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A Semiempirical Treatment of Molecular Structures. I. Electronegativity and Atomic Terms

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Iczkowski and Margrave's definition of electronegativity is critically discussed, and an alternative approach based on an antisymmetrized product of mono-electronic orbitals is described. The energies for various valency states, obtained from the barycenter of the energies of all the atomic states having a common M_s^2 value, can be calculated fairly accurately from the formula: $E = \sum_i B_x + \sum_{ij} A^+ \delta_{ij} + \sum_{ij} A^- (1 - \delta_{ij})$, where B , A^+ , and A^- are constants, and i and ij represent any electron and electron pair, respectively. The extension of this method to molecular structures, which leads to a clear understanding of the concept of electronegativity ($X_x = B_x + \sum_{s \neq r} C_{xs}^2 A_x^\pm$) and of its relationship to the Coulomb integral, can serve as a basis for a self-consistent treatment of molecular structure.

I. Introduction.—The atomic terms for an atom X can be defined 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 interactions between the electrons in the neighborhood of X .

These terms, which appear in the quantum mechanical treatment of molecules and atoms, represent in the latter case the energy of an isolated atom in a particular configuration. In Hückel's one-electron LCAO-MO approximation,¹ it reduces to the Coulomb integral

$$\alpha_x = \int \phi_x^* H \phi_x d\tau = \text{constant}$$

Under this condition, the successive addition of electrons to an atom (or a molecular orbital) produces equal energy increments, thus

$$X^+ \text{ (0 electron), } E = 0$$

$$X^0 \text{ (1 electron), } E = \alpha_x$$

$$X^- \text{ (2 electrons), } E = 2\alpha_x$$

which is never observed. For example, for hydrogen, H^+ , $E = 0$; H^0 , $E = -13.6$ e.v.; H^- , $E = -14.38$ e.v. This is a very poor approximation, and several empirical methods which usually introduce electronegativity have been proposed to account for inter-electronic interactions.²

One of the most promising methods of defining electronegativities has been developed recently by Iczkowski and Margrave,³ who drew attention to recent successful attempts to obtain electron affinities from

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

(2) H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc. (London)*, **A235**, 136 (1956).

(3) R. P. Iczkowski and J. L. Margrave, *J. Am. Chem. Soc.*, **83**, 3547 (1961).

the extrapolation of successive ionization potentials. In particular, an equation of the form

$$E(q)_A = aq + bq^2 + cq^3 + dq^4 + \dots \quad (1)$$

where q is the number of electrons in the valence shell of nucleus A , and a , b , c , and d are coefficients, is a good approximation to the true equation for the energy of atoms in various states of ionization (all the electrons belonging to the same $n - l$ shell).

The differentiation of eq. 1 with respect to q gives

$$\partial E / \partial q = a + 2bq + 3cq^2 + 4dq^3 + \dots \quad (2)$$

From the relationship between the energy increments for successive ionizations and q it is possible to determine the coefficients a , b , c , and d .

As shown in Fig. 1, these relationships are usually linear, so that only the first two terms need be considered for a limited range of ionization states. Then

$$E = aq + bq^2 \quad (3)$$

and

$$\partial E / \partial q = a + 2bq \quad (4)$$

The area below the graph (Fig. 1) for two values of q (q_1 and q_2) thus gives the energy for the addition of $q_2 - q_1$ electrons. This has been realized by Iczkowski and Margrave,³ Klixbüll-Jørgensen,⁴ and Hinze, Whitehead, and Jaffé,⁵ who derived a very interesting definition of "orbital electronegativity."

Electronegativity was originally defined by Pauling⁶ as being the tendency for an atom in a molecule to

(4) C. Klixbüll-Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, London, 1962, p. 85.

(5) J. Hinze, M. A. Whitehead, and H. H. Jaffé, *J. Am. Chem. Soc.*, **85**, 148 (1963).

(6) L. Pauling, *ibid.*, **54**, 3570 (1932).

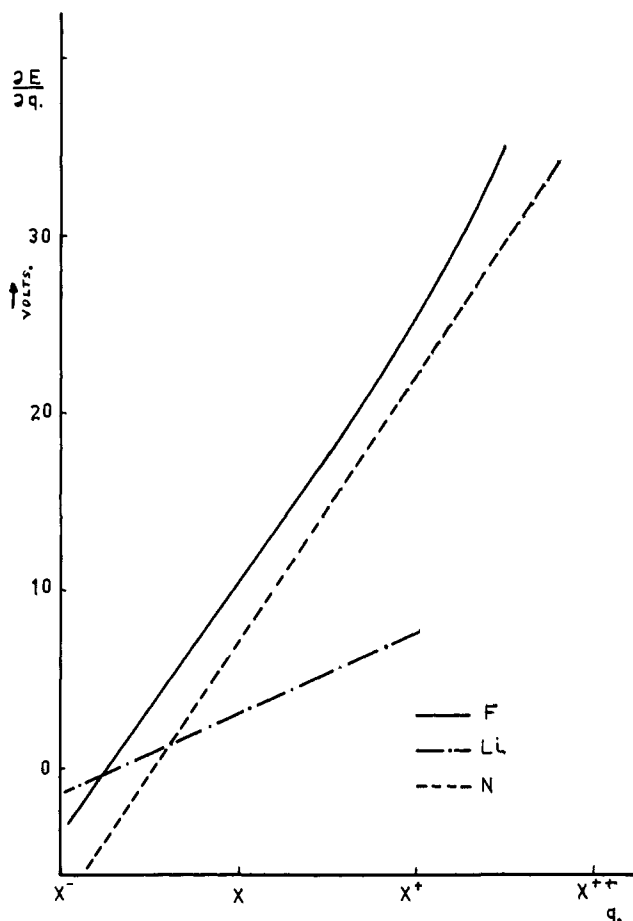


Fig. 1.—Plot of differential atomic energy with respect to the number of electrons around the core.

attract electrons to it. According to the above authors, this can be represented by $(\partial E/\partial q)$, *i.e.*, the potential around the atom. This definition implies several assumptions (see below) but has the advantage of giving a direct mathematical relationship between the energy and electronegativity of an atom, as readily shown by the following example for a monovalent atom, X.

If $q = 1$ (valency state of X), eq. 3 gives

$$E = a + b = I_V$$

Similarly when $q = 2$ (valency state of X^-)

$$E = 2a + 4b = I_V + E_V$$

from which $a = (3I_V - E_V)/2$ and $b = (E_V - I_V)/2$, where I_V is the ionization energy and E_V the electron affinity of X in its valency state.

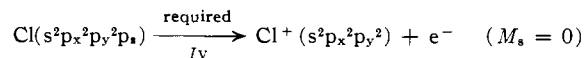
When $q = 1$ (valency state of X) the electronegativity is given by eq. 4 and leads to an expression similar to that proposed by Mulliken.⁷

$$X = (\partial E/\partial q)_{q=1} = a + 2b = (I_V + E_V)/2 \quad (5)$$

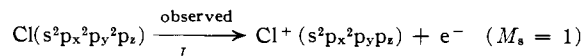
It should be noted, however, that in order to represent the electronegativity of an atom in a molecule correctly, the atom must be considered in its valency state, and this requires the introduction of electron spin. For example, the electronegativity of chlorine, calculated from Mulliken's equation with the observed ionization potential 12.9 e.v. and electron affinity 3.7 e.v., leads to a very low value of the partial ionic character of HCl

(7) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).

compared with the experimental value. This has been explained by partial sp-hybridization in the chlorine atom. An alternative explanation, which does not exclude changes in hybridization has been given by Mulliken. It takes account of the fact that electronegativity is an orbital characteristic and, therefore, both the ionization potential and the electron affinity have to be measured for the same orbital. Thus the orbital electronegativity of chlorine in its valency state is $(I_V + E_V)/2$, where I_V is given by the electronic process



and not by



Within this limitation, eq. 3 and 4 are consistent in relating the electronegativity to the charge on the atom.⁸ This definition of orbital electronegativity leads to several interesting conclusions, but also to some criticism.

(a) As suggested by Hinze, *et al.*,⁵ a molecule is stable when the tendency for an electron to go on to either atom (X and Y) is the same, *i.e.*

$$(\partial E/\partial q_A)_{q_A} = (\partial E/\partial q_B)_{q_B} = \text{group electronegativity}$$

This means that the electronegativities of both atoms in the molecule become equal, as originally suggested by Sanderson⁹; since eq. 4 relates the electronegativity to the charge density q , it becomes possible to calculate the ionic character of the bonds.¹⁰ However, care should be taken in giving a value derived from separate atoms to this average group electronegativity since E in $\partial E/\partial q$ is now a molecular energy including not only the initial atomic terms but also exchange terms.¹¹

(b) According to the above definition of electronegativity (eq. 5) the potential is determined by the total electron density around the atom. This definition implies two assumptions: (1) The occupation number q (number of electrons around the atom) may have both integral and nonintegral values. (2) The energy of an atom is a continuous and differentiable function of q . As pointed out by Hinze, Whitehead, and Jaffé, strictly speaking, neither of these assumptions is valid.

Nevertheless, from an LCAO-MO point of view, a fractional occupation number of an atomic spin orbital can be obtained. However, eq. 3 does not allow a differentiation to be made between systems where one spin orbital contains one electron (case of a

(8) Since there is a close relationship between electronegativity and the Coulomb integral α , these equations may possibly be used in calculations based, for example, on the ω -technique [A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960); G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949)]. This technique is particularly successful when applied to molecules with nonuniform charge distributions (organic ions).

If we assume that $a + 2b = \alpha_{AO}$ and $\omega\beta_0 = -2b$, eq. 4 becomes

$$\alpha = \alpha_{AO} + (1 - q)\omega\beta_0$$

which is similar to the formula proposed by Streitwieser. The coefficients α_{AO} and ω would be atomic constants instead of molecular parameters.

(9) R. T. Sanderson, *Science*, **114**, 670 (1951).

(10) R. Ferreira, *Trans. Faraday Soc.*, **59**, 1064, 1075 (1963).

(11) For the sake of completion, it is noted that an ionic interaction also contributes to the molecular potential, especially in the case of polar molecules.

hydrogen atom, where there is no repulsion) and systems in which two spin orbitals have each a fractional occupation number (case of 2 electrons with opposite spin, spending half of their life around each atom, as in the hydrogen molecule, where there is an electronic repulsion).

(c) Since an electron does not screen itself, the potential around the core should not depend upon the charge of the particle which is submitted to this potential; *i.e.*, $\partial E/\partial q \neq f(q)$. Furthermore, the law of coulombic attraction having the form Ze^2/r , it follows that the mean attraction energy of an electron by the core (considered as a central field interaction) must have the form $E = aq$ for a given core and fixed mean distance. Therefore, when only one electron is involved, the bq^2 term in Iczkowski and Margrave's equation should vanish.

Finally, it should be pointed out that the Coulomb integrals (diagonal terms in Hückel's one-electron approximation) which have the dimensions of energy, are often equated to the ionization energy of the isolated atoms,¹² although experience has shown that in order to represent the charge distribution (and even the bonding energies¹³) satisfactorily, it should be related to the electronegativities of the atoms. It is difficult to reconcile these two interpretations and, as pointed out by Coulson and Longuet-Higgins,¹⁴ it is a pity that no precise interpretation can be given to these terms.

Although the definition of electronegativity presented above can readily be criticized, it cannot be denied that it shows some interesting qualitative aspects. For this reason, an alternative way of defining the electronegativity and the Coulomb integral is proposed, according to which each electron is considered separately. This definition differs fundamentally but not formally from the preceding one and is derived directly from a theoretical approach.

II. Theoretical Approach to Atomic Structure.—

For a system of n electrons, the total wave function on which an Hamiltonian H operates, is given by the antisymmetrized product of the monoelectronic wave functions, as

$$\Phi_{\Lambda} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_{1\alpha}(1) & \chi_{1\beta}(1) & \chi_{2\alpha}(1) & \cdots \\ \chi_{1\alpha}(2) & \chi_{1\beta}(2) & \chi_{2\alpha}(2) & \cdots \\ \vdots & \vdots & \vdots & \ddots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} \quad (6)$$

where Φ_{Λ} is the wave function corresponding to a configuration Λ , with the electrons i distributed into spin orbitals $\chi_p S$ of spin $S = \alpha$ or β .

A. The Total Energy of an Atomic State.—Consider an atom containing n valency electrons (1, 2, ..., i , j , ..., n) moving in the field of a core made up of the nucleus and electrons in the inner shells. The Hamiltonian operator acting on the atomic wave function Φ_{Λ} is¹⁵

$$H = \sum_i H_{\text{core}}(i) + \sum_{ij} \frac{e^2}{r_{ij}}$$

(12) In Hückel's approximation, the total energy is given by $E = n\alpha + m\beta$ where $m\beta$ represents the bond energy and $n\alpha$ is the sum of the ionization potentials of the isolated atoms.

(13) R. G. Pearson, *J. Chem. Phys.*, **17**, 969 (1949).

(14) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947); **A192**, 16 (1947-1948).

(a) $H_{\text{core}}(i)$ is the energy operator acting on each electron i in the field of the core. This Hamiltonian involves a term $-Ze^2/r_{Ni}$ which represents the electrostatic attraction between the nucleus of charge Ze and the electron i .

According to Unsöld's¹⁶ theorem, the core electrons produce a spherically symmetrical potential,¹⁷ which can be represented by a "central field approximation." The electrostatic repulsion between the electron i and the core electrons will therefore be Ce^2/r_{Ni} where Ce is a virtual negative charge at the center of the atom. Thus

$$H_{\text{core}}(i) = -\frac{Ze^2}{r_{Ni}} + \frac{Ce^2}{r_{Ni}} = \frac{(C-Z)e^2}{r_{Ni}}$$

(b) e^2/r_{ij} is the operator for electrostatic repulsion between electrons i and j , considered as particles whose motion is described by wave functions. The total Hamiltonian is therefore given by

$$H = \sum_i \frac{(C-Z)e^2}{r_{Ni}} + \sum_{ij} \frac{e^2}{r_{ij}}$$

and the total energy for configuration Λ by

$$E_{\Lambda} = \int \Phi_{\Lambda}^* H \Phi_{\Lambda} d\tau$$

Since the atomic spin orbitals are orthogonal and normalized, the total energy of a particular configuration is given by the equation^{18,19}

$$E_{\Lambda} = \sum_q I_q + \frac{1}{2} \sum_{qr} (J_{qr} - K_{qr}') \quad (7)$$

where

$$I_q = \int \chi_q S_q^*(i) \frac{(C-Z)e^2}{r_{Ni}} \chi_q S_q(i) d\tau_i \quad (8)$$

is the core integral for the spin orbital $\chi_q S_q$

$$J_{qr} = \int \chi_q S_q^*(i) \chi_r S_r^*(j) \frac{e^2}{r_{ij}} \chi_q S_q(i) \chi_r S_r(j) d\tau_i d\tau_j \quad (9)$$

is the Coulomb integral between the orbitals $\chi_q S_q$ and $\chi_r S_r$. Finally

$$K_{qr} = \int \chi_q S_q^*(i) \chi_r S_r^*(j) \frac{e^2}{r_{ij}} \chi_q S_q(j) \chi_r S_r(i) d\tau_i d\tau_j \quad (10)$$

is the exchange integral between $\chi_q S_q$ and $\chi_r S_r$. $K_{qr}' = K_{qr}$ when χ_q and χ_r have the same spin, $S_q = S_r$ and $K_{qr}' = 0$; when χ_q and χ_r have opposite spin, $S_q \neq S_r$.

B. Procedure.—When the final objective is the calculation of molecular energies, it is not necessary to consider all the spectroscopic atomic states. We therefore propose a classification of atomic states by considering only those valence states which are necessary for the calculation of molecular properties. Accordingly, the various atomic states will be those characterized by a particular value of M_s^2 , *i.e.*, the

(15) M. G. Mayer and A. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(16) A. Unsöld, *Ann. Physik*, **82**, 355 (1927).

(17) It is understood that the inner shells containing the core electrons are complete.

(18) J. C. Slater, *Phys. Rev.*, **34**, 1293 (1929).

(19) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, Cambridge, 1953.

component of the spin angular momentum of the total system, on an arbitrarily chosen axis.

In order to define the required groups of atomic states, the electrons are allocated to the various atomic orbitals (s, p, d, etc.) and given appropriate spins in accordance with the Pauli exclusion principle.

When an atomic state cannot be defined unequivocally in this way (which happens when a common M_s^2 is found for several states, e.g., 1D and 1S), the center of gravity of the electronic levels or "barycenter" of the states having a common M_s^2 for the same configuration will be used to determine the energy. To illustrate this, the important states for elements containing only s- and p-electrons in their valency shells, classified according to this definition, are given in Tables I and II.

The theoretical calculation of the energy of the various atomic states requires a knowledge of the various integrals defined above (eq. 7, 8, 9, and 10).

Usually an analytical form²⁰ is given to the wave function $\chi_q S_q$ which is then used to solve these integrals.²¹

We suggest an alternative procedure, based on the physical interpretation of these integrals, which consists in giving them numerical values, thus providing a semiempirical method similar to that of Pariser and Parr.²²

Thus the "Core integral" I_q (eq. 8) is the energy of an electron i in the atomic orbital χ_q of spin S_q in the field of the core, and in the absence of interaction with other electrons in the same electron shell.

This energy should be similar to that calculated for hydrogen-like atoms, and, for a given core, can be equated to a constant B_x^l where l is the azimuthal quantum number, characterizing the type of orbital (s, p, d, . . .)²³ of the valency shell of atom X to which the energy B refers.

The integrals J_{qr} (eq. 9) and K_{qr} (eq. 10) represent, respectively, the Coulomb energy and the exchange energy of interaction between two electrons of two atomic spin orbitals q and r . Although the integrals J_{qr} do not depend on spin (since they are classical Coulomb interactions) the integrals K_{qr} will differ from zero only when the two electrons occupy orbitals characterized by the same spin. The total interaction energy between two electrons with the same spin, the same principal quantum number, and with azimuthal quantum numbers l and l' will be

$$J_{ll'} - K_{ll'} = A^{+ll'}$$

Similarly, between two atoms of opposite spin the energy of interaction will be

$$J_{ll'} = A^{-ll'}$$

According to our procedure of defining the various atomic states, $A^{+ll'}$ and $A^{-ll'}$ should remain constant only when orbitals l and l' have the same azimuthal quantum number (since we cannot decide which p- or d-orbital is used).

(20) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930); C. Zener, *ibid.*, **36**, 51 (1930).

(21) C. C. Roothaan, *Revs. Mod. Phys.*, **23**, 69 (1951); *J. Chem. Phys.*, **19**, 1445 (1951).

(22) R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(23) For hydrogenic orbitals, B_x^{2s} and B_x^{2p} should be equivalent. We always assume them to be different because s and p electrons interact differently with the core electrons. This agrees with experimental observation.

In order to simplify this treatment, we tentatively assume that, when the electrons belong to the same shell, $A^{+ll'}$ and $A^{-ll'}$ remain constant even if l and l' are not equal. There is no theoretical justification for this but, owing to the difficulty of treating variable A 's and since the total energy is relatively insensitive to such changes, we shall use this hypothesis. This leads to a diagonalization of the matrix, and we can define A_x^+ as the mean value of $A_{ll'}^+$, and A_x^- as the mean value of $A_{ll'}^-$ for all the values of l . A_x^+ and A_x^- are therefore, the mean interaction energies between two electrons of the same spin and of opposite spin, respectively, in each of the various states defined above. Equation 7 then reduces to the final form

$$E = \sum_i B_x^i + \frac{1}{2} \sum_{ij} A_x^+ \delta_{ij} + \frac{1}{2} \sum_{ij} A_x^- (1 - \delta_{ij}) \quad (11)$$

where δ_{ij} is the Kronecker delta with $\delta_{ij} = 1$ if the spins of i and j are parallel, and $\delta_{ij} = 0$ if the spins are antiparallel.

For the various states characterized above, the formula reduces to the expressions which are given in the fifth column of Tables I and II.

TABLE I
CLASSIFICATION OF THE ATOMIC ENERGY LEVELS (GROUND STATE AND LOWER EXCITED STATE)

| Order no. | $\pm M_s$ | Electronic distribution | "Barycenter" | Energy |
|-----------|-----------|-------------------------|----------------------------|-------------------------------|
| 1 | $1/2$ | s^1 | 2S | B^s |
| 2 | 0 | s^2 | 1S | $2B^s + A^-$ |
| 3 | $1/2$ | s^2p | 2P | $2B^s + B^p + 2A^- + A^+$ |
| 4 | 0 | s^2p^2 | $(5^1D + ^1S + 3^3P)/9$ | $2B^s + 2B^p + 4A^- + 2A^+$ |
| 5 | 1 | s^2p^2 | 3P | $2B^s + 2B^p + 3A^- + 3A^+$ |
| 6 | $1/2$ | s^2p^3 | $(10^1D + 6^3P + 2^1S)/18$ | $2B^s + 3B^p + 6A^- + 4A^+$ |
| 7 | $3/2$ | s^2p^3 | 4S | $2B^s + 3B^p + 4A^- + 6A^+$ |
| 8 | 0 | s^2p^3 | $(5^1D + ^1S + 3^3P)/9$ | $2B^s + 4B^p + 9A^- + 6A^+$ |
| 9 | 1 | s^2p^3 | 3P | $2B^s + 4B^p + 8A^- + 7A^+$ |
| 10 | $1/2$ | s^2p^4 | 2P | $2B^s + 5B^p + 12A^- + 9A^+$ |
| 11 | 0 | s^2p^4 | 1S | $2B^s + 6B^p + 16A^- + 12A^+$ |

TABLE II
EXCITED ATOMIC ENERGY LEVELS

| Order no. | $\pm M_s$ | Electronic distribution | "Barycenter" | Energy |
|-----------|-----------|-------------------------|--------------|-----------------------------|
| 12 | $1/2$ | p | 2P | B^p |
| 13 | 1 | sp | 3P | $B^s + B^p + A^+$ |
| 14 | $3/2$ | sp^2 | 4P | $B^s + 2B^p + 3A^+$ |
| 15 | 2 | sp^3 | 5S | $B^s + 3B^p + 6A^+$ |
| 16 | $3/2$ | sp^4 | 4P | $B^s + 4B^p + 6A^+ + 4A^-$ |
| 17 | 1 | sp^5 | 3P | $B^s + 5B^p + 7A^+ + 8A^-$ |
| 18 | $1/2$ | sp^6 | 2S | $B^s + 6B^p + 9A^+ + 12A^-$ |

Considering only the first two rows of the periodic table, the following atomic constants have to be determined for each atom. These constants can be de-

| | Nucleus-electron attraction | Electron-electron repulsion |
|----------|------------------------------|---|
| Hydrogen | B_x^{1s} | $A_x^- = A_x^{-1s1s}$ |
| 1st row | $B_x^{2s} B_x^{2p}$ | $A_x^- = A_x^{-2s2s} = A_x^{-2s2p} = A_x^{-2p2p}$ $A_x^+ = A_x^{-2s2p} = A_x^{-2p2p}$ |
| 2nd row | $B_x^{3s} B_x^{3p} B_x^{3d}$ | $A_x^- = A_x^{-3s3s} = A_x^{-3s3p} =$ $A_x^{-3s3d} = A_x^{-3p3p} = A_x^{-3p3d} =$ A_x^{-3d3d} $A_x^+ = A_x^{-3s3p} = A_x^{-3s3d} =$ $A_x^{-3p3p} = A_x^{-3p3d} = A_x^{-3d3d}$ |

termined by comparing the calculated and experimental values of the energies for the various states given in Tables I and II.

TABLE III
EXPERIMENTAL TRANSITION ENERGIES (IN E.V.) FOR COMMON ATOMS (GROUND STATE AND LOWER EXCITED STATE)

| Transition between the states | H | Li | Na | K | C | Si | N | P | O | S | F | Cl | Br | I |
|-------------------------------|--------|-------|-------|--------|--------|-------|--------|-------|---------|--------|---------|--------|--------|--------|
| 0-1 | 13.595 | 5.390 | 5.138 | 4.339 | 64.476 | 45.13 | 97.863 | 65.01 | 138.080 | 88.03 | 185.139 | 114.27 | | |
| 2-1 | 0.750 | 0.82 | 0.47 | [0.69] | 47.864 | 33.46 | 74.450 | 51.35 | 113.873 | 72.5 | 157.117 | 96.7 | | |
| 3-2 | | | | | 24.376 | 16.34 | 47.426 | 30.16 | 77.394 | 47.29 | 114.214 | 67.80 | | |
| 5-3 | | | | | 11.264 | 8.149 | 29.605 | 19.65 | 54.934 | 35.0 | 87.23 | 53.5 | | |
| 5-4 | | | | | 1.00 | 0.646 | 1.5047 | 0.909 | 1.990 | 1.154 | 2.475 | 1.396 | | |
| 7-5 | | | | | 1.12 | 1.46 | 14.54 | 11.0 | 35.146 | 23.4 | 62.646 | 39.90 | 35.9 | |
| 7-6 | | | | | | | 2.515 | 1.556 | 3.518 | 2.036 | 4.477 | 2.475 | 2.148 | |
| 9-7 | | | | | | | 0.05 | 0.77 | 13.614 | 10.357 | 34.98 | 23.80 | 21.6 | 19.09 |
| 9-8 | | | | | | | | | 1.558 | 0.942 | 2.056 | 1.187 | (1.22) | 1.395 |
| 10-9 | | | | | | | | | 1.465 | 2.07 | 17.42 | 13.01 | 11.84 | 10.454 |
| 11-10 | | | | | | | | | | | 3.48 | 3.69 | 3.49 | 3.21 |

TABLE IV
EXPERIMENTAL TRANSITION ENERGIES (IN E.V.) FOR COMMON ATOMS (EXCITED STATES)

| | Li | Na | K | C | Si | N | P | O | S | F | Cl | Br | I |
|-------|-------|-------|-------|-------|-------|--------|-------|--------|-------|--------|--------|--------|--------|
| 1-12 | 1.847 | 2.103 | 1.613 | | | | | | | | | | |
| 2-13 | | | | 6.488 | 6.544 | | | | | | | | |
| 3-14 | | | | 5.332 | 5.479 | 7.096 | 7.084 | | | | | | |
| 5-15 | | | | 4.181 | (4.4) | 5.846 | 6.501 | 7.475 | | | | | |
| 7-16 | | | | | | 10.924 | 7.397 | 14.868 | 9.878 | 18.860 | 12.274 | | |
| 9-17 | | | | | | | | 15.656 | 8.963 | 20.456 | 11.637 | 12.100 | 10.391 |
| 10-18 | | | | | | | | | 20.89 | | | | 10.167 |

The experimental energies of the various excited states are taken from the tables of atomic energy levels,²⁴ and the most likely values of the electron affinities, which are also necessary, have been taken from the literature.^{25,26} The differences in the energies between the various important states characterized above have been calculated for some common atoms and are given in Tables III and IV.

The final objective of this treatment being the calculation of bond properties, the method should be particularly accurate in the neighborhood of the valency state of each atom. For this reason the parameters A and B were calculated by comparing the experimental energies of the states close to the normal valency state (usually the neutral atom) with the energy values calculated from eq. 11.

TABLE V
CALCULATED VALUES (IN E.V.) OF THE COEFFICIENTS A AND B FOR SOME COMMON ATOMS

| Atom | B^* | B^p | A^- | A^+ |
|------|----------|----------|--------|--------|
| H | -13.595 | | 12.845 | ... |
| Li | -5.390 | -3.543 | 4.57 | ... |
| Na | -5.138 | -3.035 | 4.668 | ... |
| K | -4.339 | -2.726 | 3.649 | ... |
| C | -49.884 | -42.696 | 11.144 | 10.144 |
| Si | -35.2 | -28.862 | 7.335 | 6.689 |
| N | -69.593 | -58.669 | 11.975 | 10.718 |
| P | -50.759 | -43.362 | 8.674 | 7.896 |
| O | -96.247 | -80.591 | 13.707 | 12.149 |
| S | -64.523 | -55.26 | 9.229 | 8.287 |
| F | -130.174 | -109.284 | 15.996 | 13.94 |
| Cl | ... | -73.678 | 10.507 | 9.320 |
| Br | ... | -66.82 | 9.57 | 8.350 |
| I | -69.665 | -59.498 | 8.639 | 7.244 |

C. Discussion.—In principle, eq. 11 enables the energy of the barycenter of the atomic states (as de-

(24) C. E. Moore, Natl. Bur. Stand. Circ. 467, U. S. Govt. Printing Office, Washington, D. C., 1949.

(25) H. O. Pritchard, *Chem. Rev.*, **52**, 529 (1953).

(26) B. Edlen, *J. Chem. Phys.*, **33**, 98 (1960).

finned above) to be calculated, when the inner shells of the core are entirely filled.

Our results will now be compared with those given in the first section. If all the valency electrons belong to orbitals of the same type (same azimuthal quantum number)

$$B_x^l = B_x(\text{constant})$$

and if the exchange integrals K (eq. 10), which are small, are neglected

$$A^+ = A^- = \text{constant} = A_x$$

Equation 11 then reduces to

$$E = \sum_i B_x + \frac{1}{2} \sum_{ij} A_x$$

where i equals the number of electrons and ij is a pair of electrons; thus

$$E = qB_x + \frac{q(q-1)}{2} A_x$$

where q is the occupation number.

Assuming $a = B_x - (A_x/2)$ and $b = (A_x/2)$ we finally find

$$E = aq + bq^2$$

which is analogous to the empirical formula proposed by Iczkowski and Margrave (eq. 3), which thus appears to be a particular case of eq. 11. For a given orbital, the parabolic relation $E = aq + bq^2$ (eq. 3) is as valid as eq. 11. In this orbital, B_x^l is constant for the two electrons and K is exactly zero since the spins are necessarily opposed.

The close agreement observed between the empirical equation (eq. 3) and the experimental values (Fig. 1) is also found with eq. 11. It should be noted, however, that this general formula may be applied equally well to all the valency states and it eliminates the necessity of a long and detailed calculation such as was made

by Hinze, *et al.*, for each particular case.²⁷ This has been illustrated in Table VI for the particular case of oxygen.

TABLE VI
COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED ENERGIES FOR VARIOUS STATES OF OXYGEN^a

| Order no. | Electron distribution | $\pm M_S$ | Energy, e.v. | |
|-----------|---|---|---|--|
| | | | Exptl. | Calcd. |
| 15 | $2s^2p^2$ | 2 | 56.235 | 55.03 |
| 4 | $O^{+2} \begin{cases} 2s^22p^2 \\ 2s^22p^2 \end{cases}$ | 0 | 50.75 | 45.61 |
| 5 | $2s^22p^2$ | 1 | 48.76 | 44.05 |
| 16 | $\begin{cases} 2s^2p^4 \\ 2s^22p^3 \\ 2s^22p^3 \end{cases}$ | $\begin{matrix} 3/2 \\ 1/2 \\ 3/2 \end{matrix}$ | $\begin{matrix} 28.48 \\ 17.132 \\ 13.614 \end{matrix}$ | $\begin{matrix} 29.27 \\ 16.74 \\ 13.616 \end{matrix}$ |
| 6 | $O^+ \begin{cases} 2s^2p^4 \\ 2s^22p^3 \end{cases}$ | $\begin{matrix} 3/2 \\ 1/2 \end{matrix}$ | $\begin{matrix} 15.656 \\ 1.558 \end{matrix}$ | $\begin{matrix} 15.657 \\ 1.558 \end{matrix}$ |
| 7 | $2s^22p^3$ | $3/2$ | 13.614 | 13.616 |
| 17 | $\begin{cases} 2s^2p^5 \\ 2s^22p^4 \\ 2s^22p^4 \end{cases}$ | $\begin{matrix} 1 \\ 0 \\ 1 \end{matrix}$ | $\begin{matrix} 15.656 \\ 1.558 \\ 0 \end{matrix}$ | $\begin{matrix} 15.657 \\ 1.558 \\ 0 \end{matrix}$ |
| 8 | $O \begin{cases} 2s^2p^5 \\ 2s^22p^4 \\ 2s^22p^4 \end{cases}$ | $\begin{matrix} 1 \\ 0 \\ 1 \end{matrix}$ | $\begin{matrix} 15.656 \\ 1.558 \\ 0 \end{matrix}$ | $\begin{matrix} 15.657 \\ 1.558 \\ 0 \end{matrix}$ |
| 18 | $O^- \begin{cases} 2s^2p^6 \\ 2s^2sp^5 \end{cases}$ | $\begin{matrix} 1/2 \\ 1/2 \end{matrix}$ | $\begin{matrix} \dots \\ -1.465 \end{matrix}$ | $\begin{matrix} 14.19 \\ -1.465 \end{matrix}$ |
| 10 | $2s^2sp^5$ | $1/2$ | -1.465 | -1.465 |
| 11 | $O^{-2} 2s^22p^6$ | 0 | (6.77) ^b | 9.219 |

^a The zero of energy is arbitrarily put for the normal state of oxygen $2s^22p^4M_S = 1$. ^b Estimated from lattice energy calculations; see E. C. Baughan, *Trans. Faraday Soc.*, **57**, 1863 (1961).

These results show the validity of eq. 11, since the energy of many atomic states can readily be calculated to a reasonable degree of accuracy from the values of A and B alone. Similar agreement between experimental energies is obtained in other cases.

There is, however, a fundamental difference between our method and the empirical equation, because we consider the electrons as particles. There are several consequences of this approach, which answers the criticisms of the empirical method which we have discussed in the previous section.

When the system contains one electron only in the valency shell, the energy $E = B_x^i$, so that the repulsion term A appears only when several electrons are in this shell. Interelectronic repulsions are thus introduced in a correct way as required in our preliminary discussion. Moreover, the equation determining the energy is *noncontinuous* and cannot be differentiated with respect to total charge. The potential acting on an electron in the field of the other particles is obtained by dividing each term of the equation by the unit charge on the electron, *i.e.*

$$\partial E / \partial e_i = \text{potential} = E / e_i = B_x^i + \frac{1}{2} \sum_{j \neq i} A'^+ \delta_{ij} + \frac{1}{2} \sum_{j \neq i} A'^- (1 - \delta_{ij})$$

where B' , A'^+ , A'^- are the potentials, equal to B , A^+ , and A^- divided by e (the charge of an electron).

Numerically this potential is equal to the ionization energy of electron e_i , and there is, therefore, no relation between this potential and the electronegativity of the atom. This can be easily understood since electronegativity is not a measurable atomic quantity. The fact that it is well represented by an empirical equation such as eq. 3 does not show that it is a definable atomic entity with the dimensions of a potential. It is only by the examination of atomic terms in molecules that an entity such as electronegativity can be defined as will be shown in the next section.

(27) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

III. Theoretical Approach to Molecular Structures.—For the study of molecular structures, the antisymmetrized product of the wave functions remains essentially of the same form as in eq. 6, although the mono-electronic wave functions χ 's are now molecular wave functions. In the LCAO-MO method²⁸

$$\chi = \sum_P C_P \phi_P$$

where ϕ_P are atomic spin orbitals and C_P the variational coefficients.

The Hamiltonian has the form

$$H = - \sum_{X_i} \frac{e^2}{r_{X_i}} + \sum_{ij} \frac{e^2}{r_{ij}} + \sum_{XY} \frac{e^2}{r_{XY}}$$

Solution of this problem leads to two types of terms: (a) atomic terms as described above, including all the integrals representing the interactions of a nucleus with the electrons around it, and between these electrons around the nucleus; (b) molecular terms including all the integrals appropriate to two nuclei, *i.e.*, interactions between electrons localized on atomic orbitals of different atoms, interactions between a nucleus and an electron belonging to an atomic orbital of a different nucleus, and resonance integrals. These terms will be discussed in a forthcoming paper.

The atomic terms are made up of the following three types of integral with the appropriate coefficients

$$C_{X_r}^2 \int \phi_{X_r}^*(i) \frac{e^2}{r_{X_i}} \phi_{X_r}(i) d\tau \quad (12)$$

where C_{X_r} and ϕ_{X_r} represent, respectively, the coefficient and the wave function of the spin orbital r of atom X

$$C_{X_r}^2 C_{X_s}^2 \int \phi_{X_r}^*(i) \phi_{X_s}^*(j) \frac{e^2}{r_{ij}} \phi_{X_r}(i) \phi_{X_s}(j) d\tau_i d\tau_j \quad (13)$$

and

$$C_{X_r}^2 C_{X_s}^2 \int \phi_{X_r}^*(i) \phi_{X_s}^*(j) \frac{e^2}{r_{ij}} \phi_{X_r}(j) \phi_{X_s}(i) d\tau_i d\tau_j \quad (14)$$

These atomic integrals are of the type defined above, and therefore it is possible to a first approximation to give them the values already calculated, *i.e.*

$$\text{eq. 12} = C_{X_r}^2 B_X^r$$

$$\text{eq. 13} - \text{eq. 14} = C_{X_r}^2 C_{X_s}^2 A_X^{\pm}$$

The variational theorem requires that

$$\partial E / \partial C_{X_r} = 0 \text{ for each } C_{X_r}$$

which leads to

$$\partial E / \partial C_{X_r} = 2C_{X_r} [B_X^r + \sum_{s \neq r} C_{X_s}^2 A_X^{\pm} - E] + \frac{\partial E'}{\partial C_{X_r}} = 0 \quad (15)$$

E' is the energy corresponding to the molecular terms. For a homopolar molecule, *e.g.*, H_2 , the spin orbitals $1s\alpha$ and $1s\beta$ of each atom contribute one-half

(28) C. A. Coulson, *Quart. Rev. (London)*, **1**, 144 (1947).

to the two molecular spin orbitals,²⁹ so that $C_{Hr}^2 = C_{Hs}^2 = 0.5$. Substituting these in eq. 15 gives

$$\frac{\partial E}{\partial C_{Hr}} = 2C_{Hr}[B_H^r + 0.5A_{H^-} - E] + \left(\frac{\partial E'}{\partial C_{Hr}}\right) = 0$$

In the secular equation which results from the variational treatment, the diagonal terms are formed mainly³⁰ from

$$B_H^r + 0.5A_{H^-} - E$$

Now

$$B_H^r + 0.5A_{H^-} = (I_H + E_H)/2$$

is the neutral electronegativity of the atom. Our treatment thus introduces electronegativity into the diagonal terms of the secular equation in a completely consistent way. This quantity can be defined only in a molecular context, and it is important to realize that it has the dimensions of energy; it is in fact the energy of an electron in the field of the other bonding electrons and the core. When two electrons only are involved in one homopolar bond, the electronegativity is

$$B_X + 0.5A_{X^-} = (I_V + E_V)/2$$

for each electron around each atom.

It must be realized that electronegativity is not a measurable molecular constant, since it varies from molecule to molecule like the total energy (since it is a function of the variational parameters) and therefore a characteristic value cannot be given to it.

A neutral electronegativity can, nevertheless, be defined, which is the electronegativity of an atom in a homopolar molecule (where the C_{Xs}^2 for all the bonding electrons are equal to 0.5). With this restriction, the

(29) In the general case, C_X cannot be determined in advance, but starting with an initial arbitrary value the method can be made self-consistent.

(30) There is similarly a contribution from the bonding term, but this is small in comparison with the atomic term.

neutral electronegativity can be calculated. The formula developed above for atomic energies (eq. 15) is particularly suitable for these calculations, and hence the electronegativities for a large number of valency and hybridized orbitals can readily be obtained.

$$X_X = B_X^r + \sum_{s \neq r} C_{Xs}^2 A_{X^+} \delta_{rs} + \sum_{s \neq r} C_{Xs}^2 A_{X^-} (1 - \delta_{rs})$$

These are given in Table VII.

TABLE VII
NEUTRAL ELECTRONEGATIVITY OF SOME COMMON ATOMS

| Atom | Valence state | Orbital type | Electronegativity, e.v. | Atom | Valence state | Orbital type | Electronegativity, e.v. |
|------|---------------|--------------|-------------------------|------|---------------|--------------|-------------------------|
| H | s | s | 7.17 | N | s^2p^3 | p | 7.30 |
| Li | s | s | 3.10 | P | s^2p^3 | p | 5.89 |
| Na | s | s | 2.80 | O | s^2p^4 | p | 9.10 |
| K | s | s | 2.51 | S | s^2p^4 | p | 7.16 |
| C | sp^3 | s | 12.38 | F | s^2p^5 | p | 11.48 |
| | | p | 5.19 | | | | |
| | didi III | σ | 8.79 | Cl | s^2p^5 | p | 8.94 |
| | trtrtr II | σ | 7.59 | Br | s^2p^5 | p | 8.28 |
| | tetetete | σ | 6.99 | I | s^2p^5 | p | 7.53 |
| Si | sp^3 | s | 10.50 | | | | |
| | | p | 4.16 | | | | |
| | didi III | σ | 7.33 | | | | |
| | trtrtr II | σ | 6.27 | | | | |
| | tetetete | σ | 5.74 | | | | |

As already pointed out, an exact calculation of the electronegativity and hence of the bond properties requires a knowledge of the coefficients of the atomic orbitals and of the molecular terms. These will be discussed in a forthcoming paper which describes a new self-consistent treatment of molecular structures.

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The Nature of the Two-Electron Chemical Bond.¹ V. Electron Pairing and H_3^+

BY HARRISON SHULL

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Data originally calculated by Hirschfelder, Eyring, and Rosen on linear symmetrical H_3^+ are analyzed in terms of approximate natural orbitals. Every aspect of the analysis suggests that this form of H_3^+ is best described as a relatively normal single bond in which is embedded a third proton. Hopton and Linnett (*J. Chem. Soc.*, 1553 (1962)) drew the conclusion from the same data (without, however, using natural orbitals) that H_3^+ was best described by a nonpairing formulation. The present calculation and discussion does not support these authors' "propaganda against pairing."

Introduction

A recent paper by Hopton and Linnett^{2a} discusses an old wave function of Hirschfelder, Eyring, and Rosen^{2b} for linear H_3^+ in several approximations which they class as molecular orbital (MO), valence bond (VB), and nonpairing (NP) schemes, there being three of the latter considered. Hopton and Linnett maxi-

mize the overlap between the respective wave functions for these schemes and the one computed by the variational method. They conclude that since the overlap for the NP functions is 0.997–0.998 whereas the MO and VB overlaps are 0.982 the NP formalism is "best" and that there is "no particular and special energy effect involved in 'the pairing of the electrons'." This is adduced to be further support to a rather general discussion of many molecular systems in terms of a "nonpairing" formalism.³

(1) Supported in part by grants from the U. S. Air Force Office of Scientific Research and from the U. S. National Science Foundation.

(2) (a) J. D. Hopton and J. W. Linnett, *J. Chem. Soc.*, 1553 (1962); (b) J. O. Hirschfelder, H. Eyring, and N. Rosen, *J. Chem. Phys.*, **4**, 130 (1936).

(3) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961).