

frared spectrum of MgF_2 isolated in inert gas matrices and assigned a strong band near 250 cm.^{-1} to the bending vibration. While we feel that the earlier infrared spectra were carefully examined it is certainly necessary to point out that several studies are in apparent disagreement with our results. It is thus not obvious whether an ionic model is appropriate for the alkaline earth dihalides.

For group IIB dihalides an apparent disagreement sets in immediately if an ionic model is used to fit the geometry. Because the bond lengths in these species are relatively short, nonlinear geometries are predicted, unless extremely low values of the metal ion polarizabilities are used. It is evident that the linearity of HgF_2 is surprising from this point of view. Further evidence against the applicability of an ionic model is shown by the halogen quadrupole coupling constants of CH_3HgCl and CH_3HgBr . These coupling constants have been measured by Gordy and Sheridan³⁷ and are only 20% less than in CH_3Cl and CH_3Br , respectively. In view of the extremely small value of $(eqQ)_x$ found in the alkali halides and the good correlation between halogen quadrupole coupling constant and chemical bond character, it seems unlikely that an ionic model for the group IIB dihalides is applicable.

It seems, therefore, that at best an ionic model can be used for the group IIA dihalides to give an account of the general trends found. It seems unlikely that the potential function predicted by such a model is correct.

Consider next the structures of the MX_2 species in terms of directed valence theory. The ground state of the group II elements is $(ns)^2\ ^1S$, an inert structure, so that it is necessary to consider electron promotion or valence-state preparation. As has been discussed

(52) M. J. Linevsky, K. S. Seshadri, and D. White, paper presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June, 1964.

many times, the linear geometry is readily explained by considering the lowest sp configuration as the valence state. The bent geometry can then be attributed to an sd valence state. Indeed it is found that the energy of the lowest sd configuration with respect to the lowest sp configuration correlates with observed geometry. For those metals for which both geometries are found, it is necessary in addition to assume that sd is favored for short bond lengths. The linearity of MnF_2 is then surprising from this point of view since here an sd configuration is quite low lying.²⁷

In the absence of detailed and rigorous quantitative calculations it is not at all obvious in what form an explanation of equilibrium geometry should be sought. To our knowledge, it has not yet been proven that the Hartree-Fock function has its minimum energy at the same value of the molecular coordinates as obtains in reality. For diatomic molecules there are arguments, both theoretical and computational, that the difference between the Hartree-Fock and the correct internuclear separation is quite small. In view of the relatively small energy required to bend bonds compared to stretching them it is not obvious, however, that the diatomic molecule can serve as a model for the polyatomic case. Almost all of the present molecular orbital functions for polyatomic molecules are certainly very crude approximations to the Hartree-Fock functions. Thus agreement with observation can be fortuitous or the result of a particular selection of parameters. In view of these uncertainties it is apparent that any simple molecular orbital computation purporting to explain geometries should be viewed with suspicion.

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A Semiempirical Treatment of Molecular Structures. II. Molecular Terms and Application to Diatomic Molecules

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A self-consistent semiempirical method which is designed for the calculation of heats of formation and charge distribution of nonconjugated molecules is outlined. The method is based on an antisymmetrized product of molecular orbitals, simplified in such a way as to make the values of all involved integrals directly available from atomic spectra (see paper I¹ of this series where atomic terms have been described and their connection with electronegativity demonstrated) and molecular bond distances. In a preliminary study, this method has been used to calculate satisfactory values of bond energies and reasonable values of charge distributions in 80 diatomic molecules (σ -bonded).

I. Introduction

Methods based on linear combinations of atomic orbitals,^{2,3} which have proved to be particularly successful in conjugated systems, have been applied mainly in three different ways.

(a) In the case of small or highly symmetrical molecules, the calculations are made as accurately as

- (1) G. Klopman, *J. Am. Chem. Soc.*, **86**, 1463 (1964).
- (2) C. A. Coulson, *Quart. Rev. (London)*, **1**, 144 (1947).
- (3) A. Streitwieser, "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961.

possible by using either the Goeppert-Meyer and Sklar approximation⁴ or self-consistent field techniques such as the Roothaan⁵ method of solving the Hartree-Fock problem for molecules.⁶ The approximation common to these methods is giving an analytical form to the atomic orbitals.^{7,8}

- (4) M. Goeppert-Meyer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).
- (5) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
- (6) J. F. Mulligan, *J. Chem. Phys.*, **19**, 347 (1951).
- (7) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).
- (8) C. Zener, *ibid.*, **36**, 51 (1930).

The observed agreement with experimental values is unfortunately not always very satisfactory, but these methods, nevertheless, lead to some of the best approximate solutions of the Schrödinger equation. Their main disadvantage lies in the complexity of the calculation of polycentric integrals,⁹ which requires a certain number of parameters, such as the screening constant and the effective quantum number.

(b) In the one-electron approximation proposed by Hückel,¹⁰ all the unknown integrals are treated as constants. This method was developed by Coulson and Longuet-Higgins^{11,12} and leads to useful results even in its simplified form.

Several modifications have been proposed, however, such as the introduction of overlap,¹³ the influence of bond length¹⁴ on the exchange integral, and of the electronic charge¹⁵ on the Coulomb integral. These improvements allow a systematic study of the properties of conjugated hydrocarbons to be made.¹¹ The introduction of nonbonding interactions also gives a more comprehensive interpretation of the behavior of saturated hydrocarbons.¹⁶

Several attempts have also been made to calculate the energies of heteromolecules.¹² Their success depends very much on the magnitude of the parameters chosen, and a single general treatment cannot be developed.

(c) Pariser and Parr¹⁷ presented a semiempirical theory of the electronic spectra of conjugated molecules which combines the advantage of the conventional semiempirical LCAO-MO method (Hückel approximation) with the purely theoretical method of antisymmetrized products of molecular orbitals (Goepfert-Meyer and Sklar). Some atomic integrals are neglected and others are given empirical values, which are then used in the antisymmetrized product method.

The resulting theory is more successful than the purely theoretical one and has been developed in several ways by Pople,¹⁸ Dewar and Wulfman,¹⁹ Hall, and others.²⁰

Apart from purely theoretical studies of diatomic molecules few attempts have been made to calculate single bond properties by empirical or semiempirical methods.

Of these, Pauling's early suggestion that heteronuclear bond energies can be calculated from the arithmetic or geometric means of the corresponding homonuclear bond energies was particularly useful and led to the concept of electronegativity.²¹ The subsequent tendency was to adopt the values of electronegativity

(9) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

(10) E. Hückel, *Z. Physik*, **60**, 423 (1930); **70**, 204 (1931); **72**, 310 (1931); **76**, 628 (1932).

(11) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947).

(12) C. A. Coulson and H. C. Longuet-Higgins, *ibid.*, **A192**, 16 (1949).

(13) R. S. Mulliken and C. A. Rieke, *J. Am. Chem. Soc.*, **63**, 1770 (1941); G. W. Wheland, *ibid.*, **63**, 2025 (1941).

(14) J. E. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A158**, 280 (1937).

(15) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949); A. Streitwieser, *J. Am. Chem. Soc.*, **82**, 4123 (1960).

(16) C. Sandorfy, *Can. J. Chem.*, **33**, 1337 (1955); H. Yoshimizu, *Trans. Faraday Soc.*, **53**, 125 (1957); G. Klopman, *Tetrahedron*, **19**, 111 (1963).

(17) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

(18) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(19) M. J. S. Dewar and C. E. Wulfman, *J. Chem. Phys.*, **29**, 158 (1958).

(20) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc. (London)*, **A67**, 795 (1954); R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963.

(21) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960.

as a physical characteristic of the atoms and then to try to calculate the bond properties. This procedure has been applied in particular by Arnold²² in his "smoothed potential" treatment of diatomic molecules and by Pearson²³ in a first attempt to use a semiempirical LCAO treatment in these types of molecules.

The procedure we propose here is based on a normal LCAO calculation, including electron repulsion terms. Although electronegativity is not introduced as a physical characteristic of the atoms, it is interesting to note that a quantity which can be identified with electronegativity appears in the diagonal term of the matrices during the calculations.

II. Atomic Terms

In the preceding paper (hereafter referred to as paper I),¹ a semiempirical treatment of electronegativity and atomic terms was proposed. These terms were defined, for an atom X, as the sum of those integrals in which the Hamiltonian represents the interaction of the core of X with the electrons around it, together with the interaction between the electrons associated with valency atomic orbitals of X.

A formula was proposed to calculate the atomic energy, consisting in

$$E = \sum_i B_{X^l} + 1/2 \sum_{ij} A_{X^+} \delta + 1/2 \sum_{ij} A_{X^-} (1 - \delta) \quad (1)$$

where B_{X^l} is the energy of an electron belonging to an atomic orbital of azimuthal quantum number l , in the field of the core of atom X; A_{X^+} and A_{X^-} are the repulsion between electrons belonging to the same valence shell of an atom and possessing the same and opposite spins, respectively; δ is the Kronecker symbol equal to 1 if electrons i and j have the same spins and equal to 0 otherwise.

From this formula, a very convenient definition of electronegativity can be derived which has been shown to be the energy of an electron in the field of a bonded atom. We have shown that this term is automatically included in the diagonal term in an LCAO type of calculation.

In this paper, we are going to consider molecular terms, and we will show how this procedure can be applied to diatomic molecules.

III. Theory

The wave function of the ground state of a molecule with $2N$ bonding electrons is obtained by allocating each electron to one of a set of space orbitals, ψ_p , and combining the products into a complete determinantal wave function, Ψ .

In paper I, however, convenient "barycenters" of states were defined and characterized by a given value of M_S^2 (the component of the spin angular momentum of the total system on an arbitrarily chosen axis). Accordingly, we may now treat separately electrons with positive and negative spins.²⁴ The interaction between the two systems of opposite spin then gives rise to a single molecular "barycenter" from a weighted mixture of excited molecular states.

(22) J. R. Arnold, *J. Chem. Phys.*, **24**, 181 (1956).

(23) R. G. Pearson, *ibid.*, **17**, 969 (1949).

(24) A. Bristock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

Under these circumstances, two products of molecular orbitals can be obtained, describing, respectively, all the electrons with positive and negative spins

$$\begin{aligned}\Psi &= \psi_{1\alpha}(1)\psi_{2\alpha}(2)\dots\psi_{P\alpha}(i)\psi_{Q\alpha}(j)\dots\psi_{N\alpha}(n) \\ \bar{\Psi} &= \psi_{1\beta}(n+1)\psi_{2\beta}(n+2)\dots\psi_{P\beta}(n+i)\dots\psi_{N\beta}(2n)\end{aligned}\quad (2)$$

The bar is used to show that the wave function refers to negative spins: $\psi_{P\beta}(i) \equiv \bar{\psi}_P(i)$.

The total Hamiltonian operator acting on these wave functions is

$$H = + \sum_{AB} \frac{1}{r_{AB}} - \sum_i \left[\sum_A \frac{1}{r_{Ai}} \right] + \sum_{ij} \frac{1}{r_{ij}} \quad (3)$$

where A and B are constituent atoms and i and j are bonding electrons. The operator can be split into four parts

$$H_N = + \sum_{AB} \frac{1}{r_{AB}}$$

$$H^+ = - \sum_i \left[\sum_A \frac{1}{r_{Ai}} \right] + \sum_{ij} \frac{1}{r_{ij}}$$

(i and j being characterized by a positive spin)

$$H^- = - \sum_i \left[\sum_A \frac{1}{r_{Ai}} \right] + \sum_{ij} \frac{1}{r_{ij}}$$

(i and j both having negative spin)

$$H^\pm = + \sum_{ij} \frac{1}{r_{ij}}$$

(where i and j have opposite spin) leading to four components for the total energy of the system.

$$E_N = \sum_{AB} \frac{1}{r_{AB}}$$

for the core-core repulsions

$$E^+ = \frac{\int \Psi H^+ P (-1)^N \Psi d\tau}{\int \Psi P (-1)^N \Psi d\tau}$$

for the system of electrons of positive spin

$$E^- = \frac{\int \bar{\Psi} H^- P (-1)^N \bar{\Psi} d\tau}{\int \bar{\Psi} P (-1)^N \bar{\Psi} d\tau}$$

for the systems of electrons of negative spin; and

$$E^\pm = \frac{\int \Psi \bar{\Psi} H^\pm \Psi \bar{\Psi} d\tau}{\int \Psi \bar{\Psi} \Psi \bar{\Psi} d\tau}$$

for the interaction of the two systems. The total energy of any molecular system can thus be written as

$$\begin{aligned}E &= \sum_{AB} \frac{1}{r_{AB}} - \sum_P I_P + \sum_{PQ} J_{PQ} - \sum_{PQ} K_{PQ} - \\ &\quad \sum_P I_{\bar{P}} + \sum_{PQ} J_{P\bar{Q}} - \sum_{PQ} K_{P\bar{Q}} + \sum_{PQ} J_{P\bar{Q}} \quad (4)\end{aligned}$$

where

$$I_P = \int \psi_P(i) \sum_A \left(\frac{1}{r_{Ai}} \right) \psi_P(i) d\tau_i$$

$$J_{PQ} = \int \psi_P(i) \psi_P(i) \frac{1}{r_{ij}} \psi_Q(j) \psi_Q(j) d\tau_i d\tau_j$$

$$K_{PQ} = \int \psi_P(i) \psi_Q(j) \frac{1}{r_{ij}} \psi_Q(i) \psi_P(j) d\tau_i d\tau_j$$

$$J_{P\bar{Q}} = \int \psi_P(i) \psi_P(i) \frac{1}{r_{ij}} \bar{\psi}_Q(j) \bar{\psi}_Q(j) d\tau_i d\tau_j$$

As a further approximation, the molecular orbitals, ψ_P , may be represented by linear combinations of atomic spin orbitals centered on the various atoms of the molecule.

$$\psi_P(i) = \sum_A C_A^P \phi_A \quad \bar{\psi}_P(i) = \sum_A \bar{C}_A^P \bar{\phi}_A \quad (5)$$

Replacement of the wave functions in eq. 4 by their LCAO equivalents leads to a general equation for the molecular energy.

This equation, which contains many polycentric integrals, is far too complicated to be solved by a completely theoretical procedure, based for instance on Slater's atomic orbitals; it can nevertheless be greatly simplified by making semiempirical approximations.

Striking examples of this procedure are the methods of Pariser and Parr¹⁷ and of Pople¹⁸ for the calculation of ultraviolet spectra of aromatic compounds, which give excellent results. However, they treat the particular case of conjugated, alternant nonsubstituted hydrocarbons, where even a very rough approximation, like the HMO approximation, gives reasonable results.

Several hypotheses will thus be invoked, of which the following are the two most important: (i) formal neglect of differential overlap. $\phi_A(1)\phi_B(1) \equiv 0$ if the atomic orbitals ϕ_A and ϕ_B belong to two different atoms; (ii) neglect of nonbonded interactions.²⁵ These can, nevertheless, be introduced in cases such as those where steric hindrance manifestly plays a role (case of triangular heteroatomic molecules, *i.e.*, H₂O) or in crystals where all neighbors should be considered (Madelung constant).

With these main hypotheses and the definition of atomic terms given in paper I, it is now possible to simplify the general equation by considering the energetic terms in the following way.

(a) Nucleus-Nucleus Interactions

$$\frac{1}{r_{AB}} = \Gamma_{AB}$$

is, according to approximation ii, different from 0 only for neighboring atoms.

(b) Core Integrals

$$\text{(Case 1)} \quad \int \phi_A(i) \sum_A \frac{1}{r_{Ai}} \phi_A(i) d\tau_i =$$

$$\int \phi_A(i) \frac{1}{r_{Ai}} \phi_A(i) d\tau_i + \int \phi_A(i) \sum_{B \neq A} \frac{1}{r_{Bi}} \phi_A(i) d\tau_i$$

(25) This is not a restrictive hypothesis and we shall also consider in a subsequent paper the effect of all nonbonded interactions.

represents the interaction energy of electron i whose motion is described by the atomic orbital ϕ_A , respectively, with the core of A and all the other cores of the molecule. The first integral is essentially an atomic term, being equal to the constant B_A (see paper I). The second term is a sum of core-electron interactions, hereafter referred as $\sum_B \Gamma_{Ba}$. This term is again equal to 0 unless A and B are adjacent.

$$\text{(Case 2)} \quad \int \phi_A(i) \sum_A \left(\frac{1}{r_{Ai}} \right) \phi_A(i) d\tau_i$$

is the resonance integral which depends on the type and length of the bond between A and B. According to hypothesis ii, it will not depend on the neighboring bonds or atoms and can thus be treated as an empirical parameter β_{AB} , which vanishes for all nonbonded atoms.

(c) Electronic Repulsion Integrals

$$\text{(Case 1)} \quad \int \phi_A(i) \phi_A(i) \frac{1}{r_{ij}} \phi_A(j) \phi_A(j) d\tau_i d\tau_j$$

This integral represents the interaction of two electrons whose motions are described by the same wave function. This integral is also a typical atomic term and was referred to as $-A_A^-$ in part I.

$$\text{(Case 2)} \quad \int \phi_A(i) \phi_A(i) \frac{1}{r_{ij}} \phi_B(j) \phi_B(j) d\tau_i d\tau_j$$

represents the interaction of two electrons belonging to two atomic orbitals A and B and will be called Γ_{ab} . Γ_{ab} again, vanishes unless A and B are neighbors or belong to the same atom in which case $-\Gamma_{ab} = A_A^-$.²⁶

$$\text{(Case 3)} \quad \int \phi_A(i) \phi_B(i) \frac{1}{r_{ij}} \phi_A(j) \phi_B(j) d\tau_i d\tau_j$$

These repulsion integrals vanish in all cases, according to our hypotheses of neglecting differential overlap. The approximation seems here to be particularly drastic since the interaction between two electrons with opposite spin (in orbitals of the same atom)

$$A^- = -\int \phi_X(1) \phi_X(1) \frac{1}{r_{12}} \phi_Y(2) \phi_Y(2) d\tau_1 d\tau_2$$

now appears to be equal to the interaction of two electrons with the same spin

$$A^+ = -\int \phi_X(1) \phi_X(1) \frac{1}{r_{12}} \phi_Y(2) \phi_Y(2) d\tau_1 d\tau_2 + \int \phi_X(1) \phi_Y(1) \frac{1}{r_{12}} \phi_X(2) \phi_Y(2) d\tau_1 d\tau_2 = A^-$$

However, the difference between A^+ and A^- appears only for systems containing more than two bonding electrons and therefore will be introduced in a subsequent paper dealing with polyatomic molecules.

(26) This leads to an expression similar to that proposed by Pariser

$$\Gamma_{ab} = -A_A^- = I_v - E_v$$

See R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).

With these approximations, the general equation for the energy of any molecular system can be written

$$E = -\sum_A [\sum_P (C_A^{P2} + \bar{C}_A^{P2}) (B_A + \sum_{B \neq A} \Gamma_{Ba}) - \sum_P (C_A^{P2}) \sum_P (\bar{C}_A^{P2}) A_A^-] - \sum_{AB} \{ -\Gamma_{AB} + 2 \sum_P (C_A^P C_B^P + \bar{C}_A^P \bar{C}_B^P) \beta_{AB} \} - \{ \sum_P (C_A^{P2}) \sum_P (\bar{C}_B^{P2}) + \sum_P (\bar{C}_A^{P2}) \sum_P (C_B^{P2}) + [\sum_P (C_A^P C_B^P)]^2 + [\sum_P (\bar{C}_A^P \bar{C}_B^P)]^2 - \sum_P (C_A^{P2}) \sum_P (C_B^{P2}) - \sum_P (\bar{C}_A^{P2}) \sum_P (\bar{C}_B^{P2}) \} \Gamma_{ab} \quad (6)$$

C_A^P being the coefficient of atomic orbital A in the molecular orbital P.

The molecular energy can be calculated by minimization of eq. 6 with respect to all the coefficients C_X^P until self-consistency is reached. This however requires also values for the various unknowns, but since the A^- , A^+ , and B values are known from atomic spectra (see paper I), we need only find values for the β - and Γ -values.

In the following section these values are obtained by a simple empirical procedure and are then used to calculate the energies of diatomic molecules.

IV. Application to Diatomic Molecules

A. Calculation.—When the ground state of a singly bonded diatomic molecule is considered,²⁷ eq. 6 reduces to eq. 7 if the two bonding electrons are in the same molecular orbital

$$E = q_A (B_A^* + \Gamma_{Ba}) + q_B (B_B^* + \Gamma_{Ab}) + \frac{q_A^2}{4} A_A^- + \frac{q_B^2}{4} A_B^- - \Gamma_{AB} + 2\sqrt{q_A q_B} \beta_{AB} - \frac{q_A q_B}{2} \Gamma_{AB} \quad (7)$$

where $q_A (= 2C_A^2)$ is the total charge on atomic orbital A and q_B the total charge on atomic orbital B. Equation 7 can be minimized with respect to q_A and q_B in a variational procedure to give the molecular energy. The terms B_A^* and B_B^* are obtained from the following equation

$$B_X^* = B_X + \sum_i e_i A_X^\pm \quad (8)$$

where the values of B_X and A_X^\pm are those calculated from atomic spectra in paper I, and $\sum_i e_i$ is the number of electrons in the penultimate shell of the isolated atom minus one. B_X^* is thus the core attraction for the bonding electrons in the field of all the other electrons of the valency shell (Table I).

The values of B_X^* and A_X^- for alkali metals included in Table I are calculated from their ionization potentials and experimental electron affinities when available (Table II).

Calculation of the Γ -term is more difficult, and we therefore propose a point charge description of the nonbonding interactions (*i.e.*, perfect screening of the nuclear charge by all electrons belonging to the atom). This assumption, which has already been used by

(27) Hereafter, stabilizing energies will be given positive signs, repulsion energies negative ones.

TABLE I
ATOMIC PARAMETERS FOR SINGLY BONDED ATOMS

Atom X	B_X^* , e.v.	A_X^- , e.v.
H	13.595	-12.845
Li	5.39	-4.77
Na	5.138	-4.30
K	4.339	-3.65
Rb	4.176	-3.58
Cs	3.893	-3.39
F	19.476	-15.996
Cl	14.196	-10.507
Br	13.06	-9.57
I	11.849	-8.639

TABLE II
ELECTRON AFFINITIES AND IONIZATION POTENTIALS OF
ALKALI METALS

Metal	Ionization potential, e.v. ^a	Electron affinity, e.v.
Li	5.390	0.62 ^b
Na	5.138	0.84 ^c
K	4.339	0.69 ^d
Rb	4.176	(0.6) ^e
Cs	3.893	(0.5) ^e

^a C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949. ^b A. W. Weiss, *Phys. Rev.*, **122**, 1826 (1961). ^c R. Gaspar and B. Molnar, *Acta Phys. Hung.*, **5**, 75 (1955). ^d H. O. Pritchard, *Chem. Rev.*, **52**, 529 (1953). ^e Estimated (see, however, H. Ebbinghaus and H. Neuert, *Naturwiss.*, **51**, 83 (1964)).

Pople¹⁸ in his analogous treatment of conjugated molecules, leads to the identity

$$\Sigma\Gamma = -\Gamma_{AB} + \Gamma_{Ab} + \Gamma_{Ba} - \Gamma_{ab} = 0$$

This assumption, which is not strictly true, means that the interaction of nonpolarizable atoms is zero at the equilibrium distance if a bond is not formed. It should be realized, however, that $\partial\Sigma\Gamma/\partial r \neq 0$ since $\Sigma\Gamma$ includes a repulsion term, which prevents collapse of the bond and thus determines the equilibrium distance. The validity of this assumption will be discussed in a later section after the results have been considered. With this assumption and the equalities

$$q_A + q_B = 2, \quad \left(1 - \frac{q_A q_B}{2}\right) = 1/4(q_A^2 + q_B^2)$$

eq. 7 becomes

$$E = q_A B_A + q_B B_B + \frac{q_A^2}{4}(A_A^- + \Gamma_{ab}) + \frac{q_B^2}{4}(A_B^- + \Gamma_{ab}) + 2\sqrt{q_A q_B} \beta_{AB} \quad (9)$$

and the bond energy

$$E_b = E - B_A - B_B = E - I_A - I_B \quad (10)$$

is

$$E_b = \frac{q_A - q_B}{2}(B_A - B_B) + \frac{q_A^2}{4}(A_A^- + \Gamma) + \frac{q_B^2}{4}(A_B^- + \Gamma) + 2\sqrt{q_A q_B} \beta_{AB} \quad (11)$$

This treatment, therefore, involves two parameters, β and Γ (Γ_{ab}). The Pauling geometrical mean procedure²⁸ will be used to calculate β , *i.e.*

$$\beta_{AB} = (\beta_{AA}\beta_{BB})^{1/2}$$

An attempt will be made to calculate Γ (aa/bb in Slater-Condon notation) from atomic or molecular properties of the atoms. Pariser and Parr have shown that Slater orbitals usually give too large values of this integral for small distances,¹⁷ and therefore they treated it as a parameter.

If the assumption²⁹ is made that

$$\Gamma = 1/2(A_A^- + A_B^-)$$

i.e., if the repulsion between two electrons in a bond is assumed to be equal to the mean value of the repulsion between two electrons in the valence orbitals of each of the isolated atoms, then eq. 11 simplifies to

$$E_b = \frac{q_A - q_B}{2} \left[\left(B_A + \frac{A_A^-}{2} \right) - \left(B_B + \frac{A_B^-}{2} \right) \right] + 2\sqrt{q_A q_B} \beta_{AB} \quad (12)$$

In part I, terms of the kind $B_X + A_X^-/2$ were shown to be equal to the neutral electronegativity of atom X

$$X_X = B_X + \frac{A_X^-}{2} = \frac{I_v + E_v}{2}$$

Equation 11 thus becomes

$$E_b = \frac{q_A - q_B}{2}(X_A - X_B) + 2\sqrt{q_A q_B} \beta_{AB} \quad (13)$$

and minimization gives $E_b = \sqrt{(X_A - X_B)^2 + 4\beta_{AB}^2}$. This is identical with the equation given by Pearson using a one-electron LCAO approximation²³

$$\begin{vmatrix} X_A - E & \beta_{AB} \\ \beta_{AB} & X_B - E \end{vmatrix} = 0$$

However, from eq. 10 and 13 it can be shown that

$$E = B_A + B_B + E_b = I_A + I_B + E_b$$

i.e., the total energy involves ionization potentials and not the electronegativities which occurred in the matrix. This answers the criticism of Pearson's method, which we discussed in paper I.

By using this formula and Pauling's electronegativities, Pearson calculated bond energies with a reasonable degree of accuracy (second column, Table V). However, in common with many others, including Pauling's additivity rules, this method completely fails when applied to alkali metal hydrides and to very ionic molecules.³⁰ These discrepancies can almost certainly

(28) There is not really any possibility to determine the best approximation for β . The geometrical mean value, however, usually fits better with experimental values, especially for bonds between atoms having very different homopolar bond strengths and has been recommended by Pauling and Sherman (L. Pauling and J. Sherman, *J. Am. Chem. Soc.*, **59**, 1450 (1937); R. G. Pearson and H. B. Gray, *Inorg. Chem.*, **2**, 358 (1963)). An MO justification for the arithmetic mean value based on an argument of Mulliken (R. S. Mulliken, *J. chim. phys.*, **46**, 535 (1949)) is usually invoked. It can be shown, however, that this argument is based on an artefact and requires, among other hypotheses, that the overlap S_{AB} be the arithmetic mean value of S_{AA} and S_{BB} , which is obviously wrong.

(29) We do not recommend this particularly crude assumption but it turns out from the discussion which follows that this approximation is inherent in many one-electron theories.

(30) Ferreira (personal communication) has obtained much better results by taking into account electronegativity variations in the molecule

be attributed to the crude way in which Γ was calculated, since this should at least be represented as a function of bond distance.

Accordingly and in agreement with a point-charge approximation, we propose e^2/r as a trial function.¹⁸ This gives good results except when s-orbitals are used in bonding. Consequently, the alternative formula

$$\Gamma = e^2/\sqrt{r^2 + (\rho_X + \rho_Y)^2} \quad (14)$$

(where ρ represents the radius of the appropriate s-orbital) was used. This still remains a point charge approximation but the charges are no longer located at the nuclear centers, thus allowing for some kind of polarization. Under these circumstances, Γ tends to A_X^- (i.e., the repulsion between the two electrons when in the same s-orbital) when $r \rightarrow 0$ and the equation gives a useful geometrical picture of the electronic situation. The values of ρ_X , obtained from the equation

$$\rho_X = \frac{14,388}{2A_X^-}$$

are compared with the covalent radius ($R_{XX}/2$) in Table III.

TABLE III
RADIUS OF s-ORBITALS

	ρ , Å.	R_{cov} , Å.
H	0.56	0.37
Li	1.508	1.34
Na	1.673	1.54
K	1.971	1.96
Rb	2.01	2.0
Cs	2.12	2.1

The corresponding values of β given in Table IV were obtained by comparing the energy calculated from eq. 11 using these values of ρ_X to calculate Γ and the experimental homopolar dissociation energies³¹ ($q_A = q_B = 1$).

TABLE IV
HOMONUCLEAR DIATOMIC SINGLE BOND
DISSOCIATION ENERGIES

Molecule	Bond distances, Å.	Exptl. bond dissoen. energies, e.v.	β calcd. from eq. 10, e.v.
H ₂	0.7415	4.476	2.771
Li ₂	2.6725	1.084	0.842
Na ₂	3.0786	0.75	0.659
K ₂	3.923 ^a	0.514	0.523
Rb ₂	(4.1) ^a	0.47	0.504
Cs ₂	(4.3) ^a	0.45	0.477
F ₂	1.418	1.561	2.243
Cl ₂	1.988	2.475	2.055
Br ₂	2.2836	1.971	1.803
I ₂	2.6666	1.5417	1.582

^a Extrapolated from the values for Li, Na, and K.

B. Results.—The value of β_{XY} obtained from the geometric mean of β_{XX} and β_{YY} and the value of Γ obtained by introducing the bond distances given in Table VII into eq. 14 were substituted into eq. 11, which was minimized to give self-consistent values of

(according to Jaffé's equation) and by adding a Born-Landé type of term for ionic interactions.

(31) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth and Co., London, 1958; G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1959.

the bond energies and charge distributions. A National Elliott 803 computer was used for the calculations. The calculated values of the bond energies are compared with experimental values in Table V.

TABLE V
DIATOMIC SINGLE BOND DISSOCIATION ENERGIES (IN
KCAL./MOLE IN THE GAS PHASE)

Molecule	$D_{calcd.}$ Pearson ³³	$D_{calcd.}$ this work	D_{exptl}^a	Molecule	$D_{calcd.}$ Pearson	$D_{calcd.}$ this work	D_{exptl}^a
HF		135.4	134	KRb		11.4	...
HCl	97	100.4	102.2	KCs		11.6	...
HBr		85.2	86.5	KF		105.2	118
HI		70.6	70.5	KCl	145	97.1	101
HLi	88	62.3	58	KBr	132	88.5	91
HNa	89	50.5	47	KI	106	77.1	77
HK	92	46.5	43	RbCs		10.8	...
HRb	91	46.0	39	RbF		105.0	119
HCS		46.3	42	RbCl	145	97.0	102
LiNa		20.8	...	RbBr	132	88.4	90
LiK		17.9	...	RbI	106	77.3	77
LiRb		17.6	...	CsF		106.1	121
LiCs		18.2	...	CsCl	151	98.4	101
LiF		125.1	137	CsBr		90.0	91
LiCl	136	109.6	115	CsI	112	79.0	75
LiBr	122	99.0	101	FCI		56.5	60.5
LiI		84.9	81	FBr		53.4	55
NaK		15.2	14.3	FI		48.3	46
NaRb		15.2	...	ClBr	53	51.3	52.1
NaCs		16.0	...	ClI	59	47.5	49.6
NaF		106.7	107	BrI	49	40.6	41.9
NaCl	140	96.7	98				
NaBr	127	87.3					
NaI	101	75.2	71				

^a See ref. 31.

Similarly, by introducing the Madelung constant, M , $\Gamma_{cryst} = M\Gamma$, and the experimental values of ionic radii for crystals in eq. 11, the lattice energies³² and consequently heats of sublimation may be calculated (Table VI).

C. Discussion.—Although most of the results are in good agreement with experiment, some systematic discrepancies are observed. Thus, nearly all the calculated bond energies for metallic fluorides are too low, the agreement being better for chlorides, good for bromides, and the calculated values slightly too high for iodides.

Many authors³³ have discussed the particularly low bond energy of fluorine, when compared with those of the other halogens. The difference has been attributed either to strong "van der Waals" repulsions between the lone pairs of the two fluorine atoms or to the strong polarizability of iodine, which introduces a stabilizing dispersion energy. Both these terms are included in $\Sigma\Gamma$ which was originally equated to zero, and the observed discrepancies thus show the limitation of this hypothesis. Some improvement could possibly be made in the evaluation of this term, but the observed discrepancies are relatively small, and the evaluation of dispersion forces is difficult.

The calculated charge distribution obtained by minimizing E_b (eq. 11) with respect to q_A and q_B are

(32) The covalent term is again assumed to be given by $2\sqrt{q_A q_B \beta}$ although covalent bonding in crystals should take account of all neighbors. This term, however, is very small since the partial ionic character is between 92 and 98% for the alkali metal halides and between 80 and 85% for the corresponding hydrides.

(33) G. L. Caldow and C. A. Coulson, *Trans. Faraday Soc.*, **58**, 633 (1962).

TABLE VI

DIATOMIC SINGLE BOND DISSOCIATION ENERGIES OF THE CRYSTAL STATE IN KCAL./MOLE

Crystal	R _{bond} distances ^a	D _{calcd}	D _{exptl} ^{(25°)b}
LiH	2.043	116.2	110.8
LiF	2.009	197.3	201.7
LiCl	2.566	167.1	163.8
LiBr	2.747	152.3	147.5
LiI	3.002	133.4	127.5
NaH	2.44	96.3	91.9
NaF	2.31	174.3	180.3
NaCl	2.814	153.4	152.2
NaBr	2.98	141.0	138.7
NaI	3.231	124.2	120.4
KH	2.85	81.1	88.1
KF	2.664	163.0	174.3
KCl	3.138	149.4	154.7
KBr	3.285	139.2	141.9
KI	3.525	124.8	125.3
RbH	3.02	85.6	84.6
RbF	2.793	160.1	170.1
RbCl	3.267	147.6	152.4
RbBr	3.418	137.6	140.2
RbI	3.655	124.9	124.4
CsH	3.19	84.3	90.8
CsF	3.004	155.6	164.0
CsCl	3.566	143.7	151.3
CsBr	3.713	134.5	139.8
CsI	3.947	121.6	124.8

^a "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958. ^b R. T. Sanderson, "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffé, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 50, U. S. Government Printing Office, Washington, D. C., 1952.

reported in the third column of Table VII, together with the calculated and observed dipole moments. The values obtained for the ionicities of the various bonds seem at least reasonable although agreement with dipole moment values is not very good. This can be expected since no allowance has been made for polarization and secondary electronic effects including the known large lone-pair moments, and it is now widely realized that dipole moments do not represent the charge distribution in diatomic molecules satisfactorily.

The quadrupole coupling constant seems to be a far better measure of the ionicities of molecules, particularly in the case of halogen compounds, where one can expect a linear relationship to exist between the ionicity and the population of the p-orbital, at least when the molecules are not too ionic.

We find a satisfactory correlation between experimental values of quadrupole coupling constants and calculated charge densities by using the following formula (obtained from the best fit)

$$eQq = eQq_0 \left(\frac{1.887 - q_{\text{Hal}}}{0.887} \right)$$

where eQq_0 is the experimental value for the diatomic homonuclear molecule. The values obtained in this way are compared with experimental values in Table VIII.

V. Application to Single Bond Energies

Single bond energies are not only important in diatomic molecules but also in polyatomic molecules.

TABLE VII

CHARGE DISTRIBUTION AND DIPOLE MOMENT OF DIATOMIC MOLECULES

Molecule X-Y	R _{bond} distance ^{a,b,c}	Charge on atom X	qR, D.	μ _{exptl} , D.
HF	0.9171	0.5952	2.62	1.91 ^e
HCl	1.2746	0.2804	1.72	1.03 ^e
HBr	1.4138	0.1755	1.19	0.78 ^e
HI	1.6041	0.0552	0.43	0.38 ^e
HLi	1.5953	-0.5887	4.51	...
HNa	1.8873	-0.5962	5.40	...
HK	2.244	-0.6502	7.00	...
HRb	2.367	-0.6607	7.51	...
HCS	2.494	-0.6794	8.14	...
LiNa	2.87 ^d	-0.0063	0.09	...
LiK	3.27 ^d	-0.1925	3.02	...
LiRb	3.38 ^d	-0.2409	3.91	...
LiCs	3.48 ^d	-0.3159	5.28	...
LiF	1.5639	0.8825	6.63	6.28 ^e
LiCl	2.0207	0.8519	8.30	7.07 ^b
LiBr	2.1704	0.8404	8.67	6.19 ^f
LiI	2.3919	0.8123	9.33	6.25 ^f
NaK	3.49 ^d	-0.2040	3.42	...
NaRb	3.59 ^d	-0.2577	4.44	...
NaCs	3.69 ^d	-0.3406	6.03	...
NaF	1.9259	0.8807	8.14	8.37 ^g
NaCl	2.3606	0.8572	9.72	8.5 ^f
NaBr	2.5020	0.8464	10.17	...
NaI	2.7115	0.8212	10.69	...
KRb	4.01 ^d	-0.0609	1.17	...
KCs	4.11 ^d	-0.1541	3.04	...
KF	2.1714	0.9022	9.41	8.62 ^f
KCl	2.6666	0.8878	11.37	10.48 ^f
KBr	2.8207	0.8813	11.94	10.41 ^f
KI	3.0478	0.8647	12.66	11.05 ^f
RbCs	4.2 ^d	-0.0926	1.87	...
RbF	2.2655	0.9053	9.84	8.80 ^h
RbCl	2.7867	0.8918	11.93	...
RbBr	2.9447	0.8859	12.53	...
RbI	3.1768	0.8705	13.28	...
CsF	2.3453	0.9118	10.27	7.87 ^f
CsCl	2.9062	0.9002	12.56	10.40 ^f
CsBr	3.0722	0.8954	13.21	...
CsI	3.3151	0.8821	14.04	12.1 ^f
FCl	1.6281	-0.2850	2.23	0.88
FBr	1.7555	-0.3599	3.03	1.29
FI	1.985	-0.4274	4.07	...
ClBr	2.138	-0.0929	0.95	0.57 ^e
ClI	2.3207	0.2003	2.23	0.65 ^e
BrI	2.485	0.1110	1.32	...

^a See ref. a of Table VI and ref. 31. ^b D. R. Lide, *J. Chem. Phys.*, **40**, 156 (1964). ^c B. P. Dailey and C. H. Townes, *ibid.*, **23**, 118 (1955). ^d Estimated. ^e L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, *J. Chem. Phys.*, **38**, 1203 (1963). ^f A. Honig, M. Mandel, M. L. Stitch, and C. H. Townes, *Phys. Rev.*, **96**, 629 (1954). ^g R. K. Bauer and H. Lew, *Can. J. Phys.*, **41**, 1461 (1963). ^h H. Lew, D. Morris, F. E. Geiger, and J. T. Ersinger, *ibid.*, **36**, 171 (1958). ⁱ J. R. Rusk and W. Gordy, *Phys. Rev.*, **127**, 817 (1962).

We have, therefore, applied the general procedure described in the preceding sections to the calculation of the properties of single bonds. They refer, of course, to atoms where all bonds, except the one which is considered,³⁴ are assumed to be homopolar (*i.e.*, the charge density in all orbitals other than the one considered is equal to 1). Under these conditions, the

(34) We shall not treat hybridized orbitals here since this introduces an extra factor which will be considered separately.

TABLE VIII
NUCLEAR QUADRUPOLE COUPLING CONSTANTS OF
DIATOMIC HALIDES

Molecule X-Y	Total charge on Y	Calculated eQq , Mc.	Observed eQq , Mc. ^a
Cl ₂	1	(-109.74)	-109.74
BrCl	1.0929	-98.3	-103.6
ICl	1.2003	-84.9	-82.5
FCI	0.7150	-145.1	-146.0
KCl	1.8878	+0.1	+0.04
RbCl	1.8918	+0.6	+0.774
CsCl	1.9002	+1.6	+3
Br ₂	1	(769.15)	769.76
ClBr	0.9071	850.4	876.8
FBr	0.6401	1082.1	1089.0
LiBr	1.8404	40.4	37.2
NaBr	1.8464	35.2	58
KBr	1.8813	4.9	10.244
DBr (HBr)	1.1755	617.5	533
I ₂	1	(-2292.84)	-2292.84
ClI	0.7997	-2811	-2944
LiI	1.8123	-193.1	-198.15
NaI	1.8212	-170.1	-259.87
KI	1.8647	-57.7	-60
DI (HI)	1.0552	-2150	-1823

^a See ref. *c* of Table VII.

TABLE IX
ATOMIC TERMS FOR THE *n*TH VALENCE OF ATOMS COVALENTLY
BONDED IN (*n* - 1) BONDS WHERE *n* IS THE VALENCE OF
THE ATOM

Atom	B_X^*	A_X^-	R_{XX} , Å.	Bond energy of XX, e.v.	β_{XX} , e.v.
N	13.283	-11.975	1.47 ^a	1.69 ^a	1.39
P	10.222	-8.674	2.21 ^a	2.17 ^b	1.63
O	15.951	-13.707	1.48 ^a	1.52 ^a	1.76
S	11.77	-9.229	2.05 ^a	2.34 ^a	1.72

^a See ref. 31. ^b S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev.* (London), **17**, 204 (1963).

atomic terms, B_X^* and A_X^- , can be obtained directly as before (from paper I and formula 8).

$$B_X^* = B_X + \sum_i e_i \left(\frac{A_{X^+} + A_{X^-}}{2} \right)$$

These values can now be used to calculate bond properties. The results for 26 single bonds are recorded in the fourth column of Table X. These values obtained for the mean bond distances of column two are compared with observed values, when available. In the third column, the per cent ionic character is also reported.

VI. Conclusion

The results of the method developed here and in paper I for the calculation of the properties of single bonds are seen to be in satisfactory quantitative agreement with the available experimental data. It may be possible to extend it to nonconjugated polyatomic molecules. The general equation of section III provides a simple self-consistent procedure, analogous to the well-known methods for conjugated molecules, in particular that developed by Pople.

TABLE X
SINGLE BOND ENERGIES

Bond X-Y	Bond distance, Å. ^a	Charge density on X	$E_{\text{calcd.}}$ kcal.	$E_{\text{obsd.}}$ kcal.
N-P	1.49	-0.3618	67.8	69
N-O	1.36	+0.3240	52.8	53
N-S	1.74	-0.0259	44.5	...
N-H	1.01	-0.0316	91.1	93.4
N-F	1.36	+0.5484	69.9	65
N-Cl	1.79	+0.2463	45.7	46
N-Br	1.98	+0.1462	34.2	...
N-I	2.2	+0.0348	25.0	...
P-O	1.63	+0.5102	70.6	86 ^b
P-S	1.86	+0.2704	67.3	52 ^b
P-H	1.42	+0.2261	86.0	77 ^b
P-F	1.54	+0.6810	101.9	117 ^b
P-Cl	2.03	+0.4614	72.4	76 ^b
P-Br	2.23	+0.3754	58.9	62 ^b
P-I	2.46	+0.2679	46.8	44 ^b
O-S	1.5	-0.3478	66.5	...
O-H	0.96	-0.3777	106.6	110
O-F	1.42	+0.2694	44.6	45
O-Cl	1.7	-0.0207	45.6	49
O-Br	1.9	-0.1075	36.2	...
O-I	2.13	-0.2004	29.6	...
S-H	1.34	+0.0032	87.7	83
S-F	1.58	+0.5308	77.9	68
S-Cl	1.99	+0.2730	62.0	61
S-Br	2.19	+0.1748	50.9	...
S-I	2.42	+0.0595	41.9	...

^a See ref. 31. ^b See ref. *b* of Table IX.

However, it can be improved by the calculation of nonbonding interactions such as van der Waals and London forces or by introducing these interactions into the calculations in any other empirical way, for instance, by modifying the ρ -values. Actually the approximation of introducing a particular value for ρ is not an essential part of the theory, and alternative methods can be used to calculate the interelectronic repulsion terms, *e.g.*, by using multipole expansion formulas such as those proposed by Parr.³⁵

It should be emphasized also that the way in which bond energies (for polyatomic molecules) have been calculated is not completely satisfactory, since the parameters representing the resonance integrals were chosen from the experimental ($>X-X<$) bond energies, which depend on the nature of the neighboring atoms. In order to improve the treatment further the bond energy parameters should be derived from the experimental heats of formation of suitable polyatomic molecules (*e.g.*, PH₃, H₂O, H₂S). This procedure as well as the introduction of nonbonding interactions and hybridization in polyatomic systems will be developed in a forthcoming paper.

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(35) R. G. Parr, *J. Chem. Phys.*, **33**, 1184 (1960).