in terms of molecular orbitals. It is pointed out that the chemical evidence which led Lewis to his concept of the electron-pair bond can now all be explained by the quantum theory without the necessity of using such a concept. It is noted that the Heitler-London, Pauling-Slater quantum-mechanical electron-pair bond concept differs markedly from Lewis's, also that it is of more restricted application to chemical data. It is pointed out, in agreement with Hund, that properties of the H. and L., S. and P. electron-pair bond which make it useful in dealing with chemical combination are also possessed by the concept of molecular orbitals. For example, the Pauling-Slater criterion that bonds which correspond to a maximum overlapping of atomic orbitals are the strongest is just as characteristic of bonding molecular orbitals as of electron-pair bonds. An electron-pair bond is here interpreted as being little other than two electrons occupying a bonding molecular orbital. Or in general one must say that a set of n electron-pair bonds is interpreted as a set of $2n$ electrons occupying n molecular orbitals, because molecular orbitals are not necessarily localized *between two nuclei* like electron-pair bonds. It is concluded that the essential facts of molecular electronic structure can be qualitatively understood in terms of the mode of description stated in the first paragraph above and of a semi-empirical valence rule (not essentially new) which summarizes, in the light of quantum theory, the most important regularities in regard to the types of chemical compounds which are stable.

ATOMIC AND MOLECULAR ORBITALS FOR DESCRIBING MOLECULAR ELECTRONIC STRUCTURES

1. Introduction

THE series of which the present paper is the second¹ is a development of a program initiated by Hund² and the writer³ and carried forward principally by us, by Herzberg, and by Dunkel.^{4,5,6,7,8,9,10,11,21} The object

¹ A brief preliminary paper outlining some of the principles used and some of the main results has already been published: R. S. Mulliken, *Phys. Rev.* **40**, 55 (1932). In this paper, the following changes should be made in the last paragraph on p. 58. Line 8, delete "tetrahedralized but uncombined"; lines 9 and 12, delete brackets around σ , and delete "uncombined" before $2p\sigma$; lines 10-11, delete "tetrahedralized uncombined." Also on p. 59, line 10, delete brackets. Elsewhere, do not delete brackets or "tetrahedralized."

² F. Hund, *Zeits. f. Physik* **51**, 759 (1928).

³ R. S. Mulliken, *Phys. Rev.* **32**, 186, 761 (1928); **33**, 730 (1929).

of this program has been to describe and understand molecules in terms of one-electron orbital wave functions of distinctly molecular character. The first paper of the present series¹ will be referred to hereafter as I. The present paper is to a large extent a preliminary critical review rather than a presentation of new results.

2. Atomic and molecular orbitals

From here on, one-electron orbital wave functions will be referred to for brevity as *orbitals*. The method followed here will be to describe unshared electrons always in terms of *atomic orbitals* but to use *molecular orbitals* for shared electrons. This procedure was first used by Lennard-Jones¹² for diatomic molecules, and is a partial departure from the original formulation of the above program. Among the main objects of the present series are the determination of the forms of molecular orbitals and the application of a knowledge of these forms to an explanation of valence and related chemical phenomena.

Shared electrons include two types, namely *bonding* and *anti-bonding* electrons, at least in diatomic molecules; unshared electrons belong to the class of *non-bonding* electrons.^{8,9,10,11} Anti-bonding electrons occur in diatomic molecules only when accompanied by a larger number of bonding electrons. Often it is hard to draw the line between shared and unshared electrons; in such cases, the electrons in question consist of bonding and anti-bonding electrons in equal numbers, at least in diatomic molecules (cf. third following paragraph and references 8, 9).

By an atomic orbital is meant an orbital corresponding to the motion of an electron in the field of a single nucleus plus other electrons, while a molecular orbital corresponds to the motion of an electron in the field of two or more nuclei plus other electrons. Both atomic and molecular orbitals may be thought of as defined in accordance with the Hartree method of the self-consistent field, in order to allow so far as possible for the effects of other electrons than the one whose orbital is under consideration.

Every non-degenerate orbital can be occupied by at most two electrons,

⁴ F. Hund, Zeits. f. Physik **63**, 719 (1930).

⁵ F. Hund, Zeits. f. Physik **73**, 1 (1931); **74**, 429 (1932).

⁶ F. Hund, Zeits. f. Physik **73**, 565 (1932).

⁷ F. Hund, Zeits. f. Physik **74**, 1 (1932).

⁸ R. S. Mulliken, Chem. Rev. **9**, 347 (1931). On p. 351 (foot), p. 353 (middle) and p. 355 (middle), the writer gives the incorrect impression that, omitting the energy of repulsion of the nuclei, the promoted wave-function $2p\sigma$ has a *higher* energy than the original $1s$ atomic wave-function. Actually the energy is a little lower (for $R > 0$) than that of $1s$ in the H atom. This, however, does not in any essential way affect the validity of the arguments given. The fact that the energy of $2p\sigma$ goes up sufficiently rapidly *with reference* to that of $1s\sigma$, in particular the fact that the energy of $2p\sigma$ plus the nuclear repulsion energy causes a net repulsion of H and H^+ , is sufficient.

⁹ R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932).

¹⁰ G. Herzberg, Zeits. f. Physik **57**, 601 (1929).

¹¹ G. Herzberg, "Molekülstruktur," Leipziger Vorträge, 1931, p. 167. S. Hirzel, Leipzig.

¹² J. E. Lennard-Jones, Trans. Faraday Soc. **25**, 668 (1929).

corresponding to the two possible orientations of the electron spin. Orbitals having n -fold degeneracy can be occupied by at most $2n$ electrons. Examples of non-degenerate orbitals are s orbitals in atoms, σ orbitals in diatomic or linear molecules^{9,11} and most orbitals in non-linear polyatomic molecules. Examples of degenerate orbitals are p, d, \dots orbitals in atoms ($2l+1$ -fold degeneracy), π, δ, \dots orbitals in diatomic or linear molecules (2-fold degeneracy), $[\pi]$ orbitals (2-fold degeneracy), in molecules like $\text{NH}_3, \text{NO}_3^-$, etc. (cf. I), d_γ (2-fold degeneracy) d_e and p (3-fold degeneracy) in molecules having tetrahedral or octahedral symmetry (cf. I).

It should be noted that the use of atomic orbitals for describing the condition of unshared electrons in molecules often gives a false impression of the amount of degeneracy. For example if one writes $1s^2 1s^2 \sigma 2s^2$ for the electron configuration⁹ of Li_2 , the description suggests only one ionization energy for the $1s$ electrons, since $1s$ orbitals on two Li atoms are identical in energy. If one writes $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2$, however, using molecular orbitals exclusively,⁹ it is made explicit that there are two distinct energies corresponding to $\sigma 1s$ and $\sigma^* 1s$. In this particular example the energy difference is negligible, but in many cases, especially where there are electrons which are near the border line between unshared and shared, considerable energy-splittings may exist.

For example in O_2 one may perhaps best write $1s^2 1s^2 2s^2 2s^2 \dots$ but must then grant that the $2s$ type, although essentially unshared, has a markedly double ionization energy.⁹ In N_2 , the sharing of the $2s$ electrons is so strong that it is best to write $1s^2 1s^2 \sigma 2s^2 \sigma^* 2s^2$, the types $\sigma 2s$ and $\sigma^* 2s$ being very different in energy.⁹ In CF_4 , one might write $\{1s^2 2s^2 2p[\pi]^4\}_{\text{F}^4} \{1s^2\}_{\text{C}} a^2 b^6$, where a and b represent the shared electrons. In so doing, it should be recognized that four distinct energy values are to be expected for the unshared $1s$ fluorine electrons, likewise for the $2s$ and for the $2p[\pi]$,—or possibly eight values for $2p[\pi]$ because of a possible splitting up of the degeneracy implied by the symbol $[\pi]$. The four-fold splitting might be appreciable for the $2p[\pi]$ and possibly also for the $2s$, although of course negligible for the $1s$. The carbon $1s$ is of course very different in energy from the fluorine $1s$. These examples should be sufficient to show how to guard against a possible misinterpretation of the use of atomic orbitals in describing molecules.

In the present method, molecular orbitals are conceived of as entities quite independent of atomic orbitals. Nevertheless in practise molecular orbitals can usually be conveniently approximated by building up linear combinations of orbitals of the atomic type. The present method of thinking in terms of the finished molecule, used already by Lewis in his valence theory, avoids the disputes and ambiguities, or the necessity of using complicated linear combinations, which arise if one thinks of molecules as composed of definite atoms or ions.

3. One-nucleus and other viewpoints

Understanding of the electronic structure of molecules is greatly aided by introducing a set of partially overlapping descriptions whereby the electrons immediately surrounding each nucleus in a molecule are described in

terms of a set of atomic orbitals corresponding to the viewpoint of that nucleus. (Sidgwick,—reference 13, p. 98,—has used essentially this viewpoint.) Such *one-nucleus viewpoint* atomic orbitals must be taken as considerably deformed compared with ordinary atomic orbitals, the deformation being thought of as caused by the strong fields of the other nuclei. Unshared electrons, of course, are here assigned exclusively each to a particular nucleus, so that the one-nucleus viewpoints for them give the same description as that introduced in the first paragraph of section 2. Shared electrons, however, being considered as belonging to two or more nuclei, receive non-mutually-exclusive descriptions in terms of deformed atomic orbitals associated with each, or at least with several, of these nuclei (cf. descriptions of N_2^+ , HCl, and $PtCl_6^-$ in section 8 below and of CF_4 and other molecules in I as examples).

An understanding of molecular electronic structures can not infrequently be advanced by using still other auxiliary viewpoints. The well-known *united-atom* viewpoint is sometimes useful (cf. reference 9, p. 19). In hydrides especially, this or, rather, a viewpoint in which each hydrogen nucleus is at first regarded as united with a neighboring nucleus of larger charge, is valuable. This amounts to saying that in hydrogen compounds, the hydrogen one-nucleus viewpoints can often appropriately be treated as unimportant compared with the viewpoints of other nuclei in the molecule or that the hydrogen nuclei can be regarded merely as perturbing force-centers. The validity of this point of view is indicated by a number of facts concerning diatomic hydride band spectra,⁹ also by chemical data, notably the behavior of the boron hydrides.⁸

The familiar chemical method of regarding many molecules as built up of "radicals" suggests the usefulness of a point of view making use of shared orbitals belonging to *radicals* instead of, or in addition to, the viewpoint of molecular shared orbitals.

QUANTUM THEORY OF VALENCE

4. Review of theories of valence and molecular structure

A semi-historical survey of some of the theories dealing with valence and molecular structure will put the whole problem in better perspective. Incidentally, the writer hopes to show that there are no compelling reasons, either empirical or theoretical, for placing primary emphasis on electron pairs in constructing theories of valence. He hopes thereby to remove possible objections to the present method based on its lack of such emphasis.

The best chemical theory of valence covering all types of compounds is generally agreed to be that developed principally by G. N. Lewis.¹³ To a rather large extent, the essential features of this theory still stand, although their meaning has been made clearer and more specific by interpreting them in the light of the quantum theory. The most important features of Lewis's theory are perhaps the following:

¹³ G. N. Lewis, *Valence and The Structure of Atoms and Molecules*. The Chemical Catalog Co., New York, 1923. Sidgwick's excellent book should also be consulted: N. V. Sidgwick, *The Electronic Theory of Valency*. The Clarendon Press, Oxford, 1927.

(1)(a) Every atom tends so to give, take, or share electrons as to be surrounded by an outer "group of eight" electrons (reference 13, p. 79),—except that for atoms such as H, He, Li this is replaced by a group of two. (b) Electrons which are shared may be shared equally or unequally by atoms, so that one can readily account for all intermediate stages between homopolar molecules like H_2 or Cl_2 and polar molecules such as NaCl. (c) Besides the cases having a stable group of two, already mentioned, Lewis noted the existence of other probable exceptions to the "rule of eight," namely cases like those of PCl_5 , SF_6 , $PtCl_6^-$ where a central atom appears to share more than eight electrons with other atoms (reference 13, pp. 102, 114 *et seq.*). Lewis suggested that in such compounds, the shared electrons in excess of eight have "passed into a secondary valence shell" of higher energy.

(2)(a) The single bond of the old valence theory of organic chemistry is interpreted as a pair of electrons held jointly in the outer shells of two atoms, and this concept of the chemical bond is extended to inorganic compounds. This electron-pair bond may be symmetrically shared as in H_2 or Cl_2 , but more often the electron-pair is nearer one atom than the other. (b) The valence of an atom in any molecule is defined as the number of electron pairs which it shares with other atoms (reference 13, p. 104). This is Langmuir's "covalence." Lewis's definition of valence makes the numerical valence the same as the "coordination number" of Werner (reference 13, p. 114). Using this definition, atoms which form a "group of eight" (Langmuir's "octet") by sharing have a valence of four, and "we may regard the maximum valence of four as a sort of norm," although atoms sharing more than four pairs have a higher valence, e.g., S or Pt in SF_6 or $PtCl_6^-$ has a valence of six. When there is an outer shell of eight electrons, there is a strong tendency for these to be all shared. In dealing with ionic or ionized molecules, Lewis uses the term "polar number" (reference 13, pp. 70, 104), e.g., in $Co^{++}Cl_2^-$, the Co atom is said to have a polar number +2, the Cl a polar number -1. This is Langmuir's "electrovalence." (c) Usually each atomic partner in an electron-pair bond furnishes one of the two electrons, as e.g. in H_2 , CH_4 , CCl_4 , but very often one partner furnishes both: examples, $BR_3 \cdot NH_3$ and other ammonia complexes, where the N atom furnishes both electrons of a pair; SO_4^- , ClO_4^- , etc., where the central atom furnishes all the shared electrons except the ionic charges. One-sided sharing as here and in (a) causes polarity in the molecule, but does not require a really ionic conception of valence, such as Kossel has used,¹⁴ except in extreme cases. (d) Double and triple bonds are considered to involve sharing of two and three pairs of electrons, but are considered to be something very different from merely two or three ordinary electron-pair bonds. Multiple bonds are apparently rarely formed by atoms other than C, N, and O.

The fundamental ideas of Lewis's theory are perhaps the three following:

(A) each atom (better, each nucleus) in a molecule tends to become sur-

¹⁴ W. Kossel, *Ann. d. Physik* **49**, 229 (1916); *Naturwiss.* **7**, 339, 360 (1919); cf. A. E. van Arkel and J. H. de Boer, *Chemische Bindung als elektrostatische Erscheinung*, S. Hirzel, Leipzig, 1931 (German edition).

rounded by a set of closed shells of electrons; (*B*) shared electrons, forming chemical bonds of the homopolar type, are usually localized between two atoms (or nuclei) which they link together; (*C*) a chemical bond usually consists of a pair of electrons somehow rather closely united to each other. Of these three ideas, Lewis seems to have considered (*C*) as the most fundamental (cf. reference 13, pp. 79–81). Ideas (*A*) and (*B*) were already in use before Lewis's 1916 paper, although Lewis's work greatly developed them and their application. Lewis' most important contribution to the theory consisted perhaps in his introduction of the idea of the completion of closed groups by *sharings*. Idea (*A*), limited, however, to the "group of eight," was proposed by Abegg in 1904 for polar valence and was also used in the same way by Lewis and later by Parson (1915) and Kossel (1916). Idea (*B*) was adapted by Lewis from the concepts of organic chemistry. Langmuir,¹⁵ in further developing the subject in 1919, emphasized idea (*A*) and spoke of the "octet theory" of valence. Bury¹⁶ in 1921 also emphasized idea (*A*).

With the development of the quantum theory, a more fundamental theoretical background has gradually been created for the originally largely empirical ideas of the Lewis theory. Bohr's theory of the periodic system, as modified by Stoner and Main Smith, shows why idea (*A*) is important in valence theory. The group of two found in H^- , He, Li^+ is $1s^2$ and presumably the shared pair of electrons in H_2 is essentially the same, while the highly stable "octet" is ns^2np^6 . Bohr's theory also provides for less stable groups of 18 and 32 electrons. Sidgwick¹⁷ showed in a general way in 1923 on the basis of the original Bohr theory how a group of 18, containing *ns*, *np* and *nd* electrons, can be used to interpret complex ions like $PtCl_6^{=}$ or $Co(NH_3)_6^{+++}$. Revised interpretations which regard the shared electrons in such compounds as belonging to *nd*, $(n+1)s$, and $(n+1)p$, have been given later (cf. Pauling,¹⁸ also I). Knorr¹⁹ has discussed the interpretation of Lewis's theory from the standpoint of the modified Bohr theory.

Bohr's theory was unable to give a satisfactory understanding of the sharing of electrons in molecules, but the new quantum mechanics is showing itself capable of doing this.

London and Heitler, generalizing results obtained from a quantum-theoretical study of the formation of H_2 from $H+H$, attempted to construct a valence theory which has often been supposed to be the quantum-mechanical equivalent of Lewis's, and which emphasizes Lewis's ideas (*B*) and especially (*C*). This so-called spin theory of valence emphasizes the pairing of electrons and their spins, but deals primarily with the interactions of atoms as wholes. It has, however, not proved very successful.^{5,8,10} London made the suggestion that the shared electrons in excess of eight ($ns^2 np^6$) in

¹⁵ I. Langmuir, J. Am. Chem. Soc. **41**, 868 (1919); Science **53**, 290; **54**, 59 (1921).

¹⁶ C. R. Bury, J. Am. Chem. Soc. **43**, 1602 (1921).

¹⁷ N. V. Sidgwick, Trans. Chem. Soc. **123**, 725 (1923).

¹⁸ L. Pauling, J. Am. Chem. Soc. **53**, 1367, 3225 (1931); **54**, 988 (1932).

¹⁹ C. A. Knorr, Zeits. f. anorg. allgem. Chem. **129**, 109 (1923). Also W. A. Noyes (1917), and others: cf. references given by W. A. Noyes, Zeits. angew. Chem. **44**, 893 (1931).

PCl_5 , SF_6 and the like are nd electrons; this idea is more specific than the similar idea of Lewis (cf. item 1 (c) above), and seems to be a good one.^{18,1} One should distinguish carefully⁸ between Heitler and London's valence theory and their valuable *perturbation-method for calculating energies* of molecule-formation.

Pauling¹⁸ and Slater²⁰ have generalized the Heitler and London results for H_2 in a different way, considering more specifically the interactions of pairs of electrons, one electron from each of two atoms. In this way they have obtained important results on valence and valence angles in polyatomic molecules. Their work emphasizes Lewis's idea (C) in modified form but focuses attention more on idea (B). Their theory seems more limited than Lewis's in that it requires that the two electrons forming an electron-pair bond necessarily come from two different atoms. This makes it inapplicable to many chemical compounds (cf. summary of Lewis's theory, item 2c) unless one assumes them to be formed from ions, a procedure which in many cases seems decidedly artificial. The theories of Heitler and London, Pauling and Slater might be called *electron-pairing* theories if Lewis's is called an *electron-pair* theory. It should also be pointed out that the H.L.P.S. electron-pair differs very considerably from Lewis's conception of the electron-pair bond in that the electrons are much less closely associated (see below); in this respect it approaches the truth much more closely than does Lewis's conception.—Pauling and Slater consider a double bond to be merely two ordinary single bonds sticking out from each atom in different directions, and treat the triple bond in a similar way. In this they do not agree very well with Lewis (cf. summary, item 2d), nor do they agree with results obtained from the method of molecular orbitals (see below).

Dunkel²¹ emphasizes Lewis's ideas (A) and (B), and describes the shared electrons in molecules in terms of the symbols $[\sigma]$ and $[\pi]$, implying orbital wave functions having properties similar to those of σ and π orbitals in diatomic molecules. The symbol $[\sigma]$, for instance, indicates a molecular orbital concentrated in the region between two nuclei and roughly symmetrical around the line joining them. This is justified by the fact that the shared electron moves in a Hartree field which is roughly symmetrical around this line. Although shared electrons of any given kind nearly always occur in pairs in stable molecules, this seems to be incidental in Dunkel's as in the present work. Unshared electrons are classified as they would be in free atoms. Dunkel's viewpoint evidently resembles that of the present paper. Hund in his recent papers^{5,6} has used Dunkel's $[\sigma]$, $[\pi]$ classification, but has used the simple symbols σ , π .

Hund in his important recent papers^{5,6,7} concludes that the results obtained by Slater and Pauling using the electron-pair bond method can also be obtained, sometimes more easily, by the method of molecular orbitals, and that the two methods are in many respects equivalent if one restricts the use of molecular orbitals to a type localized between two nuclei,—in agree-

²⁰ J. C. Slater, Phys. Rev. **37**, 481; **38**, 325, 1109 (1931).

²¹ M. Dunkel, Zeits. f. phys. Chem. [**B**] **7**, 81; **10**, 434 (1930).

ment with Lewis's idea (*B*). Reference should be made to Hund's papers for a critical discussion of many points concerning the various quantum theories of valence.

Hund has classified valences according to a number of types, depending in part on whether they are formed by *s* or *p* electrons or involve partial hybridization of *s* and *p* (Hund's *q* type). Hund also classifies chemical bonds according to a number of types, and concludes among other things that single bonds are always of the type $[\sigma]^2$, double bonds of the type $[\sigma]^2 [\pi]^2$, triple bonds of the type $[\sigma]^2 [\pi]^4$. It will be noted that this description of double and triple bonds agrees better with Lewis's conclusions (cf. summary, item 2*d*) than does the description given by Slater and Pauling. The absence of free rotation about double bonds can be well accounted for^{8,10} by the formulation $[\sigma]^2 [\pi]^2$, which really goes back to Hückel,²² while the validity of the explanation given by Pauling and Slater seems doubtful.

Hund shows⁶ that the familiar rules of organic chemistry can be explained in terms of the quantum-mechanically predicted behavior of some of the possible types of valence and of bonds. He shows that not all of the theoretically possible types are found in ordinary organic compounds, and shows how this can be understood in terms of energy relations; in particular, by assuming that of the types $[\sigma]$ and $[\pi]$ corresponding to a *p* valence electron, $[\sigma]$ in practise nearly always has the lower energy.

In all this work, Hund's purpose has been to show how the ordinary rules of valence can be derived from the principles of the quantum theory. In doing this, he has found it necessary to specialize the concept of molecular orbitals to the case of *orbitals localized between two nuclei*. Such a localized molecular orbital occupied by two electrons he regards as corresponding to the valence bond of organic chemistry or to that of Lewis, and as being essentially equivalent in the case of ordinary stable molecules to the electron-pair bond of H.L.S.P.

Hund remarks incidentally that the use of localized molecular orbitals is a somewhat poorer approximation than the use of the non-localized orbitals which are advocated in the present series, and illustrates this⁶ by discussion of a case which corresponds to CH_2 or H_2O . He also points out that in some cases localized orbitals cannot be used at all, and illustrates this by a consideration of crystal lattices and of the benzene molecule C_6H_6 and related molecules. In his plausible and important interpretation of C_6H_6 , Hund uses the same point of view that is emphasized in the present series. His non-localized " π " type in C_6H_6 is very similar to the central-nucleus-viewpoint type $2p[\sigma]$ in CO_3^- or NO_3^- if this type is assumed to be filled by two electrons shared by the O atoms in addition to their ordinarily assumed sharing of one pair each (cf. I, p. 61).

In the present series, idea (*A*) of Lewis's theory is emphasized, idea (*B*) is adopted in generalized form (non-localized molecular orbitals), while idea (*C*) is considered as corresponding more to an incidental than to a really essential characteristic of chemical combination. While the pairing of elec-

²² E. Hückel, *Zeits. f. Physik* **60**, 423 (1930).

trons, which is a consequence of the Pauli principle combined with the fact that the electron spin can have two and only two orientations, is very important for the *general theory of atomic and molecular structure*, especially in connection with the formation of closed shells, the importance of the specific role of electron-pairs or of electron-pairing in the *formation of molecules* has, in the writer's opinion, been somewhat over-emphasized, first in Lewis's theory, then in the work of Heitler and London, Pauling and Slater. Reasons for this opinion have been given in a previous paper dealing mainly with diatomic molecules.⁸ It seems desirable, however, to take the matter up again in some detail here, approaching it historically.

5. Analysis of the origin and development of the concept of the electron-pair bond

At the outset it is important to notice that Lewis's development of the concept of the electron-pair bond preceded our present knowledge of the electron spin and its properties and of the Pauli principle.

In developing his theory, Lewis noticed that while nearly half of the known atoms contain an odd number of electrons, very nearly all stable molecules contain an even number. This and other information on atomic structure and on molecules suggested that electrons have a tendency to form stable groups of two, held close to each other (cf. reference 13, p. 82 and Fig. 22) by strong forces of unknown character. These forces Lewis for some time considered to be magnetic, since the paramagnetism characteristic of atoms or molecules with an odd number of electrons usually disappears when they combine to give molecules with an even number. Lewis considered that in the formation of a molecule from two atoms containing unpaired electrons, the electrons attract each other in pairs, and that this attraction is, to a considerable extent at least, the cause of molecule formation (cf. e.g., reference 13, p. 149, second paragraph).

The subsequent development of the quantum theory has provided adequate explanation for the above facts concerning electron-pairs. The fact that most of the electrons in atoms as well as in molecules are paired is now well understood in terms of Pauli principle and electron spin. The fact that paramagnetism goes with unpaired electrons, diamagnetism with paired electrons, is also well understood. The fact that electrons are more often unpaired in atoms than in molecules can be understood in terms of the Pauli principle, electron spin, and orbital degeneracy (see below).

According to the quantum theory an electron-pair, in a molecule or in an atom, consists of two electrons, with spins antiparallel, occupying the same orbital and "symmetrically related" so far as their orbital motion is concerned.⁸ The magnetic forces between the two electrons are very small while the electrostatic repulsion is large. It is true that the symmetrical relation keeps the electrons nearer together than they would otherwise be, and in this respect shows a similarity to Lewis's concept of a pair of electrons held together by a strong attraction. But, directly contrary to Lewis's idea, the increased nearness of the electrons usually only increases their energy of repulsion.

Thus the formation of a pair of electrons when a molecule is formed, i.e., the occupation of a shared molecular orbital by *two* electrons, far from being *per se* a cause of combination of two atoms initially having each an unpaired electron, should tend to prevent combination. According to the present point of view the two electrons concerned act as bonding electrons *in spite of* considerable repulsive forces acting between them. Further details will be found in a discussion of H_2^+ and H_2 in reference 8.

Why then, are unpaired electrons so very much rarer in stable chemical molecules than in atoms? The answer involves several distinct considerations. In the first place, every atom having an odd number of electrons has necessarily at least one unpaired, while as soon as the formation of molecules is permitted, this necessity disappears. This leaves three questions. (1) Why do atoms often have more unpaired electrons than the minimum possible number, which is zero for an even total number of electrons, and one for an odd total number of electrons? (2) Why do stable molecules nearly always have an even number of electrons? (3) Why do such molecules nearly always have all their electrons paired?

The answers to all these questions depend largely on the occurrence and behavior of non-degenerate and of degenerate orbitals. If every orbital in atoms and molecules were decidedly different from every other in energy, then no atom or molecule with an even number of electrons would contain unpaired electrons when in its normal state. The electrons would settle down into the orbitals of lowest energy, with two electrons in each such orbital.

But when there is orbital degeneracy, i.e., when two or more orbitals form a group whose members are equal in energy (cf. section 2 above), then the energy of the electron system as a whole is a minimum if every electron occupies a different orbital belonging to the degenerate group. For example in the nitrogen atom the energy is a minimum when we have the electron configuration $1s^2 2s^2 2p^3$ and the state 4S . The orbitals $1s$ and $2s$ are non-degenerate and each is occupied by two electrons, but the type $2p$ has a three-fold degeneracy, being capable for example of giving rise to three distinct orbitals, $2p_{+1}$, $2p_0$, and $2p_{-1}$ in a strong magnetic field. The state 4S corresponds to one electron, unpaired, in each of the three orbitals $2p_{+1}$, $2p_0$, and $2p_{-1}$. The energy is a minimum for this state because it permits the orbitals of the three electrons to be antisymmetrically related.⁸ The resultant spin $S(S=1\frac{1}{2}$ here) is always equal, in molecules as well as in atoms, to $\frac{1}{2}$ times the number of unpaired or antisymmetrically related electrons, here three. If two electrons occupied the same orbital, e.g., $2p_{-1}$, they would necessarily be symmetrically related; but a symmetrical relation, as already noted, forces the electrons together, and would raise the energy above that of the 4S normal state.

It remains to give reasons why stable molecules nearly always have an even number of electrons, in pairs. In the writers' opinion, this can best be explained in terms of Lewis's idea (*A*) according to which each nucleus in a molecule tends to become surrounded by an atomic closed shell of electrons.

Since such a closed shell, e.g., ns^2 or ns^2np^6 , contains an even number of electrons,—for the reason that it is in the last analysis made up of pairs of electrons, although these often belong to degenerate groups, e.g., np^6 ,—every molecule which satisfies Lewis's idea *A* must automatically contain an even number of electrons, *all paired*. The quantum-mechanical background of idea *A* will be taken up below.

A further reason why molecules with an even number of electrons much more rarely contain unpaired electrons than atoms with an even number of electrons is to be found in the fact that orbital degeneracy is less usual in molecules than in atoms (cf. section 2, above). The O_2 molecule is a good example of an "exception that proves the rule." Here the electron configuration is of a type $\cdots \pi^2$, and the normal state is ${}^3\Sigma^-$, with $S=1$ and so two unpaired electrons. The π type of molecular orbital has a two-fold degeneracy, so that with two π electrons, one can be π^+ , the other π^- , and the two can be antisymmetrically related and so give rise to the normal state with $S=1$.

From the foregoing discussion it will be seen that the empirical evidence which led Lewis to emphasize his idea (*C*), according to which the formation of electron-pairs has a peculiar importance for chemical phenomena, can now all be explained satisfactorily on the basis of general quantum-theoretical considerations without any necessity of adopting idea (*C*).

Nevertheless it must be admitted that most of the striking chemical facts are not inconsistent with an electron-pair bond theory of homopolar valence similar to Lewis's. (His idea of a special attraction between electrons as the cause of pairing must of course be dropped.) A pair of electrons occupying equivalent localized molecular orbitals appears to be on the whole the nearest quantum analogue of Lewis's bond. For the best-known stable molecules the H.L.S.P. electron-pair,—cf. Hund (section 4), and section 13,—is equally good or perhaps better, but for molecules where a pair of electrons is furnished by one atom (cf. Lewis's theory, item 2*c*, and section 6), H.L.S.P. electron-pairs are less suitable than pairs of bonding orbitals. On the other hand for describing molecules having unusually loose binding, or molecules in a high state of vibration or in process of dissociation, provided dissociation would cause the breaking up of electron-pairs into unpaired electrons, electron-pair bonds of the H.L.S.P. type should often constitute a much better approximation than bonding orbitals.

6. Advantages of the present method

The concept of the bonding molecular orbital has the following advantages over the Heitler-London, Slater-Pauling electron-pair bond. (1) It is not necessary to have two electrons to get a chemical bond; one electron occupying a bonding orbital has a bonding effect, although of course not as strong as if two were present.⁸ Such "one-electron bonds" are rarely found in stable molecules, it is true, but the concept of bonding orbitals which explains them as a special case can lay claim to greater generality than the electron-pair bond concept which has to be replaced by a different special

concept in order to deal with them. The importance of one-electron bonds¹⁸ is greatly increased if one ventures into the realm of spectroscopically observable molecular entities and of intermediate products in chemical reactions. (2) Bonding molecular orbitals can be constructed for any degree of polarity or unequalness of sharing of electrons between nuclei. H.L.S.P. electron-pair bonds, however, cannot be used for molecules of the extreme polar type, and intermediate cases can be taken care of only by forming linear combinations of wave functions of the polar and electron-pair bond types (cf. section 13). In cases like $\text{Cu}(\text{NH}_3)_4^{++}$ or CO, the H.L.P.S. method can be used only by starting with assumed states of ionization like Cu^- and NH_3^+ or C^- and O^+ , while the method of molecular orbitals can start with Cu^{++} and NH_3 or C and O. For example, the pair of electrons which any N atom in NH_3 shares with the Cu or Pt atom in $\text{Cu}(\text{NH}_3)_4^{++}$ or $\text{Pt}(\text{NH}_3)_6^{++++}$ can be assigned to a symmetrically related pair of molecular orbitals which at first belong wholly to the NH_3 but take on more and more of the character of Cu or Pt atomic orbitals as the NH_3 approaches the metal atom. Here the method of molecular orbitals is superior even for loosely bound molecules. These various possibilities make the concept of molecular orbitals more generally useful than that of H.L.S.P. electron-pair bonds. (3) Bonding molecular orbitals are not restricted, like electron-pair bonds, to holding just two nuclei together, but may be distributed between several nuclei. This makes the concept a much more flexible one than that of the electron-pair bond, and makes it possible to account rather directly for a number of phenomena, many of them more or less spectroscopic but others definitely chemical in the ordinary sense, which the electron-pair bond method does not touch. In particular, molecular orbitals can be chosen in conformity to the actual symmetry of the nuclear arrangement, while the electron-pair bond method often disregards (even though it often predicts) this.

In general it may be said that there are many phenomena which can be interpreted in terms of electron-pair bonds only if after setting up these bonds, various *linear combinations* are formed, while the molecular orbital concept goes more directly at the solution, although often seemingly neglecting certain features expressed by the electron-pair concept. It appears probable that in practise one can expect most of the phenomena expressible by the special concept of electron-pair bonds to drop out of the application of the less specialized method using molecular orbitals. This should become clear in the detailed discussion of examples in later papers. It is quite possible, however, that the electron-pair bond method may for many problems be more adapted to quantitative calculations than the present method.

7. Statement and justification of a valence rule

Most of the ordinary numerical aspects of valence, alike for homopolar, heteropolar and for intermediate types of compounds, appear to be expressible by a simple *valence rule* (cf. I): *Every nucleus in a molecule tends to be surrounded, by means of sharing or transfer of electrons, by an electron distribution corresponding to some stable configuration having a total charge ap -*

proximately equal to or somewhat exceeding the charge of the nucleus. This is essentially idea (A) of Lewis's theory together with a generalization of his idea (B). This valence rule, it will be noted, is expressed in terms of one-nucleus viewpoints, according to which the state of the electrons near each nucleus is described by means of a set of electron quantum numbers or atomic orbitals associated with the viewpoint of that nucleus.

The important tendency of many atomic nuclei to have all their outer electrons shared (cf. section 4, item 2*b*), as e.g. in the formation of NH_4^+ , $\text{BR}_3 \cdot \text{NH}_3$, or $\text{Cu}(\text{NH}_3)_4^{++}$ from NH_3 is not accounted for by this valence rule, but its explanation appears to follow incidentally from the application of the present method (cf. discussion of NH_3 and CH_3 in I).

By "stable configuration" in the valence rule is usually meant a set of atomic orbitals completely occupied by electrons (i.e., a set of closed shells) and of such type that further electrons could go only into orbitals of distinctly higher energy. Stable configurations are usually sharply marked off from other configurations with either more or fewer electrons, by virtue of large energy changes that go with a change in principal quantum number, or with the change from a penetrating to a non-penetrating type of orbit even without change in principal quantum number.

Stable configurations which are sharply defined in respect to energy tend to give sharply-defined valence relations. In the transition groups where a *d* shell is in the process of being built up, there is at first no limiting sharply-defined stable configuration, and highly variable valence is the result. As the *d* shell approaches completion, however, the complete group $d^{10}s^2p^6$ apparently begins to serve as a stable limit, which is approached or reached in a number of complex molecules.

A quantum-theoretical justification of the above valence rule follows in part from the fact that, for the electrons in the neighborhood of every nucleus in a molecule, the Pauli exclusion principle makes essentially the same requirements in regard to quantum numbers and closed shells as for the electrons in an isolated atom. This is obviously true for the unshared, inner electrons, and for the ionic structures in definitely heteropolar valence, while its truth for shared electrons appears plausible but requires further investigation. The best evidence for its correctness for shared electrons seems to be the empirical evidence of the success of the rule in interpreting chemical facts. Dunkel²¹ has justified his (more or less tacit) use of a similar rule by similar arguments (cf. also Sidgwick, reference 13, p. 98 *et seq.*).

As a result of sharing, the numbers of electrons surrounding certain nuclei sometimes very considerably exceed the numbers in the corresponding neutral atoms. In such cases the sharing is usually relatively loose and presumably is strongly one-sided, although not necessarily ionic. Thus, for example, the electrons shared by the Pt or Cu nucleus in $\text{Pt}(\text{NH}_3)_6^{++++}$ or especially $\text{Cu}(\text{NH}_3)_4^{++}$ doubtless belong much more to the N nuclei than to the metal nucleus. The shared molecular orbitals would be approximated by linear combinations containing a relatively small proportion of an orbital, —*nd*, (*n*+1)*s*, or (*n*+1)*p*,—of the metal nucleus and large proportions of *2pσ*

orbitals of the N nucleus. Nevertheless the magnetic and other properties of such molecules¹⁸ indicate that even such one-sided sharing is commonly (but not always) strong enough so that, as far as the Pauli principle is concerned, part or all the metal-nucleus-viewpoint orbitals nd , $(n+1)s$, $(n+1)p$ are effectively filled.

In general, the ability of a nucleus to hold more electrons, but a rather definitely limited number more, when in a molecule than in an atom, appears to be conditioned by the fact that shared electrons are, so to speak, electrostatically on a part-time basis for each nucleus while with respect to the Pauli principle they are serving full time.

Proceeding further with the quantum-mechanical justification of the valence rule, one needs next to show why an energy-decrease should occur when atoms or ions so combine that each nucleus becomes surrounded by a "stable configuration." The heteropolar case is fairly well understood. A qualitative understanding also of the energy decrease which occurs in homopolar sharing seems to be obtainable in terms of one-nucleus viewpoints.

8. Cause of homopolar valence forces

London and Heitler concluded that the previously mysterious homopolar valence forces are explained by "resonance" or "exchange" integrals,—like $\mp I_2$ in Eqs. (2), (3) below and similar integrals occurring in the electron-pair case,—which give rise to sharp attractions or repulsions. As will be seen in section 10, these energy integrals correspond to the fact that bonding molecular orbitals give a higher, anti-bonding orbitals a lower, electron density in the regions between nuclei than if they were formed by mere overlapping of the electron densities of the atomic orbitals from which they might be formed. In a certain sense the above simple explanation of the homopolar valence forces is an adequate one. But it is of interest to see if one can go farther in understanding the matter physically by seeking to find reasons *why* these changes in electron density and in energy should occur when molecular orbitals are formed.

The simple case of H_2^+ is instructive.⁸ If we let $E.E.$ represent the energy of the electron, taken as zero for $R = \infty$, and $N.E.$ the energy of repulsion of the nuclei, then the energy change as the two H nuclei come together is

$$\Delta E = N.E. + E.E.$$

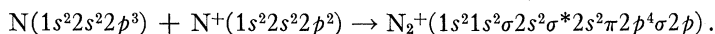
If $E.E.$ decreases with decreasing R considerably faster than $N.E.$ increases, until R reaches a fairly small equilibrium value, we have a stable molecule (negative ΔE). If it increases, or decreases less rapidly than $N.E.$ increases, we have repulsion. The two states $\sigma 1s$ and $\sigma^* 1s$ of H_2^+ correspond to these two cases. The exchange energies in the two cases are proportional respectively to $-I_2$ and $+I_2$.

The fact that ΔE is negative for $\sigma 1s$ and positive for $\sigma^* 1s$ corresponds to a rapid decrease of $E.E.$ with R for $\sigma 1s$ and a very much less rapid decrease for $\sigma^* 1s$. A good physical reason for this can be seen when we note that as $R \rightarrow 0$, the $1s$ atomic orbital of $H+H^+$ must shrink through $\sigma 1s$ to a much

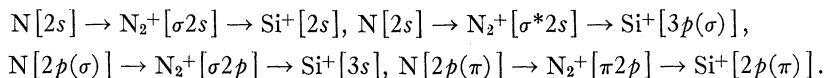
more concentrated $1s$ orbital of the united-atom, while through σ^*1s one reaches $2p\sigma$ of the united-atom, which is of about the same degree of concentration and has the same energy as $1s$ of $H+H^+$.

These considerations suggest that the behavior of bonding molecular orbitals like $\sigma 1s$ of H_2^+ is, qualitatively at least, essentially the result of an increase in effective nuclear charge without change of quantum numbers (no promotion), as R decreases. This effect must of course be intense enough to make ΔE negative in the above equation over a considerable range of R values. The fact that it actually does so for $\sigma 1s$ of H_2^+ could hardly have been predicted from our qualitative explanation, but this does not render the latter invalid, although it does show the superiority of the Heitler-London method for quantitative prediction. With anti-bonding orbitals like σ^*1s , the changed quantum numbers (promotion) more or less neutralize the effect of the increasing effective nuclear charge, thus permitting $N.E.$ always to exceed the negative of $E.E.$ in the above equation.

A somewhat more complicated case than H_2^+ is that of the N_2^+ molecule (cf. also section 10). The formation of the molecule in its normal state may be expressed as follows:



If we let $R = \infty \rightarrow R = R_e \rightarrow R = 0$ ($N + N^+ \rightarrow N_2^+ \rightarrow Si^+$), we should probably have⁹



Here the bonding molecular orbitals $\sigma 2s$ and $\pi 2p$ behave like $\sigma 1s$ of H_2^+ in that they are unpromoted as $R \rightarrow 0$, while the anti-bonding orbital behaves like $\sigma^* 1s$ of H_2^+ in that it is promoted as $R \rightarrow 0$. But $\sigma 2p$, which is promoted as $R \rightarrow 0$, is a bonding orbital, like $\pi 2p$ which is unpromoted. These results indicate that the difference between bonding and anti-bonding orbitals is not simply a difference between an unpromoted and a promoted condition if promotion is defined according to what happens in the united-atom ($R=0$).

If, however, we *redefine promotion* in terms of the *one-nucleus viewpoints* of the nuclei in the molecule, introducing the new word "*premotion*" in order to avoid misunderstanding, *bonding electrons* are essentially *unpromoted electrons* or (from an energy standpoint) sometimes slightly promoted electrons, while *anti-bonding electrons* are (strongly) *promoted electrons*. A few examples will make clear the exact sense in which *premotion* is here defined. According to the one-nucleus viewpoint of either of the two N nuclei in N_2^+ (or N_2), the seven (or eight) electrons occupying the bonding molecular orbitals $\sigma 2s$, $\sigma 2p$, and $\pi 2p$ are reckoned as $2s$, $2p\sigma$, and $2p\pi$ electrons, hence all unpromoted; in N_2 they form, from the point of view of each nucleus, a complete, although completely shared, L shell. The anti-bonding $\sigma^* 2s$ molecular electrons, however, must be reckoned as 3-quantum, hence promoted, electrons. In HCl, two bonding electrons may be considered as shared by the

H and Cl nuclei. From the H nucleus viewpoint, these represent $1s^2$, from the viewpoint of the Cl nucleus they are $3p\sigma^2$. But from both viewpoints they are unpromoted in the sense that their quantum numbers are the same as those of electrons already present in the H and Cl atoms. In PtCl_6^- (cf. I), two bonding electrons may be considered as shared between each Cl and the Pt nucleus. From the point of view of each Cl nucleus, the electrons it shares are $3p[\sigma]^2$. From the point of view of the Pt nucleus, the twelve electrons it shares are $5d, 4s^2, 6p^6$, while $5d_e^6$ is also present but unshared. The shared $5d$ and $6s$ electrons are unpromoted, the $6p$ electrons are promoted in the sense that the Pt atom alone, in its normal state, has a configuration $5d^96s$ without $6p$ electrons. But the fact that $6p$ electrons are only a little less easily ionized than $5d$ or $6s$ in the Pt atom makes it possible for the Pt nucleus in PtCl_6^- to use them as bonding electrons of a slightly promoted type.

The results of the preceding paragraphs can be formulated in part as follows. *Chemical combination of the homopolar type is a result of the shrinkage and consequent energy-decrease of atomic orbitals in the fields of neighboring nuclei, when such orbitals are shared with little or no promotion.*

A condition which is necessary for successful sharing is that the binding energy shall not be too different in the atomic orbitals involved. Otherwise the sharing becomes a one-sided affair: either an electron is almost completely transferred from one nucleus to another, or else almost no sharing or transfer at all takes place (cf. Hund⁸ for further discussion and details). Polar molecules like Cs^+F^- approximate the former and loosely bound molecules like $\text{Cu}(\text{NH}_3)_4^{++}$ the latter case; unstable molecules like HeH are extreme examples of the latter case.

9. Valence saturation

The important phenomenon of valence saturation can now be somewhat understood. It should first be pointed out that saturation is usually a relative rather than an absolute matter. Whether an atom or molecule acts in a saturated manner usually depends on the other atoms or molecules with which it is placed in contact, and furthermore it depends very much on circumstances such as temperature, pressure, and presence or absence of light. In practise, however, a molecule is generally considered saturated if it is stable at room temperature in the presence of others of its own kind and of air and diffused sunlight and perhaps of certain common chemicals. With this definition, a given atom can occur in many different saturated molecules.

A state of saturation usually exists when each nucleus in a molecule is surrounded by a set of closed shells which is stable with respect both to gain and to loss of electrons, including gain by sharing. A set of closed shells is stable toward loss of electrons if it has a high ionization potential; toward gain of electrons if a fairly large energy would be required to transfer an electron to an orbital outside the set. Closed shells ending with ns^2np^6 , also the shell $1s^2$, usually fulfill both criteria, while closed shells ending with nd^{10}

fulfill neither since the ionization potential is relatively low and the energy of excitation required to get $nd^9 (n+1)s$ is always small, or even negative. Even "stable" closed shells do, however, often take part in further sharing, usually by allowing two of their electrons to be shared by another nucleus (cf. section 4, item 2*b* and the examples of NH_3 combinations cited in section 7). Closed shells ending with ns^2 , $n > 1$, are relatively stable toward gain of electrons, but not toward loss. Atoms which are surrounded by stable closed shells when alone do not form molecules, because their electrons are too strongly held for either transfer or sharing and at the same time their outer shells contain no vacant places of low energy for receiving transferred or shared electrons. From the preceding discussion it will be seen that the property of saturation is not a property of closed shells as such, but depends on the occurrence of marked energy discontinuities, which often but not always are associated with closed shells.

Electrons are not accepted beyond the point of saturation simply because the unfavorable energy effect corresponding to promotion to a vacant position is greater than the normal favorable energy effect corresponding to sharing without promotion. The quantum-mechanical forces which cause saturated molecules to repel other molecules if they come too close may be described as *promotion forces*. The action of the promotion forces in polyatomic molecules is of the same nature as the anti-bonding action^{8,9} of anti-bonding electrons in diatomic molecules.

In diatomic molecules there is sometimes a forced sharing of anti-bonding electrons, incidental to the sharing of bonding electrons, which may be considered as a sort of supersaturation. That is, electrons are included in the molecule in promoted orbits which would not be expected from the valence rule. An example is the N_2 molecule with the electron-configuration $1s^2 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p^4 \sigma 2p^2$. From the point of view of each nucleus, that nucleus is surrounded by $1s^2$ unshared, then by $2s^2 2p\pi^4 2p\sigma^2$ (shared, cf. section 8), forming a complete *K* and *L* shell, and in addition by two (partially) promoted electrons probably classifiable as 3-quantum electrons, corresponding to the shared $\sigma^* 2s^2$. The molecule NO is even more supersaturated, by the inclusion of a $\pi^* 2p$ electron in its configuration.⁹ This functions very decidedly as a promoted 3-quantum electron from the point of view of one or both nuclei.

More commonly one finds an opposite condition in which nuclei in molecules are surrounded by less than a complete stable shell. This often results from a competition of different nuclei for electrons, or an inability of certain nuclei to share enough electrons to complete the shells of all the other nuclei. Probable or possible examples of nuclei with incomplete outer shells are B in BCl_3 , C in CO_3^- , N in NO_3^- , S in SO_3 (cf. I).

COMPARISON OF PROPERTIES OF MOLECULAR ORBITALS AND ELECTRON-PAIR BONDS

10. Properties of molecular orbitals

It has been stated in previous sections that the concept of molecular

orbitals possesses all the important properties which make the concept of electron-pair bonds valuable in explaining and predicting molecular structures, and further, is less specialized and so adapted to explain a wider variety of phenomena. The characteristics of the two concepts can be well understood by developing them for the simple molecules H_2^+ and H_2 , then generalizing.—The reader should also refer to Hund's valuable discussion^{5,6} of molecular orbitals (Hund's concept *c* in reference 5) and their relation to electron-pair bonds (Hund's concept *b*).

Pauling²³ was the first to apply the Heitler-London method, developed originally for H_2 and there yielding among other things the Heitler-London electron-pair bond, to the one-electron molecule H_2^+ . Applied to H_2^+ , it helps one to understand molecular orbitals. One finds that when $\text{H}(1s)$ and H^+ approach, either attraction with formation of normal H_2^+ , or repulsion, may occur. The two modes of interaction correspond to the two energetically distinct states one would have for $\text{H}(1s) + \text{H}^+$ if the two H nuclei were slightly different in charge.

Let the two H nuclei be designated *A* and *B* and the corresponding 1s atomic orbitals ϕ_A and ϕ_B . The molecular orbitals resulting when H and H^+ are brought together can be expressed in zeroth approximation as follows:

$$\phi_0 = c_0(\phi_A + \phi_B), \quad \phi_1 = c_1(\phi_A - \phi_B), \quad (1)$$

where the normalizing factors *c* depend on the distance *R* between the nuclei. The energy changes ΔE are in first approximation as follows:²³

$$\phi_0: \Delta E = e^2/R + [e^2/(1 + S)](-I_1 - I_2) \quad (2)$$

$$\phi_1: \Delta E = e^2/R + [e^2/(1 - S)](-I_1 + I_2). \quad (3)$$

Here

$$I_1 = \int [\phi_B^2/r_A] d\tau, \quad S = \int \phi_A \phi_B d\tau, \quad I_2 = \int [\phi_A \phi_B/r_A] d\tau, \quad (4)$$

where r_A is the distance of the electron from nucleus *A*. The "resonance" term $\mp I_2$ turns the scales in favor of attraction in the case of ϕ_0 , of repulsion in that of ϕ_1 .

The orbital ϕ_0 , whose presence leads to formation of a stable molecule, belongs to the class of bonding orbitals and may in fact be taken as the prototype of these, at least for diatomic molecules with equal nuclei. Similarly ϕ_1 may be taken as a prototype for diatomic anti-bonding orbitals. It will be noted that ϕ_0 is symmetrical in the nuclei while ϕ_1 is antisymmetrical, and that ϕ_0 is nodeless while ϕ_1 has a nodal plane half-way between the nuclei.

The behavior of the ΔE 's for ϕ_0 and ϕ_1 (Eqs. 2, 3) is easily understood when one considers the mean charge density $e^2\phi^2$ corresponding to each. One finds

$$\phi_0^2 = c_0^2(\phi_A^2 + \phi_B^2 + 2\phi_A\phi_B), \quad \phi_1^2 = c_1^2(\phi_A^2 + \phi_B^2 - 2\phi_A\phi_B). \quad (5)$$

²³ L. Pauling, Chem. Rev. 5, 173 (1928).

This shows that $e^2\phi_0^2$ is relatively more concentrated in the region between the nuclei than if one had a mere overlapping of the densities $e^2\phi_A^2$ and $e^2\phi_B^2$, which would give $\frac{1}{2}e^2(\phi_A^2 + \phi_B^2)$ for $e^2\phi^2$. On the other hand ϕ_1 is much less concentrated between the nuclei than for a mere overlapping of $e^2\phi_A^2$ and $e^2\phi_B^2$. With mere overlapping of densities, one would have a slight repulsion between H and H⁺, corresponding to $e^2/R - e^2I_1$ in Eqs. (2) and (3). It is the added concentration between the nuclei or withdrawal from this region, in ϕ_0 and ϕ_1 , which expresses itself in $\mp I_2$ in Eqs. (2) and (3) and is decisive in making ϕ_0 bonding and ϕ_1 anti-bonding.

The above results for molecular orbitals in H₂⁺ can be generalized to other molecules. N₂⁺, obtained by the union of N⁺(1s² 2s² 2p²) + N(1s² 2s² 2p³), will serve as an example. Strictly, we should use also a certain admixture of N⁺⁺ + N⁻, and should consider various excited states of N⁺ + N, but it is unlikely that this would seriously affect the results. Also, it should be noted that in this discussion we are treating the group of three states of N⁺ (³P, ¹D, and ¹S) and of N(⁴S, ²D, ²P), which arise from the electron configurations mentioned, as if each group were a single state. This is, however, legitimate because of the large energy of formation of N₂⁺. N₂⁺ in its normal state contains one $\sigma 2p$ electron, which may be considered, approximately at least, as going over on dissociation to a $2p$ atomic orbital of the neutral N atom. This may be on either nucleus A or nucleus B, so one gets approximately

$$\phi_{\sigma 2p} = c(\phi_{A2p} + \phi_{B2p}),$$

where of course it is understood that the $2p$ atomic orbitals are based on a suitable atomic Hartree field. Instead of the bonding orbital $\sigma 2p$, one could also get the anti-bonding orbital $\sigma^* 2p$, which should occur in some excited, perhaps unstable, state of N₂⁺: $\phi_{\sigma^* 2p} = c^*(\phi_{A2p} - \phi_{B2p})$. The bonding orbitals $\sigma 2s$ and $\pi 2p$ in N₂⁺ could similarly be shown to be capable of being respectively approximated by sums $\phi_A + \phi_B$ made up of atomic $2s$ or $2p$ orbitals, and the anti-bonding orbital $\sigma^* 2s$ could be approximated by a difference $\phi_A - \phi_B$.

Also in *unsymmetrical diatomic molecules*, molecular orbitals can be approximated by linear combinations of atomic orbitals: bonding type, $\phi = a\phi_A + b\phi_B$. In strongly ionic molecules, $a \gg b$ or vice versa. The results stated in this and the preceding paragraph have already been given by Hund^{5,6} and need not be further discussed here.

It seems clear that molecular orbitals in polyatomic molecules also can be approximated as linear combinations of atomic orbitals (cf. I for examples), and that bonding orbitals are additive linear combinations. In general, polyatomic bonding orbitals may be expected to surround several nuclei, although in special cases such orbitals may be largely confined to the neighborhood of two nuclei.

11. Maximum overlapping as a criterion of bonding power

It is now of interest to learn how the bonding power of a molecular orbital depends on its form. This can be seen from expressions like that for ϕ_0 in

Eq. (1). Since the lowered energy of bonding orbitals results from the fact that they are relatively concentrated between the nuclei, one readily sees that in order to have the bonding energy as large as possible, products such as $\phi_A\phi_B$ in Eq. (4) should be as large as possible, which is true if the atomic orbitals ϕ_A and ϕ_B overlap as much as possible. This can also be seen directly from the energy equations (cf. Eqs. 2, 4). This is Pauling's and Slater's *criterion of maximum overlapping of atomic orbitals*. The process of applying this criterion to the problem of determining the zeroth approximation atomic orbitals which give *strongest bonding* (Pauling's "best bonding eigenfunctions"), when ϕ_A and (or) ϕ_B belong originally to degenerate orbitals, seems to be the essence of the method used by Slater and Pauling (cf. reference 20, p. 1141).

Slater's and Pauling's original derivations of this criterion from the equations for electron-pair bonds (cf. Eq. (8) and related ΔE equations) give the impression that the existence of the criterion depends on the overlapping of the *orbits of two actual electrons*. The present approach shows, however, that the criterion for finding a *best bonding molecular orbital* for a pair of atoms depends only on the overlapping of two atomic orbitals, regardless of whether the resulting molecular orbital is occupied by two electrons, by one electron, or by none; the validity of the procedure, used in the present series, of regarding such an orbital occupied by two electrons as essentially equivalent to an electron-pair bond will be considered shortly.

Furthermore, the present approach shows that the criterion of maximum overlapping is just as applicable to molecular orbitals which are approximate linear combinations of atomic orbitals of several atoms as to those which are formed from orbitals of just two atoms. The present use of molecular orbitals which connect several nuclei is perhaps the most essential difference between the present method and that of Slater and Pauling.

12. Doubly- or multiply-occupied molecular orbitals

In nearly all chemically stable molecules, every bonding molecular orbital which is occupied at all is occupied by the full quota of electrons allowed by the Pauli principle, namely two if the orbital is non-degenerate, $2n$ if it is degenerate and n is the degree of degeneracy. The most important properties of such multiply-occupied bonding orbitals can easily be generalized from a consideration of the doubly-occupied $\sigma 1s$ orbital in normal H_2 . Omitting constant factors and spins, the wave function χ for normal H_2 may be approximated by the following expression:

$$\chi = \phi_0(1)\phi_0(2) \quad (6)$$

Eq. (6) implies that the two electrons move entirely independently, in the $\sigma 1s$ orbital, here denoted by ϕ_0 ; the numbers 1 and 2 refer to the coordinates of the two electrons. This, however, is true only as a rough approximation. Although the agreement of Eq. (6) with the truth can be made rather good by making the best possible choice of the form of ϕ_0 ,—the simple form given in Eq. (1) can be greatly improved on by adjusting it to correspond

to a one-quantum orbit in a suitable Hartree field,—it can never be made exactly right without adding a correction term. This is necessary in order to take care of detailed effects of the two electrons on each other's motions. The same kind of problem is met with in atomic spectra, for example in the He atom. Eq. (5) is a fairly good approximation for this atom if ϕ_0 is taken to refer to the 1s atomic orbital in a suitable Hartree field.

Slater²⁴ has found, in a paper preceding the work already referred to above, that if ϕ_0 is approximated by $c_0(\phi_A + \phi_B)$ in accordance with Eq. (1), the corrected expression for χ can be closely approximated by:

$$\chi = a\phi_0(1)\phi_0(2) - b\phi_1(1)\phi_1(2), \quad (7)$$

where ϕ_1 is as given in Eq. (1). For the molecule in its equilibrium condition ($R = R_e$), Slater finds $a/b = 8$, approximately; but for a molecule in the process of dissociation ($R \rightarrow \infty$), a/b approaches 1. This indicates that Eq. (6), even with ϕ_0 taken as $c_0(\phi_A + \phi_B)$, and of course all the more so if a better ϕ_0 is used, is a good approximation for H_2 in its ordinary stable state.

Reflection indicates that it is safe to generalize the type of approximation contained in Eq. (6) to unsymmetrical and to polyatomic molecules (cf. also reference 5). It even appears that the approximation may often be relatively better for polyatomic molecules than for H_2 . Hence the general use of molecular orbitals in describing shared electrons in stable molecules seems to be justified as a good approximation. In the case of chemical bonds with large R and small dissociation energy, however, cases may occur where the use of molecular orbitals as in Eq. (6), although still formally possible, does not constitute a good approximation.

The nature of the correction required in Eq. (6) is somewhat different for the case of H_2 than for that of He, because of the non-centralness of the Hartree field in H_2 . The nature of this difference can be seen if we consider what would happen if we increased R to a large value in H_2 . One would then find that the molecule would usually be very much like two H atoms with one electron on each, which means that χ would be essentially of the form $\phi_A(1)\phi_B(2)$ or $\phi_A(2)\phi_B(1)$. There would, however, be a small possibility of finding both electrons attached to one H nucleus, in which case χ would be essentially $\phi_A(1)\phi_A(2)$ or $\phi_B(1)\phi_B(2)$, corresponding to $H^- + H^+$ or $H^+ + H^-$. Returning to $R = R_e$, it would seem reasonable that the true χ should be approximately a linear combination of the four expressions just given.

13. Comparison with Heitler-London electron-pair bond

Heitler and London's original approximation²⁵ for normal H_2 , omitting constant factors, was

$$\chi = \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1). \quad (8)$$

²⁴ J. C. Slater, Phys. Rev. **35**, 514-5 (1930).

²⁵ W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927); Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

This expresses a state of affairs in which if one electron is in ϕ_A , the other is necessarily in ϕ_B . For large R , this would keep the electrons separated, with one near each nucleus, but for $R = R_e$, where ϕ_A and ϕ_B overlap strongly, the effect is much less pronounced.

Slater²⁴ has found that the true state of H_2 for $R = R_0$ is better expressed by

$$\chi = \alpha[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] + \beta[\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)], \quad (9)$$

with α/β roughly equal to 8. [That the ratio α/β here is nearly the same as a/b in Eq. (7) is accidental.] Eq. (9) allows the two electrons to be close together near the same nucleus oftener than Eq. (8) would permit.

Eq. (9) is a step from Eq. (8) toward Eq. (6); Eq. (6) implies that the probability of any stated position for one electron is independent of the position of the other. On the other hand, Eq. (7) is a step from Eq. (6) toward Eq. (8), if ϕ_0 and ϕ_1 are as given in Eq. (1). In fact, Eqs. (7) and (9) become identical if Eq. (1) is used and if the coefficients a, b, α, β , are properly related. Slater (private communication concerning details of Ref. 25) found that for $R = R_e$ in H_2 , the ratio of the coefficients c_0 and c_1 in Eq. (1) is about that given by $(c_1/c_0)^2 = 6.21$. Substituting this, also $a/b = 8$, in Eq. (7), the latter reduces to the form of Eq. (9) with $\alpha/\beta = 14.21/1.79$, which happens to be very nearly the same as a/b .

Eq. (8) is the expression, in terms of wave functions, of the Heitler-London, Pauling-Slater concept of the electron-pair bond, for the case of H_2 . Eq. (6) is the expression in terms of wave functions, for H_2 , of the concept of a bonding orbital occupied by two electrons. Slater's Eqs. (7) and (9), in view of his result that a/b and α/β are nearly equal, suggest that the two concepts, while departing from the truth in opposite ways, are about equally good approximations to it in their ability to describe the positions of two equivalent bonding electrons relative to each other and to two nuclei. Other considerations, pro and con, may enter besides the values of the ratios a/b and α/β , and of course such ratios would be different for other examples than H_2 , but it seems fairly safe to assume that the molecular orbital concept ordinarily does not give too bad an approximation in its description of the electron positions. We have already seen that in two other important properties,—the fact of concentration between the nuclei and the existence of the criterion of maximum overlapping,—the concept of bonding molecular orbitals gives the same results as that of electron-pair bonds.

For electron-pair bonds, the first of these properties follows if one determines the electron density for a single electron; this is given by $\int \chi^2 d\tau_2$ and comes out proportional to

$$\phi_A^2 + \phi_B^2 + 2S\phi_A\phi_B, \quad (10)$$

where S is as in Eq. (4). The concentration term here is less by a factor S than in Eq. (5). When one takes $\int \chi^2 d\tau_2$ using Eq. (6), however, one gets the same result as is expressed in Eq. (5). The existence of the criterion of maximum overlapping follows in the case of the electron-pair bond by a considera-

tion of the above electron density expression, or of ΔE expressions,²⁵ in much the same way that it does for bonding orbitals.

It is instructive to compare the application of the method of H.L.P.S. electron-pairs and that of molecular orbitals to molecules which have unequal nuclei and are partly polar, such as LiH, HF or HCl. If one uses electron-pair bonds, one forms a linear combination of polar and electron-pair wave functions:¹⁸

$$\chi = \alpha[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] + \beta\phi_B(1)\phi_B(2), \quad (11)$$

where B is the more negative atom. Using molecular orbitals, Eq. (6) applies, with

$$\phi_0 = a\phi_A + b\phi_B, \quad b > a. \quad (12)$$

Using Eq. (12), Eq. (6) becomes identical with Eq. (11) if we put $ab = \alpha$, $b^2 = \beta$, except that Eq. (6) gives an extra term $a^2\phi_A(1)\phi_A(2)$. This term is relatively unimportant if the molecule is strongly polar; for example if $b = 2a$, the coefficient of $\phi_A(1)\phi_A(2)$ is only one fourth that of $\phi_B(1)\phi_B(2)$. As in the case of equal nuclei discussed above, however, the truth must lie between Eq. (11) and Eqs. (6), (12). If both forms represent about equally good approximations, as seems likely, Eq. (6) may well be preferred for many purposes because of its simpler conception and formulation.