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# CHEMICAL BONDING

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## INTRODUCTION

### *Theories of Chemical Bonding*

In this paper *chemical bonding* is taken to refer mainly to the electronic structures of stable chemical molecules in their ground states. However, to a lesser extent, radicals and molecular compounds and complexes are also considered.

For a full understanding of chemical bonding, the application of quantum mechanics, dating from 1925–1926, is essential. It seems unnecessary to review the development of chemical theory up to that time: Let Figure 1 serve as a summary that includes the earlier history (1). To be sure, ionic binding had already become fairly well understood following Bohr's 1922–1923 quantum theory of atoms and the periodic system, but the nature of covalent bonding still remained essentially a mystery.

Historically, chemical bonding was long formulated in terms of interactions between atoms. Gradually it was recognized that electrons are the active agents in forming bonds, but just how they act could not be clarified without quantum mechanics. Typical stable molecules contain an even number of electrons and are diamagnetic. This fact led to the idea of electron pairs as typical of most chemical bonds. G. N. Lewis, in particular, developed this idea in a fruitful way (2).

In 1926, in Schrödinger's establishment, Heitler and London used quantum mechanics to show how one could arrive at a good theoretical understanding of the formation of the hydrogen molecule with its electron pair from two atoms (3). The theory was generalized by Slater and Pauling to deal with covalent electron-pair bonds in general. This approach is generally known as valence-bond theory. In 1938 Pauling published his well known book, *The Nature of The Chemical Bond* (4). This book fitted into the traditional view that molecules are *composed of atoms*.

Meanwhile, an alternative approach, the molecular orbital theory, was developed (Hund and Mulliken, beginning in 1927–1929: see Reference 5). Here the molecule is viewed as an independent unit, even though it is formed by the coming together of atoms, and although the molecule in its inner electron shells (as contrasted with its valence shell) still largely preserves the same structures as in its separated atoms.

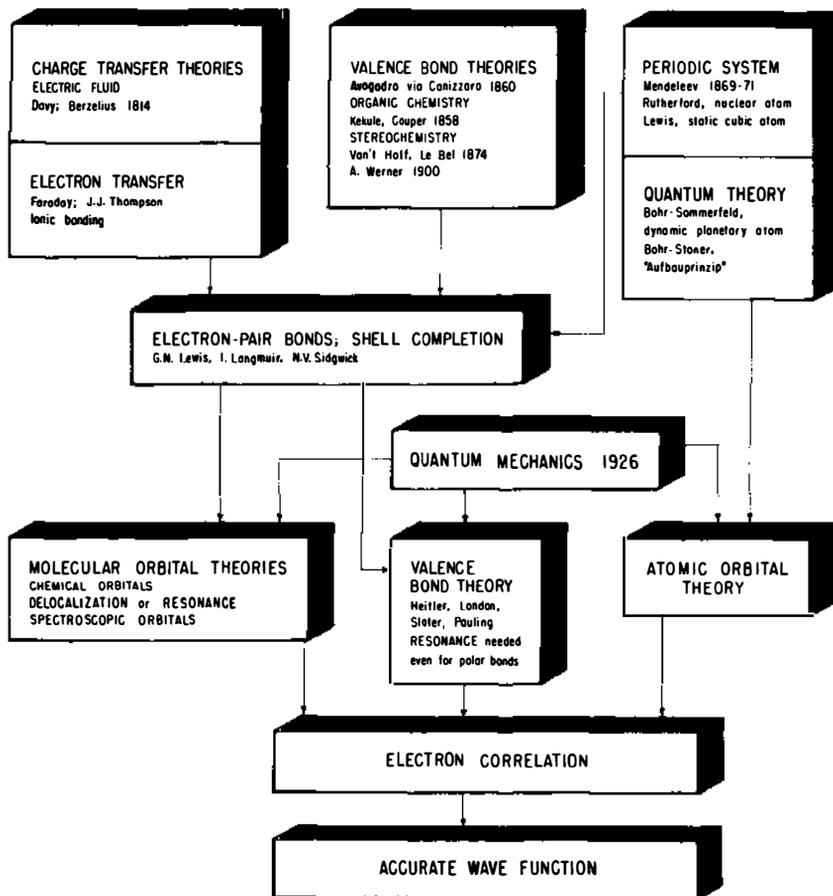


Figure 1 Survey of early history of chemical bonding leading up to present quantum-mechanical era.

In molecular orbital theory, the fact that most molecules contain electron *pair* bonds is explained as a consequence of the Pauli principle, according to which in the stable state of any system, any given orbital can be occupied by two (and only two) electrons with opposite spins. This fact greatly favors the stability of even-electron as compared with odd-electron molecules. Besides bonding electron pairs and inner-shell electrons in pairs (or multiples of pairs because of degeneracy), many molecules contain more or less atomlike "lone pairs."

The valence-bond method is limited in that it deals only with electron pair bonds. It is limited also in that it does not take care of heteropolar or ionic bonding. For this, it must be supplemented by adding an ionic term to the wave function. The

molecular orbital (MO) method, on the other hand, while suitable for molecules in their stable equilibrium form, in most cases does not permit following them correctly out to dissociation, so that its calculated dissociation energies are usually very poor. Both methods can be improved by variational adjustment of parameters corresponding to effective nuclear charges and by other adjustments. But something more (electron correlation) is necessary that goes beyond a combination of the advantages of the two methods. This matter is taken up in a later section.

In the first few years after the advent of quantum mechanics, many of the world's leading theoretical physicists engaged in calculations on molecules (for review see 6). Great progress was made in qualitative and semiempirical understanding. The greatest quantitative success of the theory was attained in 1933 by James & Coolidge (7) in their computations on the hydrogen molecule. They used a 13-term function containing the interelectronic distance explicitly to obtain a dissociation energy within experimental error of the empirical value. But except on the simplest systems, the computations, mostly by the valence-bond approach, were complicated and laborious without yielding more than very approximate results. Typically, the far-from-negligible overlap integral was neglected. Frustrated and repelled, many of the theorists turned to other problems.

There occurred a qualitative and semiempirical period (1931–1935) in which I used the LCAO method to develop MO electron configurations for the prototypes of important classes of molecules (8). Meanwhile (1931), Hückel introduced his semiempirical theory for  $\pi$ -electron systems (9), which set in motion a wealth of studies and calculations by Lennard-Jones, Coulson, Longuet-Higgins, Dewar, and others.

Until about 1950 it appeared that we must be content for quantitative results with rather rough semiempirical computations done on old-fashioned desk machines. Before long, however, this bottleneck began to be broken with the development of electronic digital computers. A second major bottleneck was that of the evaluation and numerical computation of certain integrals representing the energies of repulsion between electrons in different orbitals. In 1951–1956 this problem was solved through the effort of groups led by Kotani in Japan, Boys in Cambridge, Coulson in Oxford, Löwdin in Uppsala, Slater at MIT, and Roothaan in Chicago. Soon the first *ab initio* computations of the modern type were under way, at first with desk machines but before long with digital computers.<sup>1</sup> The pioneering work in this field was that of Boys (11). Meantime in 1950 Roothaan published his classic paper (12) on the use of the LCAO method in self-consistent field computations.

From 1955 on, although semiempirical methods are still extensively used, especially for larger molecules, the use of *ab initio* methods has increased rapidly and even explosively, especially from 1970. These are reviewed by Schaefer (13, 128).

### *The Role of Spectroscopy*

While ionization processes played a part, our initial understanding of the electronic structure of atoms resulted mainly from an analysis of the data furnished by atomic

<sup>1</sup> For a survey of the outlook in 1958, see Reference 10.

spectroscopy. This study contributed largely to the development of the old quantum theory and its successor, quantum mechanics. It is worth noting here that the role of electronic spin in spectroscopy was not understood until about the same time that quantum mechanics appeared.

Molecular spectroscopy can be divided into two parts: (a) nuclear, which deals with vibrations and rotations, and (b) electronic. The main outlines of vibrational and rotational spectroscopy were intelligible in 1925 in terms of the old quantum theory. Some rough analogies of molecular-to-atomic electronic spectra were also found (5). But a real understanding of molecular electronic structure and spectra, and of the details of vibrational and rotational motions and their interaction with electronic motions, became possible only by the application of quantum mechanical theory.

Throughout this century, spectroscopy in increasingly varied forms has continued to supply empirical information to give flesh to the theory. Empirical potential curves (of ground and excited states) have been constructed from spectroscopic data of various kinds.

### *The Born-Oppenheimer Separation and Potential Surfaces*

Let us turn now to quantum mechanics in the form of the Schrödinger wave equation. After dealing briefly with the element of time, the first step in the solution for a molecule is to separate, as far as possible, the nuclear from the electronic motions. Through this now familiar process (Born & Oppenheimer 14), the electronic part is expressible in terms of a multidimensional potential surface (or curve in the diatomic case) that forms a locus for the vibrations and rotations of the molecule. This surface corresponds to a hypothetical situation in which the nuclei are held fixed, but the electrons are left free to adjust themselves to the demands of their part of the Schrödinger equation. Of greatest relevance, of course, is the portion of the potential surface near the equilibrium configuration of a stable molecule. More remote regions, however, are also relevant if we wish to pursue a molecule out to dissociation, to consider chemical reactions, or to study the effects of high-energy collisions. In principle, the potential surface of a given set of atoms extends all the way from the "united atom," where all the nuclei and electrons have coalesced into a single atom, out in a great variety of directions to various assemblies of separate atoms from which molecules might be composed.

In the diatomic case the separation is, of course, just into two atoms. Here the potential curve leads in many cases to atoms in their ground states, but sometimes one or possibly both atoms are in excited states. For a really complete understanding of the electronic structure of a molecule, one should know the complete surface from the united atom out to all possible combinations of separate atoms. Such a surface would include all the isomers of any molecule. In practice we have as yet attained only the merest beginning of such a program for a few relatively simple molecules. In nearly all cases we have no more than a few fragments of the surface that can be associated with a particular isomer. For diatomic molecules

our information is, of course, more complete, but it is still limited. How do we obtain these surfaces? Slowly, but with increasing speed, through the modern development of computers.

### Terminology

The current diatomic notation  $\sigma, \pi, \delta, \dots {}^1\Sigma, {}^2\Sigma, \dots$  was introduced by Hund in 1928 (15). The notations  $\Sigma_g^+$  and  $\Sigma_u^-$  and so on were introduced a little later (16), although the distinction involved had already been recognized by Wigner & Witmer (17) and by Hund.

In 1933 (18) I adapted orbital and state notation for polyatomic molecules from vibrational state symbols introduced by Placzek for Raman spectra. With minor modifications, this system is currently in use (19, 20). One difficulty in the system is that for certain symmetry species bearing  $B_i$  or  $b_i$  labels with numerical subscripts the choice of subscripts depends on the choice of labels for coordinate axes, which generally is arbitrary. Recommendations for dealing with this difficulty were made in a report (20) that has received some official approval.

In 1932 (21) I proposed the term "orbital" as an abbreviation for *one-electron orbital wave function*; I discussed atomic orbitals and molecular orbitals, meaning *exact* AOs and MOs in terms of the Hartree-Fock self-consistent field theory. The abbreviation symbols MO and AO first appeared in a 1939 paper (22). However, LCAO MOs as rather rough approximations to exact MOs were discussed in 1935 (23). At that time "LCAO" referred to what now in *ab initio* calculations means the use of a *minimal basis set* of AOs.<sup>2</sup> I introduced the term "spinorbital" in 1948 (25).

## DIATOMIC MOLECULES

### Molecular Orbital Theory

To begin with, much can be learned by an examination of our understanding of diatomic molecules (26). Even the simplest molecule,  $\text{H}_2^+$ , is very instructive and leads naturally to the use of MOs. When an  $\text{H}^+$  and a ground state H atom approach each other, the resulting wave function can be expressed in the LCMAO (linear combination of modified atomic orbital<sup>3</sup>) form

$$\phi(1\sigma_g) = \sigma_g 1s = (1s_a + 1s_b)/2^{1/2}(1 + S)^{1/2}. \quad 1.$$

Here  $1\sigma_g$  is the customary symbol used in modern computations for the lowest-energy MO in a homopolar molecule;  $\sigma_g 1s$  is a convenient abbreviation for what follows in Equation 1. The whole wave function here is nothing but an MO.  $S$  is the overlap integral between the  $1s$  AOs on the two nuclei  $a$  and  $b$ . Equation 1 remains accurate at all values of the internuclear distance  $R$ , provided that  $1s$  is interpreted as an MAO. The modifications, varying with  $R$  so as to minimize the

<sup>2</sup> For further discussion, see Reference 24.

<sup>3</sup> See Reference 27.

energy, consist of scaling and suitable polarization, in a manner discussed in some of the early quantum-mechanical papers on  $H_2^+$  and  $H_2$ .

The excited MOs of  $H_2^+$  are of interest mainly for the light that they throw on MOs that are occupied in heavier diatoms. The lowest of these are as follows; for simplicity, the appropriate normalizing factors have been omitted.<sup>4</sup>

$$\begin{aligned}\phi(1\sigma_u) &= \alpha\sigma_u1s + \beta2p\sigma = \alpha(1s_a - 1s_b) + \beta2p\sigma \\ \phi(2\sigma_g) &= \alpha\sigma_g(2s - \lambda2p\sigma) + \beta2s = \alpha[(2s_a - \lambda p\sigma_a) + (2s_b - \lambda2p\sigma_b)] + \beta2s \\ \phi(2\sigma_u) &= \alpha\sigma_u(2s - \lambda2p\sigma) + \beta3p\sigma = \alpha[(2s_a - \lambda2p\sigma_a) - (2s_b - \lambda2p\sigma_b)] + \beta3p\sigma \\ \phi(3\sigma_g) &= \alpha\sigma_g(2p\sigma + \lambda2s) + \beta3d\sigma = \alpha[(2p\sigma_a + \lambda2s_a) + (2p\sigma_b + 2s_b)] + \beta3d\sigma \\ \phi(1\pi_u) &= \pi_u2p + \beta2p\pi = 2p\pi_a + 2p\pi_b + \beta2p\pi \\ \phi(1\pi_g) &= \alpha\pi_g2p + \beta3d\pi = \alpha(2p\pi_a - 2p\pi_b) + \beta3d\pi \\ \phi(3\sigma_u) &= \alpha\sigma_u(2p\sigma + \lambda2s) + \beta4f\sigma = \alpha[(2p\sigma_a + \lambda2s_a) - (2p\sigma_b + \lambda2s_b)] + \beta4f\sigma\end{aligned}$$

Equation(s) 2 are written in a form and in an energy order appropriate to first row molecules, where they represent valence-shell MOs. In the special case of  $H_2^+$ , because of the degeneracy of  $2s$  and  $2p$  in the H atom,  $\lambda = 1$  in all MOs; the energy order, which also varies with  $R$ , is different than that given above (28). The terms in  $\lambda$  represent *hybridization*, which is really an extreme special case of polarization. Instead of writing them explicitly, one *could* omit them and consider them merely as parts of the modification involved in forming MAOs; for example,  $\phi(3\sigma_g)$  could be written as  $\alpha\sigma_g2p\sigma + \beta3d\sigma$ , and the  $\lambda2s$  would be considered as merely a part of the necessary polarization to form a  $2p\sigma$  MAO.

In all cases,  $\alpha \rightarrow 1$  and  $\beta \rightarrow 0$  as the atoms separate ( $R \rightarrow \infty$ ), while in the united atom ( $R = 0$ ),  $\alpha \rightarrow 0$  and  $\beta \rightarrow 1$ . The increased value of the principal quantum number  $n$  in going from the separated atoms to the united atom is called *promotion*;  $1\sigma_g$ ,  $2\sigma_g$ , and  $1\pi_u$  are unpromoted MOs, the rest are promoted MOs. At intermediate  $R$  values, in particular at the equilibrium distance of a stable molecule, there is partial promotion, its extent varying from case to case. As promotion approaches completion (but this happens only in certain excited states) one may speak of Rydbergization, since at small  $R$  the promoted MOs often become Rydberg MOs (29). The scaling in the conversion from AOs to MAOs in Equations 1 and 2 involves *shrinkage* (increased effective nuclear charge) in the case of unpromoted MOs and the opposite in the case of promoted MOs; the scaling regularly increases as  $R$  decreases. Correspondingly, the energy increases or decreases with decreasing  $R$  in the two respective cases. Hence unpromoted MOs tend to be bonding and promoted MOs antibonding.

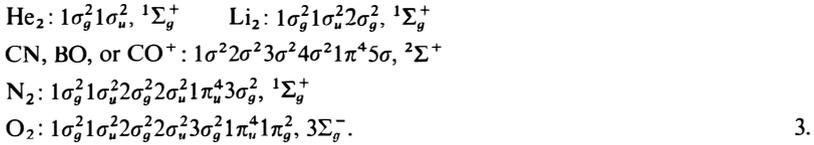
In Hund's earliest paper on molecules inspired by quantum mechanics, absence or presence of promotion was taken as the criterion for bonding or antibonding. However, Lennard-Jones (30) in 1929 pointed out that a better criterion for *bonding* is the occurrence of an *additive* LCAO form as in  $1\sigma_g$ ,  $2\sigma_g$ ,  $3\sigma_g$ , and  $1\pi_u$  in Equations

<sup>4</sup> In Equation(s) 2, it is assumed that the *positive lobe* of any  $2p\sigma$  AO on atom  $b$  is taken to face *toward* the positive lobe of  $2p\sigma$  on atom  $a$ . Some such assumption is necessary to give meaning to the + or - signs in such expressions as  $2s - \lambda2p\sigma$  or  $2p\sigma + \lambda2s$ .

tions 1 and 2. On the other hand, a *subtractive* form as in  $1\sigma_u$ ,  $2\sigma_u$ ,  $3\sigma_u$ , and  $1\pi_g$  may be said to cause *antibonding*.

In 1929 Herzberg (31) proposed that the number of bonds in a molecule like  $N_2$ ,  $O_2$ , or  $F_2$ , or  $NO$ , may be obtained by taking the difference between the number of pairs of bonding and antibonding electrons. The validity of Herzberg's method is illustrated in Table 1.

In summarizing the approximate electronic structure of a molecule, one writes an electron configuration and the overall state symbol. For example, for ground states, we have



In the unstable molecule  $\text{He}_2$ , the antibonding  $1\sigma_u$  electrons overpower the corresponding  $1\sigma_g$  bonding pair. This behavior is typical. To be stable, a molecule must have more bonding than antibonding electrons. In heteropolar molecules, the two atoms contribute unequally to the LCMAO, and we have

$$\phi = a\chi_a + b\chi_b, \tag{4}$$

where  $\chi_a$  and  $\chi_b$  are the MAOs of the two atoms.

**Table 1** Net numbers of bonding electron pairs, and dissociation energies<sup>a</sup>

Molecule	Valence shell	$N_B$	$N_A$	Bonds	$D_0(\text{eV})$
$\text{H}_2^-$	$1\sigma_g$	$\frac{1}{2}$	—	$\frac{1}{2}$	2.6508
$\text{H}_2$	$1\sigma_g^2$	1	—	1	4.4781
$\text{He}_2^+$	$1\sigma_g^2 1\sigma_u$	1	$\frac{1}{2}$	$\frac{1}{2}$	2.365
$\text{He}_2$	$1\sigma_g^2 1\sigma_u^2$	1	1	0	0.00090
$\text{Li}_2$	$2\sigma_g^2$	1	—	1	1.05
$\text{C}_2$	$2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	3	1	2	6.21
$\text{N}_2^-$	$2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g$	$3\frac{1}{2}$	1	$2\frac{1}{2}$	8.713
$\text{CO}^+$	$3\sigma^2 4\sigma^2 1\pi^4 5\sigma$	$3\frac{1}{2}$	1	$2\frac{1}{2}$	8.34
CN	$3\sigma^2 4\sigma^2 1\pi^4 5\sigma$	$3\frac{1}{2}$	1	$2\frac{1}{2}$	7.8
$\text{N}_2$	$2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$	4	1	3	9.759
CO	$3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$	4	1	3	11.09
$\text{O}_2^+$	$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g$	4	$1\frac{1}{2}$	$2\frac{1}{2}$	6.663
NO	$3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi$	4	$1\frac{1}{2}$	$2\frac{1}{2}$	6.497
$\text{O}_2$	$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$	4	2	2	5.116
$\text{F}_2$	$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^4$	4	3	1	1.602

<sup>a</sup>  $N_B$  and  $N_A$  are the respective numbers of bonding and antibonding electron pairs.  $D_0$  is the dissociation energy in electron volts.

Conceptually, the structure of MOs in terms of MAOs is very simple. Originally, one spoke of LCAO MOs implying the use of free-atom AOs, but with MAOs one can attain much better, in fact close to the best possible, solutions of the SCF (self-consistent field) or Hartree-Fock-Roothaan approximation to the molecular electronic structure. In practical computations, however, each AO and MAO is further broken up into a number of bits called STFs (Slater-type functions). The process is now familiar and need not be further described here.

To obtain an accurate wave function, it is necessary to go beyond the SCF approximation, by introducing *electron correlation*. The most usual method is by *configuration mixing* (CM), commonly called configuration interaction. Thus for an accurate MO wave function for  $H_2$ , one has

$$\Psi = c_1(1\sigma_g)^2 - c_2(1\sigma_u)^2 - c_3(1\pi_u)^2 - c_4(2\sigma_g)^2 \cdots, \quad {}^1\Sigma_g^+, \quad 5.$$

where  $(1\sigma_g)^2 = 1\sigma_g(1)1\sigma_g(2)S_{12}$ , with  $S_{12} = 2^{-1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ . In the molecule at equilibrium,  $c_1(1\sigma_g)^2$  is the major term, and the others are progressively smaller.<sup>5</sup> Comparison with HL (Heitler-London) theory can be made by writing out  $1\sigma_g$  and  $1\sigma_u$  in accordance with Equations 1 and 2 but omitting the  $\beta 2p\sigma$  component in  $1\sigma_u$  and omitting the further terms in Equation 5. The result is

$$\Psi = d_1[1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)] \\ + d_2[1s_a(1)1s_a(2) + 1s_b(1)1s_b(2)], \quad 6.$$

where  $d_1 = \frac{1}{2}c_1/(1 + S) + \frac{1}{2}c_2/(1 - S)$ ;  $d_2 = \frac{1}{2}c_1/(1 + S) - \frac{1}{2}c_2/(1 - S)$ . On dissociation ( $R = \infty$ ),  $c_1 = c_2$  and  $S = 0$ , hence  $d_2 = 0$ , leaving an expression that is identical with the HL wave function (see next section). One sees that  $\Psi$  of Equation 6 consists of a HL plus an ion-pair term, the adjustment of whose coefficients provides the accurate wave function except for further relatively small terms including those in Equation 5. These are of some importance at intermediate  $R$  values but vanish on dissociation.

For molecules with more than two electrons, CM can be approximated by forming a linear combination of terms each corresponding to a particular electron configuration. In general, however, there are many configurations in which the electrons are no longer all in pairs as in Equation 5 (6). For each configuration MOs and spins are usually combined into one or more Slater determinants in a familiar way (12).

### Valence-Bond Theory

The HL wave function (3) for the ground state of  $H_2$  is

$$\Psi = (1s_a \cdot 1s_b)S_{12} = \{[1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)]/2^{1/2}(1 + S^2)^{1/2}\}S_{12} \quad 7.$$

Here  $1s_a \cdot 1s_b$  is a convenient abbreviation to indicate a *normalized* form  $u(1)v(2) + v(1)u(2)$ . For accuracy at  $R < \infty$ ,  $1s$  should be taken as an MAO.

Coulson & Fischer (32) proposed a more general expression that is a compromise between the simple uncorrelated MO and VB expressions and that serves to im-

<sup>5</sup> The relatively simple form of Equation 5 is valid only if "natural" MOs are used.

prove very considerably on both:

$$\Psi = (1s_a + \lambda 1s_b) \cdot (1s_b + \lambda 1s_a) S_{12}. \quad 8.$$

For  $\lambda = 0$ , Equation 7 is reproduced; for  $\lambda = 1$ , the MO expression  $1\sigma_g^2$  (Equation 6 with  $d_1 = d_2$ ) is obtained. In general,  $\lambda$  is to be determined as a function of  $R$  so as to minimize the energy. By a suitable choice of  $\lambda$ , Equation 8 can be put into the same form as Equation 6.

Equation 8 can be further generalized for the heteropolar case (cf Equation 4):

$$\Psi = (\chi_a + \lambda \chi_b) \cdot (\chi_b + \mu \chi_a) S_{12}. \quad 9.$$

Here, the advantage of the MO method in dealing with the heteropolar case is absorbed into a still more general formulation (33). This formulation goes part way, but not all the way, toward providing electron correlation.

Goddard has made many computations using a generalized valence-bond theory (GVB) somewhat in the philosophy of Coulson & Fischer, plus additional configuration mixing (see 129).

### *Ionization Potentials, Bonding, SCF Orbital Energies, and Photoelectron Spectroscopy*

How do we decide that an MO is bonding, antibonding, or nonbonding? The usual empirical criterion is to see whether the dissociation energy  $D$  respectively decreases, increases, or remains unchanged on removing an electron from the given MO. An alternative criterion is to see if  $R_e$  increases, decreases, or remains unchanged; *usually* the two criteria give the same answer.

Intrinsically related to the  $D$  criterion is an ionization potential ( $I$ ) criterion. As can be seen from a simple diagram of potential curves for a molecule AB and its ion  $AB^+$ ,

$$I_M - (I_A \text{ or } I_B) = D - D^+, \quad 10.$$

where  $I_M$  and  $I_A$  or  $I_B$  are the molecular and corresponding atomic ionization potentials. Equation 10 is unambiguous for homopolar molecules but can be used for moderately heteropolar molecules by taking the mean of  $I_A$  and  $I_B$  or, more accurately, a mean weighted in favor of the more electronegative atom. Valence-state  $I$ s should be used (see section on bond energies and electronegativity), and in some cases (e.g. MgH, MgO)  $D$ s for dissociation to an excited state of AB are required. In spite of these complications (34a, b), Equation 10 is a useful empirical guide, especially for homopolar molecules.

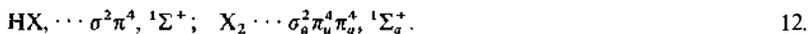
Theoretically, independent of the limitations of Equation 10, there is an approximate agreement between the molecular  $I$ s and the negatives of the orbital energies  $\epsilon$  of SCF MO theory; this is an application of Koopmans' theorem (35). This theorem would be exact if (a) the SCF approximation were exact, and (b) all the other orbitals were unchanged when an electron is removed from one. Actually,

$$I = -\epsilon + (CE - CE^+) - RE^+, \quad 11.$$

where CE is correlation energy and  $RE^+$  is relaxation or reorganization energy of the ion as a result of ionization. The term  $(CE - CE^+)$  is normally positive, while  $RE^+$  (taken positive) represents a decrease of energy. Thus the two terms supplementing  $-\varepsilon$  in Equation 11 usually tend to cancel, and in any event the relation  $I = -\varepsilon$  for any MO is usually correct to a fairly good approximation.

What may be described as an empirical result of ab initio SCF calculations is that for MOs of additive LCAO form  $(\chi_A + \chi_B)$ ,  $-\varepsilon$  is always larger for the MO than for the corresponding AO, whereas for subtractive LCAO MOs  $(\chi_a - \chi_b)$ ,  $-\varepsilon$  is smaller for the MO than for the AO. By Equation 11,  $I_{\text{mol}}$  is, then, usually larger than  $I_{\text{at}}$  for the additive MOs, which then are bonding, and smaller for the subtractive MOs, which are antibonding. A theoretical explanation in terms of the virial theorem for these empiricotheoretical relations is given in a later section.

The upshot of the foregoing discussion of  $D$ ,  $I$ , and  $\varepsilon$  values, and Equations 10 and 11, is that we may expect  $I_{\text{mol}}$  to be greater than  $I_{\text{at}}$  for bonding, less for antibonding, and about the same for nonbonding MOs. These relations are quite generally found to be empirically verified. Table 2 gives some examples for halogen and hydrogen halide molecules. The electron configurations are:



Here in HX,  $\sigma$  is a bonding MO of approximate LCAO form  $a(1s_{\text{H}}) + b(np\sigma_{\text{X}})$ , whereas in  $\text{X}_2$ ,  $\sigma_g$  is bonding of the form  $(np\sigma_a + np\sigma_b)$ , while  $\pi_u$  and  $\pi_g$  are, respectively, bonding and antibonding of LCAO forms  $(np\pi_a + np\pi_b)$  and  $(np\pi_a - np\pi_b)$ . Table 2 shows good agreement with our expectations. In the case of the nonbonding  $\pi$  MO of HF, the fact that  $I_{\text{mol}}$  is less than  $I_{\text{at}}$  can be understood as a result of strong  $\text{H}^+\text{F}^-$  polarity that decreases  $I$  because it is essentially located on the F atom, which is now partially negative. A similar effect seems not to be observed in the other HX, but perhaps it would be if more care were taken to use valence-state  $I$ s.

Until the advent of X-ray and optical photoelectron spectroscopy (PES) in 1962, relatively little was known experimentally other than minimum ionization potentials. Strictly speaking, AOs and MOs are nothing but convenient theoretical building blocks, yet photoelectron spectroscopy has given them a new empirical reality by connecting them fully with measurable ionization potentials. The progress of the subject was surveyed in the 1975 volume of this series (36).

Relatively recently, increasing attention has been given to the fact that, in addition to the main PES transitions that correspond to ionization from an individual MO, there are numerous weaker satellite transitions. These fall into two groups: (a) shake-up transitions, in which the primary ionization is supplemented by excitation of an additional electron or electrons; (b) correlation transitions, which proceed from or into states that correspond to CM (configuration mixing) terms (cf Equation 5) in the molecule and especially its positive ion (37a, b, for theory see 38a, for application to HF see 38b). In general, the use of X-ray PES (ESCA) favors shake-up peaks. The simple identification of PES transitions with individual MO excitation has been put in question in the case of *inner* valence shell MOs, e.g.  $2\sigma_g$  of  $\text{N}_2$ , by the conclusion (for  $\text{N}_2$  and CO see 37b) that the somewhat broad peak observed there is a composite due to superposition of several peaks involving CM.

**Table 2** Ionization potentials of halogens, hydrogen halides, and their atoms<sup>a</sup>

Molecule	Ion state	Ionization Potential (eV) <sup>b</sup>		Atomic <i>I</i> (eV)
		adiabatic	vertical	
HF	<sup>2</sup> Π	16.06	—	17.42
	<sup>2</sup> Σ <sup>+</sup>	18.6	20.0	13.61, 17.42
HCl	<sup>2</sup> Π	12.75	—	13.01
	<sup>2</sup> Σ <sup>+</sup>	16.25	—	13.61, 13.01
HBr	<sup>2</sup> Π	11.69	—	11.84
	<sup>2</sup> Σ <sup>+</sup>	15.30	—	13.61, 11.84
HI	<sup>2</sup> Π	10.41	—	10.45
	<sup>2</sup> Σ <sup>+</sup>	13.24	14.3	13.61, 10.45
F <sub>2</sub>	<sup>2</sup> Π <sub>g</sub>	15.70	15.83	17.42
	<sup>2</sup> Π <sub>u</sub>	18.39	18.80	17.42
Cl <sub>2</sub>	<sup>2</sup> Π <sub>g</sub>	11.51	11.59	13.01
	<sup>2</sup> Π <sub>u</sub>	13.96	14.40	13.01
	<sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	15.72	16.08	13.01
Br <sub>2</sub>	<sup>2</sup> Π <sub>g</sub>	10.51	10.56	11.84
	<sup>2</sup> Π <sub>u</sub>	12.41	12.77	11.84
	<sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	14.28	14.56	11.84
I <sub>2</sub>	<sup>2</sup> Π <sub>g</sub>	9.22	9.35	10.45
	<sup>2</sup> Π <sub>u</sub>	10.74	11.01	10.45
	<sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	12.66	12.95	10.45

<sup>a</sup> For the <sup>2</sup>Π states, the <sup>2</sup>Π<sub>3/2</sub> *I*'s are given. For the atoms, the minimum *I*'s (from <sup>2</sup>P<sub>3/2</sub> to <sup>3</sup>P<sub>2</sub> for the halogens) are given. A more careful comparison would use valence-state *I*'s with suitable mean values where multiplet components are involved. The data are from Reference 130.

<sup>b</sup> For HX, the <sup>2</sup>Π and <sup>2</sup>Σ<sup>+</sup> states correspond respectively to removal of a π nonbonding or a σ bonding electron. For X<sub>2</sub>, the <sup>2</sup>Π<sub>g</sub>, <sup>2</sup>Π<sub>u</sub>, and <sup>2</sup>Σ<sub>g</sub><sup>+</sup> states correspond respectively to removal of a π<sub>g</sub> antibonding, a π<sub>u</sub> bonding, and a σ<sub>g</sub> bonding electron. In each case, it is the *vertical I*'s that are appropriate.

As an example of a satellite peak that is simply explained by CM, consider the ground state of N<sub>2</sub><sup>+</sup>, with the dominant configuration  $\cdots 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g, 2\Sigma_g^+$ , which contains a substantial admixture of  $\cdots 2\sigma_g^2 2\sigma_u 1\pi_u^3 3\sigma_g^2 1\pi_g, 2\Sigma_g^+$ . Here, in addition to the main peak, the PES contains a satellite peak of considerable intensity that can be identified with two transitions that proceed to the second of the two configurations just mentioned.

### Correlation Diagrams

A correlation diagram shows how the orbital energies  $\epsilon$  of MOs change with internuclear distance. Simple diagrams were introduced by Hund in 1927. I presented qualitative and semiempirical diagrams for first row molecules in 1932 (39). In

1972 I published the result of moderately accurate SCF MO calculations on the occupied MOs in the ground state of  $N_2$  from the united atom ( $R = 0$ ) to  $R_e$  (40). Similar calculations on  $N_2$  and CO have been made (41), also some less accurate calculations on other atom pairs.

These correlation diagrams if extended to  $R = \infty$  would have to assume that a single electron configuration gives an adequate approximation to the wave function for all  $R$  values. In general this is not true, and one can properly speak only of a pseudocorrelation except in the case of inner electrons (34b). However, the correlation diagram for all MOs should usually be valid from  $R = 0$  to about  $1.5 R_e$ , where CM is becoming fairly strong.

### Population Analysis and Charge Density Distributions

To obtain the charge distribution corresponding to a normalized MO  $\phi$ , one takes the square (or  $\phi\phi^*$  if the MO is complex). If the MO is occupied by  $N$  electrons (most often  $N = 2$ ), this population is, according to Equation 4,

$$N\phi^2 = Na^2\chi_a^2 + 2NabS(\chi_a\chi_b/S) + N_b^2\chi_b^2. \quad 10.$$

Each of the three terms in Equation 8 is a normalized distribution. On integrating over all space, one obtains

$$N = Na^2 + 2NabS + Nb^2. \quad 11.$$

The first and last terms may be called the *net populations* on  $a$  and  $b$ , and the middle term the *overlap population*. If one divides the overlap population equally between  $a$  and  $b$ , one obtains *gross populations*

$$N_a = N(a^2 + abS) \quad \text{and} \quad N_b = N(b^2 + abS) \quad 12.$$

on  $a$  and  $b$ . While open to objections, this procedure gives definite results and satisfies a natural desire to distribute the charge between  $a$  and  $b$  (42).

In Equations 4 and 10,  $\chi_a$  and  $\chi_b$  are MAOs. Or each MAO may be written out as an LCMAO of the form  $\sum_i c_i\chi_i$ , where  $\chi_i$  is a suitably scaled AO. In practice, each  $\chi_i$  is broken up into a linear combination of STFs (Slater-type functions). Equations 11 and 12 then each break up into a number of terms associated with STFs of the two atoms and with overlaps of these. One obtains gross populations for each atom corresponding to each type of AO or STF.

In this way, one can write a summary of (M) AO populations in electron configuration form; for example (42) for CO, considering only  $s, p$  hybridization,

$$1s_C^{2.00}2s_C^{1.40}2p\sigma_C^{1.40}2p\pi_C^{1.02}1s_O^{2.00}2s_O^{1.86}2p\sigma_O^{1.25}2p\pi_O^{2.98}. \quad 13.$$

If hybridization is treated as merely a special case of modification by polarization, Equation 13 might be replaced by

$$1s_C^2 2s_C^2 2p\sigma_C 2p\pi_C 1s_O^2 2s_O^2 2p\sigma_O 2p\pi_O^3. \quad 14.$$

where the symbols now represent strongly modified AOs.

In a molecule with many electrons, one has merely to sum over all the electrons to get overlap and gross populations for the molecule as a whole, or for its  $s$ ,  $p$ ,  $d$ , . . . or  $\sigma$ ,  $\pi$ , . . . gross populations or their individual overlap populations. From the gross populations, atomic charges are readily obtained. When electron correlation is taken into account in terms of a generalization of Equation 5, it is necessary to determine the populations for each individual configuration and to add these with multiplying coefficients equal to the squares of the coefficients (cf the  $c_i$ 's in Equation 5) in the mixed configuration (43).

As already mentioned, the procedure for obtaining gross populations embodied in Equation(s) 12 is open to objections (26). This can be seen from the fact that Equation 12 occasionally gives (usually slightly, but sometimes significantly) negative values of  $N_a$  or  $N_b$ , or sometimes values  $> N$ . Such answers are obviously absurd. The difficulties are greatest for antibonding MOs and heteropolar molecules (26). For most stable molecules, however, the method of population analysis outlined above probably makes good sense qualitatively and perhaps semiquantitatively. But in spite of many attempts, no satisfactory solution of the problem of finding the "true" charges on atoms in a molecule has been found, and it is very questionable whether there is any such solution. An MAO viewpoint may be helpful (44).

Instead of seeking to break down a molecular electron population into overlap and gross populations, a very instructive alternative is to compute the charge density distribution  $N\phi^2$  in each MO, and its sum  $\sum_i N_i\phi_i^2$  for the molecule as a whole. The latter can then be compared with the sum of the charge density distributions of the atoms in the molecule or with the distribution for the united atom (difference charge densities). Many density and difference density contour maps obtained from ab initio SCF computations have now been published (see e.g. Reference 26), and are worthy of careful study. Figure 2 is a charge density map

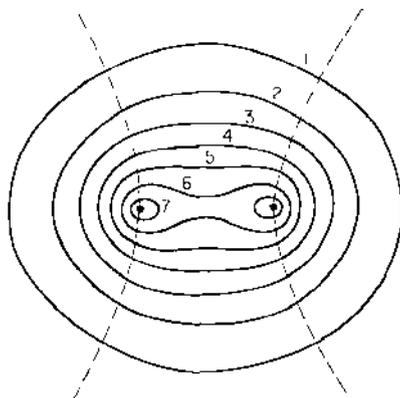


Figure 2 Contour map for the charge density distribution in  $H_2^+$ . The quasi-hyperbolic dashed lines divide the density distribution between an inner "binding" region and two outer "antibonding" regions (see section on bonding and binding).

for the electron in  $\text{H}_2^+$ . Reproduction and discussion of more of these would be appropriate here, but space does not permit.

### *Bond Energies and Electronegativity*

Pauling has given extensive tables of bond energies for atom pairs in polyatomic as well as diatomic molecules (4). He did this by suitably breaking up the total dissociation energy of the molecule into energies for dissociating atom pairs. Pauling noticed that for a heteropolar atom pair (A-B) the bond energy is always greater than the average (or in general, greater than the geometric mean) of the bond energies for A-A and B-B. From the differences, he set up his well-known scale of relative electronegativities:

$$\Delta = D(\text{A-B}) - \frac{1}{2}[D(\text{A-A}) + D(\text{B-B})]$$

or, better,

$$\Delta' = D(\text{A-B}) - [D(\text{A-A}) + D(\text{B-B})]^{1/2} = 30(x_{\text{A}} - x_{\text{B}})^2 \quad 15.$$

where the  $x$ s are the Pauling electronegativities if  $\Delta$  and  $\Delta'$  are in kcal mole<sup>-1</sup>.

Later, I introduced my scale of absolute electronegativities, where for any atom  $A$ ,

$$M_A = \frac{1}{2}(I_A + E_A), \quad 16.$$

with  $I_A$  and  $E_A$ , respectively, a *valence state* ionization potential or electron affinity (45). For meaningful results, valence state quantities, first used by Van Vleck (46), are necessary. The quantities  $M_A - M_B$  are approximately proportional to Pauling's  $x_A - x_B$ . This proportionality made it possible for Pauling to assign absolute values for each atom on his scale.<sup>6</sup>

Several more refined treatments have since been published. A paper by Klopman (51) includes a review and references.

### *Potential Curves*

For most diatomic molecules, the potential curves  $U(R)$  out to dissociation can be fitted rather well by the well-known Morse function proposed in 1929 (47):

$$U(R - R_e) = D_e[1 - \exp(-\beta(R - R_e))]^2, \quad 17.$$

where  $\beta$  can be calculated from  $D_e$  and the spectroscopic constant  $\omega_e$ . Much more accurately, when more spectroscopic data are available, the left and right branches (relative to  $R_e$ ) of the potential curve can be plotted up to the limit of the data by means of the familiar Rydberg-Klein-Rees method developed in 1932 and 1947 (48).

For most molecules, spectroscopic data extending out to dissociation are lacking. Birge-Sponer extrapolations of vibrational data out to dissociation, first used in 1926 (49), are then helpful but not very reliable. To fill the gap, ab initio calcula-

<sup>6</sup> Pauling deviates somewhat from this proportionality in his choice for the H atom. One may note also that in comparing the two scales, Pauling has set  $E_A$  equal to zero for the alkali atoms, which is appreciably untrue.

tions including electron correlations have promise, although not many are yet available, and the highest accuracy is not obtained (26). For an example, see Guberman's recent paper on  $O_2$  (50).

In general, the species of atomic states into which a molecule in a given species of state can dissociate are restricted by the correlation rules of Wigner & Witmer (17), well known since 1928.

### *The Virial and Chemical Bonding; Scaling*

The individual behavior of the potential and kinetic energies when atoms form a bond is of interest for an understanding of the physical nature of chemical bonding. For stable states, the potential curve  $U(R)$  has a minimum at  $R_e$ . In general

$$U(R) = [T_{e1}(R) + V(R)] - [T(\infty) + V(\infty)] = T_{e1}(R) + V(R) - E(\infty), \quad 18.$$

where  $V$  is the total potential energy, but  $T_{e1}$  is only the electronic part of the kinetic energy  $T$ . The  $U(R)$  curve is an effective potential for the motions of the nuclei, whose kinetic energy is excluded from  $U(R)$ .

In quantum, as in classical, mechanics the virial theorem holds:

$$T = -\frac{1}{2} \sum_i \overline{q_i \dot{F}_i}, \quad \text{where } F_i = -\frac{1}{2} \partial V / \partial q_i. \quad 19.$$

In an isolated atom or molecule (inverse-square electrostatic forces), Equation 19 yields the Coulombic virial theorem

$$\bar{T} = -\frac{1}{2} V = -E. \quad 20.$$

Equation 20 cannot be applied to  $U(R)$ , except at  $R_e$ , because otherwise  $U(R)$  requires that hypothetical external forces must be applied to hold the nuclei fixed, and these must be included in the  $F_i$  of Equation 19. When these are considered, one obtains (51)

$$\begin{aligned} T_{e1}(R) - T(\infty) &= -U(R) - R(dV/dR), \\ V(R) - V(\infty) &= 2U(R) + R(dV/dR). \end{aligned} \quad 21.$$

In 1933 Slater (52) discussed the application of Equations 21 to typical stable  $U(R)$  curves. For  $R$  values that are not too small, these can be approximated in the Lennard-Jones form

$$U(R) \approx -aR^{-n} + bR^{-m}, \quad m > n. \quad 22.$$

Using Equations 21, one obtains

$$\begin{aligned} T_{e1} - T(\infty) &= -(n-1)aR^{-n} + (m-1)bR^{-m}, \\ V - V(\infty) &= (n-2)aR^{-n} - (m-2)bR^{-m}. \end{aligned} \quad 23.$$

As two atoms approach at large  $R$ , the first term on the right predominates, hence  $T_{e1}$  falls and  $V$  rises with decreasing  $R$ . At smaller distances, long before  $R_e$  is reached, the second term predominates, and these relations are reversed.

Ruedenberg (53) has discussed in detail the foregoing behavior of  $T_{e1}(R)$  and  $V(R)$  for the ground states of  $H_2^+$  and  $H_2$ . He gives computed curves for  $H_2^+$ , here

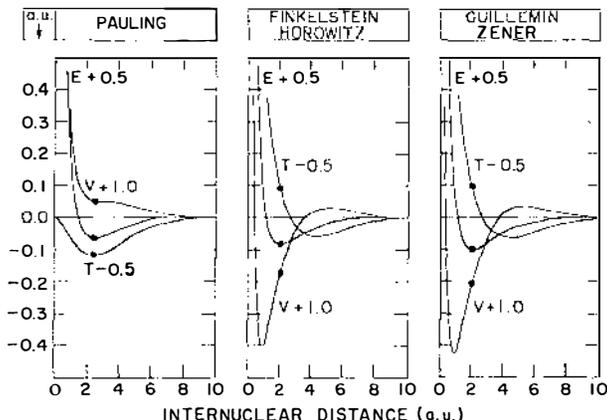


Figure 3 Potential energy and electron kinetic energy components of the ground state  $U(R)$  curve of  $H_2^+$  (from Reference 131).

reproduced as Figure 3, for three successfully improved approximations to  $\phi(1\sigma_g)$  of Equation 1. It is simplest to substitute the AO of the free H atom for  $1s$  in Equation 1 ( $\zeta = 1$  in Equation 24), as was done by Pauling (1928):

$$1s = (\zeta^3/\pi)^{1/2} \exp - (\zeta r). \quad 24.$$

A much improved MAO is obtained by scaling ( $\zeta > 1$ , varying with  $R$ , to the value 1.2387 at  $R_e$ ): this was introduced by Finkelstein and Horowitz (FH) in 1928. Further improvements can be made in the  $1s$  MAO by polarization (Guillemin and Zener 1929) or, still better, by an LCMAO of the form  $\sum_i c_i \chi_i$ .

As Ruedenberg has emphasized, however, scaling is most crucial. Inspection of Figure 3 shows that only for a variable  $\zeta(R) > 1$  in Equation 24 can the requirements of the virial theorem, e.g. Equation 20 at  $R_e$ , be satisfied. The FH curves in Figure 3 are adequate for this purpose, even though quantitatively they can be improved by polarization. As Ruedenberg has emphasized for  $H_2^+$  and  $H_2$ , the shrinkage of the free-atom AOs corresponding to  $\zeta > 1$  in Equation 14 is a necessary virial theorem requirement associated with chemical bonding. This shrinkage of the free-atom AOs necessarily involves increased  $T_e$  and decreased  $V$  near  $R_e$ , even though at large  $R$  the opposite behavior is equally characteristic.<sup>7</sup>

It seems fairly certain that the same characteristics are typical for the bonding electrons in chemical bonds in general. In these respects, then, the bonding in  $H_2^+$  is a prototype for chemical binding in general. The fact that shrinkage (increased  $\zeta$  compared with free-atom AOs) is characteristic of bonding MOs is a fact well known both empirically from ionization potentials (cf Table 2) and theoretically from SCF computations (see section on ionization potentials). Equally characteristic

<sup>7</sup> For further details see Reference 26.

is swelling or expansion (decreased  $\zeta$ ) for antibonding MOs, as shown both empirically and theoretically.

Let us return to the virial theorem. For a repulsive  $U(R)$  curve, e.g. in the interaction of two He atoms, Equations 22 and 23 are still valid, but the region where  $T_{\text{el}}$  decreases and  $V$  increases is confined to large  $R$  values mostly outside the van der Waals minimum, with  $T_{\text{el}} - T_{\infty}$  and  $V - V_{\infty}$  small. At smaller  $R$ ,  $T_{\text{el}}$  rises strongly and  $V$  falls.

For an ion-pair curve one has  $U(R) \approx -e^2/R$ ,  $T_{\text{el}} = 0$ ,  $V = -e^2/R$ . However, in actual ion-pair molecules  $U(R)$  is an atom-pair curve for larger  $R$  values until this curve crosses the ion-pair curve. Hence as two atoms (e.g. Na + Cl) approach to form an ionic molecule,  $T_{\text{el}}$  falls at first and  $V$  rises just as for a stable covalent state.

The virial theorem deals with the average or overall total kinetic energy. The local kinetic energy density can also be evaluated. Interesting details are given by Bader & Preston (54).

### Bonding and Binding

When two atoms are far apart, there is no net force between them. If the atoms approach each other the charge distributions of the electrons are distorted so as to give a net force of attraction or repulsion. According to the Hellmann-Feynman theorem (55), the attractive force of the electrons on a nucleus of charge  $Z_A e$  in a molecule AB is, in atomic units,

$$F_A = Z_A Z_B / R^2 - Z_A \int [\rho(r_A, \theta_A) \cos \theta_A / r_A^2] dV. \quad 25.$$

Here  $\rho$  is the electronic charge density at a location  $r_A, \theta_A$  measured from nucleus  $A$ , with  $\theta_A = 0$  on the axis in the direction of  $B$ . A similar expression holds for  $F_B$ . Further,  $F_A = F_B = -dU/dr$ , if repulsive forces are taken as positive. At  $R_E$ , we have  $F_A = F_B = 0$ .

As Berlin has pointed out (56), the electronic charge distribution in a molecule can be divided into *binding regions*, where the electronic forces pull the nuclei together, and *antibinding regions*, where they push them apart. At  $R_e$ , the effects of these regions balance exactly. The boundaries of the two regions are shown by dashed lines in Figure 2 for  $\text{H}_2^+$ . For heteropolar molecules, the boundaries are of course less symmetrically disposed.

In a many-electron molecule, the net Hellmann-Feynman forces can be broken up into contributions from the individual MOs and, still further, into contributions from the partial (net and overlap) populations in each MO. These matters have been discussed in detail by Bader et al (57) and are reviewed in Reference 26.

### Ab Initio Computations

In a few early calculations integrals were estimated or neglected, or other assumptions were made. Then, in 1956 C. W. Scherr published the first, accurate, all-electron, ab initio (purely theoretical), molecular computation on  $\text{N}_2$ , under the sponsorship of C. J. Roothaan (58). This was an SCF LCAO computation that

used a minimal basis set [one each of the AOs ( $1s$ ,  $2s$ ,  $2p\sigma$ ,  $2p\pi$ )].<sup>8</sup> Shortly thereafter, Sahni published an all-electron calculation on BH, begun earlier at Cambridge in the laboratory of S. F. Boys (59). The computations were done on desk machines. Before long, electronic digital computations were being published (26). Meantime, S. F. Boys had been using computing machines in atomic, and then molecular, calculations (11, 61).

In 1951 a notable conference was held at Shelter Island, Long Island, New York, in which a number of chemists and physicists participated (62). At that time the problem of the evaluation of interelectronic repulsion integrals was acute. After the conference, our laboratory made good progress with two-electron integrals. Before long, these could be satisfactorily calculated with the aid of computing machines. Subsequent progress is summarized in recent books (13, 26) and in a review by Schaefer (128).

## POLYATOMIC MOLECULES

### *Structures of Prototype Molecules*

From 1928 to 1932, my work focussed upon the MO structures of typical diatomic molecules (34a, 39, 63). Then, during 1932–1935, I turned to a survey of the structures of prototype polyatomic molecules (8):  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}^+$ ,  $\text{NH}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{R}_2\text{O}$ ,  $\text{CX}_4$ ,  $\text{CH}_3\text{X}$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{ClO}_3^-$ ,  $\text{SO}_3$ ,  $\text{BF}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{PtCl}_4^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{MnO}_4^-$ ,  $\text{CH}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{RX}_n$ ,  $\text{CH}_3\text{X}$  (including  $\text{X} = \text{NH}_2$ ,  $\text{OH}$ ),  $\text{H}_2\text{S}$ ,  $\text{PH}_3$ ,  $\text{N}_2\text{H}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2\text{O}$ , aldehydes and ketones,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CS}_2$ ,  $\text{NO}_2^+$ ,  $\text{N}_3^-$ ,  $\text{NCO}^-$ ,  $\text{NCS}^-$ ,  $\text{HgCl}_2$ , etc. Ionization potentials and spectra were used as diagnostic tools in LCAO descriptions of the MO electron configurations of the molecules considered. The discussion of  $\text{C}_2\text{H}_4$  was especially thorough.

In the meantime Pauling (4, 64), Slater (65), and others developed the application of the valence-bond method in qualitative and rough quantitative form (6). Pauling used resonance structures for qualitative and semiquantitative considerations. Slater and Pauling introduced the principle of maximum overlapping of AOs in the formation of a valence bond. I pointed out that the same criterion is applicable to the overlap of the AOs in an LCAO MO (66). The magnitudes of overlap integrals were at first known only qualitatively, until the publication of some tables of computed overlap integrals in connection with a study of overlap integrals and chemical bonding (67).

Somewhat earlier (1930) Hückel had discussed the structure of double-bonded compounds and proceeded to a thorough consideration of benzene and related compounds by both MO and valence-bond methods (68). In other papers he considered naphthalene, diphenyl, and other aromatic and unsaturated compounds, including free radicals (69). He proposed the  $4n + 2$  criterion for aromaticity ( $4n + 2$  is the number of  $\pi$ -electrons) (68).

<sup>8</sup> In 1943, Coulson & Duncanson had computed  $\text{Li}_2$  by the LCAO MO method, rather inaccurately, since they included only  $1s$  and  $2s$  in the basis set ( $2p\sigma$  is also needed) (60). Coulson had earlier discussed  $\text{H}_2$ .

## Semiempirical Methods of Calculation

At first the valence-bond resonance structure method became popular with organic chemists who dealt with aromatic and other  $\pi$ -electron systems (70). Then the HMO (Hückel MO) method, with its solutions of secular equations to obtain the orbital energies  $\epsilon$ , was increasingly adopted (71a, b). In this LCAO MO method, the total  $\pi$ -electron energy was put equal to the sum of the one-electron energies without specific allowance for interactions between electrons. However, a purely empirical choice of two negative parameters roughly took care of the theory's imperfections: the atomic Coulomb integral  $\alpha_A = \int \chi_A \mathcal{H} \chi_A d\tau$  and the resonance integral  $\beta = \int \chi_A \mathcal{H} \chi_B d\tau$ , where  $\mathcal{H}$  is an effective Hamiltonian that includes the effects of the  $\sigma$  electrons, and the  $\chi$ s are AOs. Although the overlap integral  $S = \int \chi_A \chi_B d\tau$  entered into the equations, and can be included specifically, it was generally neglected (71a, b). However, it could be shown (72b, c) that the empirical integral  $\beta$  really corresponds not to  $\int \chi_A \mathcal{H} \chi_B d\tau$ , but to  $\int \chi_A \mathcal{H} \chi_B d\tau - S\alpha$ , a numerically much smaller quantity, so that *in this respect*  $S$  was not being neglected.

Many papers were written about various ramifications of the HMO method, especially by Coulson & Longuet-Higgins (71a, b, 73a, b). An important distinction was the classification of unsaturated hydrocarbons into alternant and nonalternant (74). At first, in the HMO theory all carbon atom  $\alpha$ 's were made equal, and all  $\beta$ 's were made equal regardless of bond multiplicity or length. Later, the variation of  $\beta$  with bond length was taken into account and, also, the effects of charges on the atoms (Wheland's  $\omega$ -technique) (75).

In 1938 Goeppert-Mayer & Sklar (76) discussed the  $\pi$ -electron structure and spectrum of benzene in terms of an antisymmetrized wave function, taking into account electronic interactions. In further discussion going beyond the HMO theory (25), I introduced, in 1949, the simple but rather good approximations

$$\int aa|bb \approx \frac{1}{2}S[J_{aa} + J_{bb}]; \quad \int ab|ab \approx S \int aa|ab, \quad 26.$$

where  $J_{aa} = \int aa|aa$ ,  $\int aa|ab = \int \chi_a(1)\chi_a(2)[e^2/r_{12}]\chi_a(1)\chi_b(2)$ , and so on. In 1953, Pariser & Parr introduced their semiempirical antisymmetrized LCAO MO theory using empirical parameters and the approximation of zero differential overlap. Pople independently introduced a similar theory (77).<sup>9</sup>

The next attempt was to include all the valence electrons in the theory, instead of only  $\pi$ -electrons.<sup>10</sup> In 1965 Pople et al proposed the useful CNDO theory and the more exact NDDO theory (79), followed in 1966 by the improved CNDO/2 theory (80), and in 1967 by the still better INDO theory (81). All these depend on the use of a carefully chosen set of empirical parameters and can be applied to molecules quite generally. Further efforts were made by Dewar et al in 1968 in the MINDO method (82) and in 1974 with the MINDO/3 method (83a). In 1976

<sup>9</sup> I showed (78) that very little more is needed than Equation(s) 26 to justify the approximation of "zero differential overlap."

<sup>10</sup> A brief review and references are given in the introduction to Reference 79.

Dewar & Thiel proposed a further improvement, the MNDO method, a simplification of NDDO, and obtained and tested empirical parameters for H, C, N, and O compounds (84a).

A quite different semiempirical method initiated by Slater in 1965 and extensively developed and applied by Johnson is the SCF- $X\alpha$  scattered wave method (83b). This method is especially adapted to larger systems. It has been used rather extensively.

### *Bond Orders, Bond Lengths, Conjugation, and Hyperconjugation*

In 1939 Coulson (84b) introduced the partial bond order  $p_{rs}^j$  for the  $r$ - $s$  bond in the  $j$ th  $\pi$  MO in a conjugated system, as

$$p_{rs}^j = c_j c_{js}, \quad \text{where } \phi_j = \sum_k c_k \chi_k. \quad 27.$$

For the total  $\pi$  bond order  $p_{rs}$ ,  $p_{rs}^j$  is summed over the  $\pi$  MOs  $\phi_j$ , and each  $p$  is multiplied by the number of electrons in  $\phi_j$ . For example, if in butadiene the  $\pi$  AOs are numbered from 1 to 4, a simple HMO calculation that neglects overlap gives

$$\begin{aligned} \phi_1 &= 0.371\pi_1 + 0.600\pi_2 + 0.600\pi_3 + 0.371\pi_4, \\ \phi_2 &= 0.600\pi_1 + 0.371\pi_2 - 0.371\pi_3 - 0.600\pi_4, \end{aligned} \quad 28.$$

where  $\phi_1$  and  $\phi_2$  are each occupied by two electrons. Then

$$\begin{aligned} p_{12} &= p_{34} = 2(0.371)(0.600) + 2(0.600)(0.371) = 0.894 \\ p_{23} &= 2(0.600)(0.600) + 2(0.371)(-0.371) = 0.447. \end{aligned} \quad 29.$$

At first overlap was neglected in such calculations, but later Chirgwin & Coulson (85) discussed the redefinition of bond orders when overlap integrals are no longer neglected. Another assumption made in the early HMO calculations was that  $\beta$  is the same for all C-C bonds. Actually, it varies with bond length (86), roughly proportional to  $S$  (25, 72b), and refined calculations took this into account.

In a discussion of various definitions of bond orders as a measure of bonding, I advocated the use of overlap population  $n$  for this purpose (87a). I suggested in effect that the bond dissociation energy  $D$ , for not too heteropolar bonds, might be roughly proportional to  $\sum n_i \bar{I}_i$ , where  $\bar{I}_i$  is the mean value (over the two atoms concerned) of the ionization energy for the MO  $\phi_i$ :

$$D \approx \sum N_i n_i \bar{I}_i. \quad 30.$$

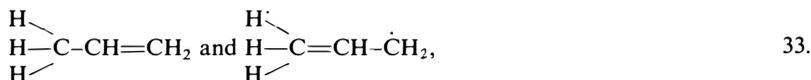
Recently, Jug further discussed the definition of bond orders (87b).

In conjugated systems, any single bond interposed between double or triple bonds shows some shortening as compared with isolated single bonds. Two explanations have been proposed to explain this shortening: (a) the fact that the  $s$ - $p$  hybridization in the  $\sigma$  bonds that take part in multiple bonds differs in isolated

bonds (approximately tetrahedral hybridization), in double bonds (trigonal), and in triple bonds (digonal): increasing  $s$  character in this order causes shortening; (b) the presence of  $\pi$  bond order in conjugated single bonds. Theory shows that both effects must participate, but does not readily say how much each contributes. The question was actively discussed in 1959 (88). An additional smaller factor in bond lengths and energies is hyperconjugation (70).

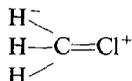
After a little prehistory, hyperconjugation (HCJ) came to the fore in 1941 (72a-c). For a helpful review, see Reference 73a. Out of a group of  $\sigma$  MOs, e.g. as in  $\text{CH}_3$  or  $\text{CH}_2$ , one can construct group MOs that in MO theory can function as quasi- $\pi$  group MOs to interact conjugatively with neighboring  $\pi$  MOs (67). The nature of the interaction is suggested by writing groups of  $\sigma$  bonds as if they were  $\pi$  bonds, for example  $\text{H}_3\equiv\text{C}-\text{C}\equiv\text{CH}$  (here there are two quasi- $\pi$  group  $\text{CH}_3$  MOs: a  $\pi_x$  and a  $\pi_y$ ), or  $\text{H}_3\equiv\text{C}-\text{CH}=\text{CH}_2$  (here there is one quasi- $\pi$  group MO). Other varieties of HCJ can also occur, for example, with lone pairs as in  $\text{H}_3\equiv\text{C}-\text{Cl}$ , where the Cl contains a  $\pi^+$  double lone pair. In general, instead of  $\text{CH}_3$  or  $\text{CH}_2$  one may have  $\text{CR}_3$  or  $\text{CR}_2$ , where R is any atom or radical.

For computations it is necessary to use MO theory, but it is instructive also to write valence-bond resonance structures. Thus in propylene one has the structures:



where  $\cdot$  indicates either a free electron (biradical structure), or a  $+$  or  $-$  charge on the H with  $-$  or  $+$  on the  $\text{CH}_2$  carbon.

HCJ with  $\pi$  lone pairs also occurs as in  $\text{CH}_3\text{Cl}$  (resonance structures

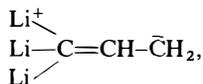


with either  $\pi_x$  or  $\pi_y$  of Cl) and in various other situations (72c).

The energetic effects of HCJ ("delocalization energy") of  $\text{CR}_3$  or  $\text{CR}_2$  (or  $\text{CH}_2\text{R}$  or  $\text{CRR}'\text{R}''$ , etc) groups can be reliably predicted to vary according to the nature of R. They are also much enhanced in carbonium cations and anions and, to a lesser extent, in radicals (72c). A number of relatively recent ab initio calculations are superseding the old HMO calculations, even though the latter have been improved by including  $S$  and allowing for variation of  $\beta$  with bond length. An interesting example of this is contained in a recent paper that also contains a review of earlier work (89). Here the geometry of substituted ethyl ions  $\text{RH}_2\text{X}-\text{CH}_2^+$  is studied for varying X (Li, BeH,  $\text{BH}_2$ ,  $\text{CH}_3$ ,  $\text{NH}_2$ , OH, and F). Two conformations are possible whose relative stability and the sometimes considerable energy barrier that exists between them depend on the electronegativity of X (90).

The large effect of Li here could be qualitatively predicted from HMO theory or from valence-bond resonance structures. Consider, for example, HCJ in propylene or in propylene with Li substituted for H in  $\text{CH}_3$ . As a principal resonance

structure one would have



with much stronger stabilization than with  $\text{CH}_3$ . According to the simplest HMO theory (72b), modified ( $\omega$  technique) to take account of the net charges on Li and the  $\text{CH}_2$  carbon, two  $\pi$ -electron MOs are occupied that are the lowest-energy ( $E$ ) solutions of the secular equation:

$$\begin{vmatrix} \alpha - E & \beta^* & 0 & 0 \\ \beta^* & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta' \\ 0 & 0 & \beta' & \alpha - E \end{vmatrix} = 0. \quad 31.$$

For  $\text{CH}_3$ , with  $-\beta^* \gg -\beta'$  corresponding to the fact that C-H  $\sigma$ -bonds are much stronger than C-C  $\pi$ -bonds, the lowest-energy  $\pi_x$ -electron MO's (72b) are

$$\begin{aligned} 0.701(\text{H}_3) + 0.707(\text{C}_1) + 0.092(\text{C}_2) + 0.023(\text{C}_3), \\ 0.092(\text{H}_3) + 0.023(\text{C}_1) - 0.701(\text{C}_2) - 0.707(\text{C}_3). \end{aligned} \quad 32.$$

But with  $\text{CLi}_3$ ,  $\beta^*$  and  $\beta'$  are roughly equal, and so are the coefficients in (32). The result is clearly that the delocalization energy (72b) is vastly enhanced with  $\text{CLi}_3$ ; also a large dipole moment is developed.

In general,  $\text{CH}_3$  substituents lead to very weak delocalization energies, dipole moments, etc (much stronger in carbonium ions). The effects are somewhat changed in  $\text{CR}_3$  when R is an alkyl group (Baker-Nathan effect) (91). They can be much larger in other cases, e.g.  $\text{R} \equiv \text{Li}$ . Many ab initio SCF papers involving HCJ have appeared fairly recently, but they generally use minimal basis sets. There are also recent SCF papers using extended basis sets for calculations on HCJ in the benzenium ion ( $\text{C}_6\text{H}_7^+$ ), toluene, and toluenium (92). The first ab initio calculation on HCJ was in 1971 for the ethyl ion (93). An extended basis set was used that gave a delocalization energy of 12 kcal mole<sup>-1</sup>. A later paper (94) gave 24 kcal mole<sup>-1</sup> and a HCJ  $\pi$  population on the  $\text{CH}_2$  carbon of 0.11 electron.

### Ab Initio Calculations

Since about 1970, ab initio calculations with electronic digital machines, first used on diatomic molecules (26), have been rapidly extended to a wide range of polyatomic molecules (13, 95, 96). The work includes both SCF computations and, increasingly, CM calculations, with configurations often extending into the thousands in number.

The master of conventional CM calculations, I. Shavitt, who began his work with S. F. Boys, has reviewed the subject (cited in 96). Recently some promising, unconventional CM methods have been initiated (26, 95).

Thus far, polyatomic CM calculations have been confined to relatively small molecules ( $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{B}_2\text{H}_6$ ,  $\text{C}_2\text{H}_6$ ,  $\text{HCOOH}$ , cyclopropane, buta-

diene,  $\text{H}_2\text{CO}$ ,  $\text{N}_2\text{H}_2$ ,  $\text{NO}_2$ ,  $\text{CH}_2$ , etc). In view of the impossibility of including all configurations, a valuable method of extrapolation has been introduced by Buenker & Peyerimhoff (97). In this method, calculations are made at several levels of CM completeness, followed by extrapolation to infinite CM.

Most calculations now use an extended basis set of Gaussian-type functions (26); Boys first proposed in 1950 that they be used instead of Slater-type functions. Gaussian-type functions were used by Foster & Boys in a paper on formaldehyde in 1960 (98). Much used is a procedure in which Slater-type functions are first approximated by an expansion in terms of Gaussians (99). Pople in particular has used what he calls the STO-3G or, more accurately, the 4-31G expansion (100).

Comprehensive minimal basis SCF calculations have been made by Pople and his group on numerous small organic molecules (e.g. all molecules of the form  $\text{H}_m\text{ABH}_n$  with C, N, O, or F atoms), on  $\text{C}_4$  hydrocarbons, and on carbonium ions (101, 102, 103). SCF calculations of varying accuracy have been made on molecules as large as the DNA bases, porphyrin (104), and even on the guanine-cytosine base pair that includes H bonding (105). Rather accurate SCF calculations on benzene and toluene, and on the benzenium and toluenium ions, are available (92). SCF calculations on a variety of complexes have been made (see the section on molecular complexes). SCF calculations on TCNQ (tetracyanoquinodimethane) and its ions have been made (106).

### *Walsh's Rules*

In 1942 I noted that  $\text{AB}_2$  molecules with 16 or less valence-shell electrons are linear and those with 17–20 are bent. I explained this in terms of the ionization energies  $I$  of MOs as a function of apex angle (107). (In view of Koopmans' theorem, for ionization energies one can read SCF MO orbital energies  $\epsilon$ .) The apex angle was seen to be a result of a competition between occupied MOs whose  $I$ 's rise or fall with variation in it. For example,  $\text{CO}_2$  is linear, but with addition of another electron in  $\text{NO}_2$  the molecule is bent; this is explained by supposing that the  $I$  of the added electron in  $\text{NO}_2$  decreases rapidly in energy as the molecule becomes bent. A diagram was given showing roughly how the  $I$  of each MO varies with the apex angle.

In 1953 Walsh presented a somewhat revised and very extensive generalization of these ideas that covered the geometries of various types of polyatomic molecules (108). The resulting specifications are generally known as Walsh's rules. Recently, Buenker & Peyerimhoff have given a comprehensive review of the interpretation of Walsh's rules in the light of ab initio theory and computations (109). As they point out, these rules seem to imply that (e.g. in the case of  $\text{AB}_2$ ) energy as a function of apex angle can be measured by  $\sum I$  or  $\sum \epsilon$  taken over the occupied MOs. Instead, the variation of the nuclear repulsion with angle should be included; also,  $\sum \epsilon$  includes interelectronic repulsions twice, whereas they should be included only once. However, these difficulties prove not to be very significant for the qualitative comparisons for which Walsh's rules are used. On the other hand, correction terms become important in certain extreme cases (e.g.  $\text{Li}_2\text{O}$ , which is linear and not bent like  $\text{H}_2\text{O}$ ). Buenker & Peyerimhoff also point out that the same rationale

of using the variation of  $\epsilon$  values as an indication for angles could be extended to their use for predictions about other geometrical coordinates.

### *Localized Molecular Orbitals*

To represent chemical bonds, chemists usually draw lines connecting adjacent atoms in a polyatomic molecule. Following Hund's 1931 discussion of  $\sigma$  and  $\pi$  bonds (110), one can easily construct corresponding localized LCAO MOs that connect each pair of atoms. These have valuable flexibility in that varying degrees of polarity can be represented just as in heteropolar diatomic MOs.

However, an electron configuration composed of electrons assigned to such MOs cannot be made to provide a wave function as accurate as one built from the conventional "canonical" or "spectroscopic" (1) SCF MOs that are generally delocalized over the whole molecule. The relation between localized and delocalized MOs has been discussed in a very readable manner by Coulson (111).

Conventional SCF MOs form an orthonormal set, whereas fully localized MOs generally do not. On the other hand, by a unitary transformation the conventional set of MOs can be converted (in an infinite variety of ways) into other sets without changing the energy. By a suitable choice, one can often obtain an orthogonal set of MOs that approximate rather closely to fully localized MOs but differ by having a small, nonlocalized tail.

Coulson refers to this tail effect as  $\sigma$  hyperconjugation, since it resembles e.g. the small admixture of  $\text{CH}_3$  orbitals into the  $\pi$  MO in  $\pi$ -hyperconjugation in propylene. As an example, Coulson discusses the orthogonal transformation whereby linear combinations of the conventional delocalized MOs of  $\text{CH}_4$  are converted into four equivalent MOs that are largely localized in the four CH bonds. Each of the resulting MOs contains a weak tail consisting of AOs of the three H atoms other than the one primarily concerned. The tail effect can never be eliminated if one wishes to keep an orthogonal set of MOs. One can simply cut off the tail, but then the wave function as a whole, and its energy, become poorer approximations.

If one could fully localize bonds (or, more generally, groups of atoms like  $\text{CH}_3$  or  $\text{CH}_2$ ) in polyatomic molecules, one could build up such molecules piecewise, in agreement with the familiar additivity relations well known to chemists. A number of attempts have been made in this direction, but because of the tail effect they must remain imperfect. A related endeavor is to assign a dipole moment to an individual bond, e.g. the CH bond in a hydrocarbon.

Much of the early discussion (112) of localized MOs was devoted to sets of equivalent orbitals in symmetrical molecules: examples include the two localized OH bond MOs in  $\text{H}_2\text{O}$  and the four tetrahedral bond MOs in  $\text{CH}_4$ .

S. F. Boys developed a systematic localization procedure (113), and Peters has written extensively on methods of obtaining localized MOs (114). However, the tail effect generally turns up, often in awkward ways.

A systematic localization procedure was developed by Edmiston & Ruedenberg (115). Their objective is to confine each MO to as small a space as possible, while keeping these MOs as far from each other as possible. They do this by setting up unitary transformations so as to maximize the repulsion energy between the elec-

trons occupying the MO (for the common case of an electron pair in the MO) and, simultaneously, to minimize the repulsion energy from electrons in other localized MOs. The procedure can even be applied to give increased localization of AOs in atoms. Good results are obtained, but the tail effect cannot be eliminated.

Edmiston & Ruedenberg depart in one way from the now customary segregation between  $\sigma$  and  $\pi$  MOs. Namely, when both of these are present among the delocalized MOs, they make localized MOs that are mixtures of  $\sigma$  and  $\pi$ ; for example in  $N_2$ , instead of a localized  $\sigma$  bond and a double  $\pi$  bond, they make three equivalent bonds in a trigonal arrangement. While this procedure maximizes localization, it goes farther than most modern chemists would wish to go.

### *Alternant Molecular Orbitals*

In the alternant MO method, applicable to alternant hydrocarbons, different but complementary forms are given for MOs with  $\alpha$  and  $\beta$  spins. The method has the advantage of providing part of the correlation energy, but is rather complicated and is perhaps of less value nowadays in view of the development of relatively efficient methods for obtaining more complete correlation. Introduced by Löwdin in 1955 (115), the method has been thoroughly discussed in a book by Pauncz (116).

### *Coordination Chemistry, Complex Ions, Sandwich Compounds, and Molecular Complexes*

A multitude of composites are now known in which atoms, ions, or molecules are combined with other molecules in a way that cannot be described simply in terms of ordinary single and multiple bonds (117). These compounds can be understood to a considerable extent in terms of charge-transfer forces between molecules acting as electron donors and others as electron acceptors (118). MO theory gives a more thorough understanding by combining AOs or MOs of the constituents in a complex structure to give a preponderance of bonding MOs to hold the whole together. A helpful feature is that most of these complex structures involve the union of partners whose MO structures consist wholly or partly of closed shells. Under these circumstances the SCF MO approximation for the complex should be relatively good without much correction for correlation energy.

The classical donors and acceptors are the lone-pair ( $n$ ) donors and the vacant-orbital ( $v$ ) acceptors. Their mutual interaction gives rise to relatively strongly bonded molecular complexes or compounds. These donors and acceptors have been called increvalent (118) because in their interaction new bonds are (partially) formed. Weaker complexes are formed involving sacrificial ( $b\sigma$  and  $b\pi$ ) donors and sacrificial ( $a\sigma$  and  $a\pi$ ) acceptors: sacrificial because their functioning involves loss of bonding ( $b$ ) or the incurrance of antibonding ( $a$ ) in their MOs. For example the  $R_3N \cdot I_2$  complexes of the  $n \cdot a\sigma$  type are rather stable, but they display antibonding in the  $I_2$  molecule by very appreciable increases in the I-I bond length in the complexes.

Besides these one-way complexes, there are many that are stabilized by two-way action, each partner serving simultaneously as donor and acceptor in a manner

first discussed by Dewar in 1951 (119). Well-known examples of such amphidonors and amphiceptors (118) are CO in the carbonyls, PF<sub>3</sub>, and C<sub>2</sub>H<sub>4</sub>. Very many such two-way actions occur in complex ions of the transition elements. The sandwich compounds, of which ferrocene [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] was the first discussed (in 1951) involves two-way action between metal atoms and  $\pi$ -electron amphidonors.

For a given prototype molecule, donor or acceptor action can be greatly enhanced (fortified) by introduction of substituent groups. Thus the weak amphidonor C<sub>2</sub>H<sub>4</sub> can be converted into a very strong donor by substituting N(CH<sub>3</sub>)<sub>2</sub> groups for the four H atoms. The resulting compound with Br<sub>2</sub> even forms a Mg<sup>2+</sup>-like salt [C<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>]<sup>2+</sup>(Br<sub>3</sub><sup>-</sup>)<sub>2</sub> according to Wizinger (120). On the other hand, replacement of the four H by CN leads to the strong acceptor tetracyanoethylene (TCNE). Similarly, the weak  $\pi$  amphidonor benzene (C<sub>6</sub>H<sub>6</sub>) can be converted into a strong donor by substituting CH<sub>3</sub> for H atoms or into a strong acceptor by substituting NO<sub>2</sub> groups.

Environmental cooperation is another important influence (118). An example is the system NH<sub>3</sub> + HCl. Clementi has made an SCF MO calculation that follows these two molecules from their union in the vapor state down to a stable combined structure that may be described briefly as (NH<sub>4</sub>)<sup>+</sup><sup>‡</sup>Cl<sup>-‡</sup> (121). When NH<sub>3</sub> and HCl vapors are mixed, a cloud of crystalline NH<sub>4</sub><sup>+</sup>Cl<sup>-</sup> is produced. This can be understood as a result of the polymerization of (NH<sub>4</sub>)<sup>+</sup><sup>‡</sup>Cl<sup>-‡</sup>, present in small amounts in the vapor, under the action of the electrostatic forces of the crystal, which causes charge transfer to the Cl to become complete. The cooperative effect of polymerization has induced complete charge transfer. A further cooperative effect occurs if the NH<sub>4</sub><sup>+</sup>Cl<sup>-</sup> crystal is dissolved in water: NH<sub>4</sub><sup>+</sup>(aq) and Cl<sup>-</sup>(aq) ions are formed.

Although  $b\pi \cdot a\pi$  complexes are generally weak, with little charge transfer, transfer can be enhanced by cooperative action. Thus the  $b\pi$  donor TMPPD (tetramethylparaphenylene diamine) and chloranil form a weak  $b\pi \cdot a\pi$  complex, but if allowed to form a crystal this has the structure TMPPD<sup>+</sup>Chl<sup>-</sup>, and on solution in water TMPPD<sup>+</sup>(aq) and Chl<sup>-</sup>(aq) ions are formed (118).

Both moderately strong and weak molecular complexes are characterized by charge-transfer spectra in which charge transfer is usually much more complete in the excited state. These spectra often give rise to visible color, even (or especially) in very weak complexes. In some cases ("contact charge-transfer spectra") there is such a spectrum even when there is no evidence of more than contact between a donor and an acceptor molecule. An example is the behavior of aniline, which is colorless when pure but turns brown when oxygen is bubbled through it (and becomes colorless again on sweeping out the oxygen). Yet there is no evidence of formation of a stable ground-state complex.

Following Benesi & Hildebrand's discovery of an intense absorption in I<sub>2</sub> solutions of benzene and methylated benzenes (122), I introduced the intermolecular charge-transfer spectrum interpretation in 1950 (123). This involved extensive charge transfer in the excited state and a small amount ( $b\pi \cdot a\sigma$  type) in the ground state of the benzene-iodine complex. In subsequent years, such weak complexes were often called charge-transfer complexes, although Briegleb (124) rather more

properly called them electron donor-acceptor complexes. More recently several writers have emphasized that the stability of the weaker of these complexes in their ground states may be due more to electrostatic than to charge-transfer forces. The matter has been thoroughly studied by Morokuma and associates, who have broken down the relevant contributions into exchange repulsions together with attractions due to direct electrostatic polarization, charge transfer, dispersion, and mixed effects (125). For several complexes including H bonding, they have obtained, with the help of SCF calculations, quantitative computed values for these various contributions.

### *Electron-Deficient Molecules*

These, in particular the boranes and carboranes, are well reviewed in text books (117).

### *Multiple Bonds*

A facet of transition-metal chemistry first recognized by Cotton in the early 1960s is the ability of d electrons in transition metal atoms to form multiple (up to quadruple) bonds. The subject has been expanding very rapidly (126).

### *Van der Waals Molecules*

This subject, which has become very active, has recently been reviewed in this series (127).

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