

Electronic Structures of Molecules XI. Electroaffinity, Molecular Orbitals and Dipole Moments

Robert S. Mulliken

Citation: [The Journal of Chemical Physics](#) **3**, 573 (1935); doi: 10.1063/1.1749731

View online: <http://dx.doi.org/10.1063/1.1749731>

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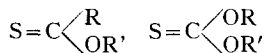
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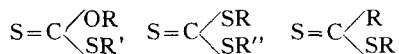


fact that the H atom may be labile and tend to jump from one O atom to the other, or to locate itself between them. These expectations seem to be confirmed by the experimental evidence, but a detailed consideration will not be undertaken here.

Similarly, molecules like



etc., should have characteristic S=C absorption¹⁵ like that in S=CCl₂. The same is true of molecules like



etc.¹⁵ In all these cases, the molecule must *also* be regarded as a derivative of H₂O or H₂S, and there should be absorption regions, but at shorter wavelengths than the first absorption region of the C=O or C=S, associated with excitation of *np* nonbonding electrons of the single-bonded O or S atoms.¹ It is interesting to note that, although the most easily excited electron in both $\begin{array}{c} \diagup C=O \\ \diagdown \end{array}$ and $\begin{array}{c} \diagup O \\ \diagdown \end{array}$ is found to be a nonbonding *2p* electron of the O atom, excitation is easier in the former case, partly because *I* is lower there for the nonbonding electron, and partly because *I* is higher for the lowest available excited orbital there. Analogous statements hold, of course, for the S compounds.

SEPTEMBER, 1935

JOURNAL OF CHEMICAL PHYSICS

VOLUME 3

Electronic Structures of Molecules

XI. Electroaffinity, Molecular Orbitals and Dipole Moments

ROBERT S. MULLIKEN, *Ryerson Physical Laboratory, University of Chicago*

(Received June 25, 1935)

A convenient criterion for defining equal electronegativity of two atoms is stated in terms of coefficients in LCAO approximate molecular orbitals. Connections between relative electronegativities, coefficients in LCAO orbitals, effective charges on atoms in partially polar molecules, and dipole moments, are then analyzed, and various equations are obtained expressing these connections. The discussion is largely applicable to polyatomic as well as to diatomic molecules. A theoretical derivation is given for an empirical equation, found by Pauling, which forms a basis for the latter's approximate scale of relative electronegativities. Pauling's and other possible approximate scales are discussed, and it is shown how an approximate "absolute electroaffinity" can conveniently be defined on each scale. A very rough theoretical justification is given for the empirically observed proportionality between relative electronegativities obtained from Paul-

ing's and from the writer's scale. The necessary existence of a "homopolar dipole" contribution to the electric moment of any bond is shown, provided the atoms forming the bond are of unequal size. By "homopolar dipole" is meant a contribution which would not vanish, for atoms of unequal size, even if they are of equal electroaffinity. Dipole moments of H₂O, NH₃ and HX are briefly discussed. It is concluded that the dipole moment scale of electronegativity is probably not well founded. An important object of the paper is to show how electroaffinity and other data can be used in the approximate determination of the polarities of molecular orbitals and so of bonds, the results being expressed both in terms of coefficients in LCAO molecular orbitals and in terms of effective charges transferred. Applications are made to the electronic structures of various diatomic molecules, especially HI, HI⁺, HO⁻, ClO⁻.

1. INTRODUCTION

IN determining the electron configurations of molecules, we may proceed semi-empirically by considering alternative possibilities based on rough theoretical schemes, and then making choices in harmony with empirical data. The most convenient simple and generally applicable

way of working out such theoretical schemes with molecular orbitals is to use LCAO approximations for the latter, at least for the normal and some of the low excited states. By using these in connection with certain semi-empirical rules it is possible even to make approximate predictions of *I*'s (ionization potentials) for the real (Hartree-

field) orbitals to which the LCAO forms¹ are approximations.

To a considerable extent, the vital coefficients which appear in an LCAO form, i.e., the coefficients of the atomic orbitals used, are determined by symmetry considerations (cf. IV, V of this series^{2, 3}). Even when rigorous symmetry is lost the existence of an approximate symmetry is often sufficient to guarantee that the coefficients are nearly the same as for a related case with exact symmetry. Another important principle similar to the foregoing is that,—even aside from symmetry considerations,—if the approximate form and energy of an orbital are known in one molecule, then these may be expected to be approximately preserved in many cases in other related (e.g., "derivative") molecules. A necessary condition for this preservation is of course that the field of force in the region of the orbital in question shall be nearly the same in the parent and derivative molecules (for examples, cf. VII, IX, and others of this series).⁴

The coefficients in LCAO forms depend in an important way, however, not only on symmetries of molecules and their parts, but also on the polarities of the bonds. This fact has been used in earlier papers in a rough qualitative way. The present paper is devoted primarily to a more careful consideration of the effects of polarity on LCAO coefficients, so that our knowledge of the LCAO forms and thereby our understanding of the real molecular orbitals may be made more precise.

It will be shown that electronegativity scales^{5, 6} can in many cases be made use of qualitatively and even semi-quantitatively in determining how the LCAO coefficients are affected by polarities of bonds. It should be mentioned, however, that the existing scales have a meaning only in the cases of neutral molecules with electron-pair bonds and not too strongly polar. For strongly polar or heteropolar molecules, and for molecule-ions, the

same qualitative principles can still be applied as in the less polar cases, but the values of LCAO coefficients must be estimated in other ways than by the electroaffinity scales hitherto proposed.

2. A NEW BASIS FOR THE ELECTROAFFINITY SCALE FOR THE CASE OF NEUTRAL UNIUNIVALENT DIATOMIC MOLECULES

In papers where electronegativity scales have been set up,^{5, 6} the discussion has been given wholly in terms of atomic orbital approximations for molecular electronic structures. It is equally possible, in fact simpler, to set up an electroaffinity scale in terms of molecular orbital approximations, at least if we use LCAO forms for the latter.

It is best to begin with neutral uniunivalent diatomic molecules. Suppose we have a bonding molecular orbital (ordinarily occupied by two electrons) approximated by the LCAO form

$$\phi_{AB} = a^{\times}\phi_A + b^{\times}\phi_B. \quad (1)$$

If $a^{\times} = b^{\times}$, or $a^{\times^2} = b^{\times^2}$, we may say that the atoms A and B are of equal electroaffinity or electronegativity; or if $a^{\times^2} > b^{\times^2}$, that A is the more electronegative. Conversely, if we know the relative electroaffinities of two atoms, we can determine whether $a^{\times^2} > b^{\times^2}$ or $b^{\times^2} > a^{\times^2}$. Either $a^{\times} = b^{\times}$ or $a^{\times^2} = b^{\times^2}$ may be taken as a criterion of equal electroaffinity, but it will be shown below that, when we consider differences in electroaffinity, these can be more simply related to $a^{\times^2} - b^{\times^2}$ than to $a^{\times} - b^{\times}$ (cf. Eqs. (21), (22)).

The criterion of equal electroaffinity just set up is ordinarily nearly but not exactly equivalent to the criterion⁶ $\alpha = \beta$ based on atomic orbitals. As a matter of fact it is probably inherently impossible to define equality of electronegativity other than approximately, except for $A \equiv B$.

The use of (1) with $a^{\times} = b^{\times}$ or $a^{\times^2} = b^{\times^2}$ implies, as one sees from perturbation theory, an effective equality of term values, i.e., an effective degeneracy, between the atomic orbitals ϕ_A and ϕ_B . In other words, equal electronegativity of two atoms A and B implies effective degeneracy between their respective valence orbitals.

As can be seen, however, from work of Hund,⁷

¹ R. S. Mulliken, J. Chem. Phys. **3**, 375, 514 (1935): VI, VIII of this series.

² R. S. Mulliken, Phys. Rev. **43**, 279 (1933): IV.

³ R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933): V.

⁴ R. S. Mulliken, J. Chem. Phys. **3**, 506, 517 (1935): VII, IX.

⁵ L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932); L. Pauling and D. M. Yost, Proc. Nat. Acad. Sci. **18**, 414 (1932).

⁶ R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934).

⁷ F. Hund, Zeits. f. Physik **73**, 1 (1931): especially pp. 18–19, 25–26.

the effective degeneracy for $a^\times = b^\times$ is not in general between the orbitals ϕ_A and ϕ_B as they exist in the free neutral atoms A and B. The case of H_2 illustrates the point. In constructing an LCAO bonding orbital for H_2 , one of the two electrons is thought of as replaced by a continuous charge distribution, of which half (i.e., a charge $-\frac{1}{2}e$) is near each nucleus. This gives the Hartree field whose Schrödinger equation is to be solved for the molecular orbital. As the distance r between the nuclei goes to infinity this field becomes that of two centers each with a net charge $+\frac{1}{2}e$. The mean effective charge is, however, somewhat greater, say Z^*e , because the second electron penetrates the region occupied by the first.

The LCAO approximation (1) is obtained by, so to speak, taking r out to infinity and then back again. If we follow the real molecular orbital of the above-defined Hartree field to $r = \infty$, it is seen there to take on the form $2^{-1/2}(\phi_A + \phi_B)$, where ϕ_A and ϕ_B are 1s atomic orbitals, although not of ordinary H atoms ($Z=1$) but of certain central fields (*roughly* Coulomb fields with $Z_{eff}=Z^*$). If now we return from $r = \infty$ to the actual r , i.e., r_0 , it will be seen that the form $a(\phi_A + \phi_B)$ should still serve as a more or less good zeroth approximation (LCAO approximation) to the actual molecular orbital. The error involved in the LCAO form, or at any rate in the energy, is considerably reduced by now using orbitals corresponding to a revised value of Z^* (obtainable, e.g., by a variation method) rather than to the value of Z^* which would be appropriate for $r = \infty$. In the case of H_2 , for instance, Hund finds the best such Z^* to be about 0.85.⁷ Now when two electrons are assigned to such an LCAO orbital, a basis is obtained for a tolerable approximation to the actual H_2 normal state wave function, provided r is not allowed to be large. For large r the approximation becomes very poor (regardless of Z^*) because of overionicity,¹ since really as $r \rightarrow \infty$ the molecule dissociates into two neutral atoms.

If A and B are two different univalent atoms, their orbitals ϕ_A and ϕ_B in ϕ_{AB} of (1) correspond to two different Z^* 's, i.e., Z_A^* and Z_B^* . As in the case of H_2 , each of these should be somewhat less than the corresponding Z^n , where Z^n is the effective Z of the orbital ϕ for the neutral atom

($Z^n = Z = 1$ for H, but for other atoms $Z > Z^n > 1$). Of more interest than the Z^* 's, however, are the corresponding term values, since if these are equal we have effective degeneracy and equal electroaffinity of ϕ_A and ϕ_B .

Here we can be guided by Hund's calculation⁷ on H_2 , where the term values of ϕ_A and ϕ_B corresponding to the best Z^* , giving an energy for H_2 agreeing with experiment, were found to be a little less than $(I_H + E_H)/2$, where E = electron affinity. Generalizing from this example, it seems likely that in any molecule AB which is not too strongly heteropolar, the desired LCAO term value of, e.g., ϕ_A may be fairly well approximated by $(I_A + E_A)/2$, or at least be *proportional* to the latter, which is all that is needed for our purpose. This suggests that a quantity proportional to $(I + E)/2$ may be taken as a more or less good measure of the "absolute electroaffinity" of an atom, as was proposed in a previous paper⁶ on the basis of an even rougher argument than that given here. The argument is of course still merely one of plausibility, the real justification for the use of $(I + E)/2$ remaining essentially empirical.⁶ Nevertheless it shows that the appearance of $(I + E)/2$ as electroaffinity is reasonable.

The foregoing considerations will be refined by a more careful treatment below, especially in section 6. In connection with the use of the quantity $(I + E)/2$, it should be recalled⁶ that it is necessary to take I and E values not for the ordinary normal state of atom and ion, but in general for suitable "valence states."

The discussion given in the next-to-last paragraph is in one respect not quite adequate. On going back, it will be noted that we are dealing with a pair of equivalent bonding electrons, each of which in turn may be used to produce a Hartree field for the other. Now if say $a^\times > b^\times$ for the resulting orbital (atom A more electronegative than B), then the basis of the Hartree field must be a charge distribution having more negative charge near atom A than near B. [Incidentally, it is not advisable to worry about how this charge distribution would actually change as $r \rightarrow \infty$, if allowed to adjust itself continuously. The best LCAO form here is one based on a partition of charge between A and B which corresponds to the situation for the actual small value of r , but which would have no real significance for $r = \infty$.]

The polarity of the Hartree field produced by the first electron thus makes the net positive charge less than $\frac{1}{2}e$ on atom A and greater than $\frac{1}{2}e$ on atom B, i.e., it diminishes Z^* for the former and increases it for the latter, as compared with the homopolar case. Thus it decreases the effective difference in electronegativity between the two atoms, and makes the orbital ϕ_{AB} less polar than one might at first have anticipated. It can be shown, however (see near end of section 6) that the difference in electronegativity, i.e., in effective term values, between A and B remains approximately *proportional* to what it would be without allowance for the transfer of charge from A to B. Thus the occurrence of charge transfer does not affect the validity of the argument given above indicating that the difference in electronegativity is approximately proportional to the difference between the quantities $(I+E)/2$ of the neutral atoms A and B.

3. DIATOMIC MOLECULAR IONS

Let us next consider positively charged molecules in which there is only one bonding electron (examples: H_2^+ , Li_2^+ , $(LiK)^+$, $(HI)^+$). In such cases the LCAO approximation remains valid, in fact becomes *increasingly good*, as $r \rightarrow \infty$. Here $Z^* = Z^n$ for each atom ($=1$ for H), at least for $r = \infty$, hence the quantity I rather than $(I+E)/2$ is a proper measure of electroaffinity; a correction ought to be made, however, if possible, to get effective I 's appropriate to $r = r_e$ instead of to $r = \infty$. Valence state rather than ordinary I 's should of course be used. Other things being equal, the polarity of a given molecular orbital when occupied by only one electron should be greater than when occupied by two, since the mutual polarity-shielding effect discussed above in section 2 is absent.

An interesting application of the foregoing is to the bonding orbital of HI. The electron configuration,⁸ omitting inner electrons, is

$$(5p\sigma_1 + 1s_H, \sigma)^2(5p\pi_1)^4, {}^1\Sigma^+. \quad (2)$$

Here $(5p\sigma_1 + 1s_H)$ represents the bonding orbital, given in LCAO approximation by

$$a(5p\sigma_1) + b(1s_H). \quad (3)$$

In neutral HI, this has a pronounced H^+I^-

polarity ($a > b$), corresponding to the fact that $(I+E)$ is greater for I than for H, if the proper valence states of I^+ , I, and I^- are used in computing $(I+E)$ for I.^{8, 6}

In the $(HI)^+$ state

$$(1s_H + 5p\sigma_1, \sigma)(5p\pi_1)^4, {}^2\Sigma^+, \quad (4)$$

however, with only one bonding electron, the polarity of the bonding orbital may be mildly reversed (H^-I^+ , $a < b$), since the valence I is somewhat less for I than for H (about 12.93 for I as compared with 13.53 volts for H; the value 12.93 is the $V_1 \rightarrow V_0$ valence I , which is considerably larger than the ordinary $I^8, 6$). This reversal of polarity is not certain, however, since the relative values of the effective I 's might perhaps be reversed at $r = r_e$ as compared with $r = \infty$.

As another example, we may consider LiH and $(LiH)^+$. For neutral LiH , there is evidence that the molecule is a little nearer to the homopolar than to the ionic ideal case: the bonding orbital $a(1s_H) + b(2s_{Li})$ may have a/b perhaps about 2. The molecule is too strongly polar to permit use of the electroaffinity scale in more than a qualitative way; it may be noted that $(I+E)/2$ has the respective values 7.12 and about 2.86 for H and Li.

For $(LiH)^+$, we have to consider the I values 13.53 for H and 5.37 for Li. These tend to indicate a much greater polarity of the bonding orbital, and of the molecule, than in neutral LiH . It seems possible that the polarity of the orbital may even be so great (i.e., a^\times nearly 1, b^\times nearly 0) that the orbital becomes practically non-bonding, the molecule being then simply an atom-pair $H^+ + Li^+$. There would also be an excited state with a^\times then nearly 0, b^\times nearly 1 (cf. Eqs. (7) below) of type $H^+ + Li$. Pauling⁹ considers that $(LiH)^+$ and other molecules $(AB)^+$ containing a single bonding electron, unlike the corresponding neutral molecules with an electron pair, are unstable unless the term values of ϕ_A and ϕ_B are "essentially" equal, i.e., differ by less than the amount of the resonance energy. However, it would appear that the polarization energy should be comparatively large in most such cases and so should often suffice to give at least a modicum of stability, and make b^\times appreciably larger than zero. Equations whereby the

⁸ R. S. Mulliken, Phys. Rev. **46**, 549 (1934).

⁹ L. Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).

energy and coefficients can be approximately calculated for molecules $(AB)^+$ with one bonding electron are given below (Eqs. (7)–(11) and (16)–(17)).

Quite different is the case of positively charged molecules in which the bonding electron pair is left intact, but a nonbonding electron has been removed. As an example we may consider $(HI)^+$ in the (normal) state

$$(5p\sigma_I + 1s_H, \sigma)^2 (5p\pi_I)^3, {}^2\Pi_{1/2}, \uparrow. \quad (5)$$

Since the electron which has been removed comes from the I atom, the primary effect on the bonding orbital should be to increase Z^* for $5p\sigma_I$. The H^+I^- polarity ($a^* > b^*$) of the bonding orbital should thus be increased as compared with the same orbital in neutral HI.

In seeking to determine the degree of polarity of the bonding orbital in (5) a comparison of the $(I+E)/2$ values for I^+ and H, it can be shown, is not appropriate. A helpful method here is to approximate the wave function of (5) using entirely atomic orbitals, and then to compare with (5). In terms of atomic orbitals, (5) corresponds essentially to the ${}^2\Pi$ of $H(1s) \cdot I^+(p\sigma p\pi^3, V_2)$ with only a little admixture of the ${}^2\Pi$ of $H^+ \cdot I(p\sigma^2 p\pi^3, V_1)$; V_1 and V_2 are valence states.⁶ The conclusion that $H^+ \cdot I$ is relatively unimportant here is reached in view of the fact that the energy of $H(1s) + I^+(V_2)$ at $r = \infty$ is about 2.37 volts lower⁶ than that of $H^+ + I(V_1)$, noting also that according to HLPS (Heitler-London-Pauling-Slater) theory the binding energy should be greater in the former case. For values of r corresponding to the stable molecule there should be only a small or moderate perturbation between the wave functions of the $U(r)$ curves of these two states. Hence the ${}^2\Pi$ normal state of HI^+ is mainly $H \cdot I^+(V_2)$, and we conclude that the polarity of the bonding orbital after all cannot be much greater than in neutral HI.

Similar methods can be applied in other cases where a nonbonding electron has been removed or excited: examples, $(5p\pi_I)^{-1}$ in $(ICl)^+$; $(3p\pi_{Cl})^{-1}$ in $(ICl)^+$. In I_2^+ , of course, the bonding orbital remains homopolar, since the charge is shared equally by (or rapidly "resonates between") the two I's.

Negatively charged ions can be treated in similar ways; let us consider HO^- and ClO^- as

examples. (CN^- is similar, but the presence of more than one bonding electron pair complicates matters.) HO^- and ClO^- each have a single bonding pair. Their electronic structures are qualitatively the same as those of HF and ClF.

$$\begin{aligned} HO^-: & (2p\sigma_O + 1s_H, \sigma)^2 (2p\pi_O)^4, {}^1\Sigma^+ \\ ClO^-: & (2p\sigma_O + 3p\sigma_{Cl}, \sigma)^2 (2p\pi_O)^4 (3p\pi_{Cl})^4, {}^1\Sigma^+. \end{aligned} \quad (6)$$

The wave function of HO^- may also be approximated, by using atomic orbitals, by a mixture of those of $H(V_1) + O^-(V_1)$ and $H^-(V_0) + O(V_0)$. Since the energy at $r = \infty$ is about 4.3 volts lower for the former, and since also the potential energy curve of the former should go down and that of the latter up according to HLPS theory, it appears that the wave function must be nearly pure $H \cdot O^-$. There should, however, be some admixture of $H^+ \cdot O=$, but it is impossible to estimate how much. Comparison with (6) indicates that the bonding orbital $a(2p\sigma_O) + b(1s_H)$ is nearly homopolar ($a \approx b$), or perhaps shows some inequality $a > b$ if the effect of $H^+ \cdot O=$ is important. Thus it is probable that the strong inequality $a > b$ which is present in this orbital in neutral OH is much reduced by the negative charging of the O atom. (Note that neutral OH differs from OH^- in that one π_O electron is missing from (6).)

In building up the wave function of OCI^- using atomic orbitals, we may consider $O^-(V_1) + Cl(V_1)$, $O(V_0) + Cl^-(V_0)$, and $O^-(V_0) + Cl^+(V_0)$. For $r = \infty$ the first named is probably only a little lower than the second (1.3 volts estimated⁶), but according to HLPS theory its $U(r)$ curve should go down while that of the second should go up. Thus $O^- \cdot Cl$ should predominate strongly over $O \cdot Cl^-$ in the wave function. The importance of $O^- \cdot Cl^+$ is difficult to estimate; it may or may not exceed that of $O \cdot Cl^-$. On the whole, we conclude that the bonding orbital is probably nearly homopolar in ClO^- .

Absorption spectra of OH^- and OCI^- (also SH^- etc.) are known in water solution, but as in the cases of Cl^- , Br^- and I^- , the explanation of these spectra (probably electron removal spectra) is complicated by the presence of the solvent. The most easily removed electron should be the nonbonding $2p\pi_O$ in the case of OH^- , and either $3p\pi_{Cl}$ or $2p\pi_O$ in the case of OCI^- .

Reviewing the results of the preceding discussion, it may be concluded that while the concept of relative electronegativity may possibly always be used, the ordinary scales $((I+E)/2$ and Pauling's) cannot be used except for normal states of neutral molecules of not too great polarity and with a pair or pairs of bonding electrons. In the case of positive molecule-ions with one bonding electron, I may be used as a measure of electroaffinity.

4. EVALUATION OF COEFFICIENTS IN LCAO MOLECULAR ORBITALS

Given orbitals ϕ_A and ϕ_B of the two atoms, one can set up a perturbation problem and solve for the energies and the coefficients a^\times and b^\times in the LCAO form Eq. (1). This can be done in the same way for neutral or ionized molecules, provided only the sizes and forms of ϕ_A and ϕ_B are properly chosen. The discussion is also applicable if one or both of the atoms are polyvalent. One or both of the orbitals ϕ_A and ϕ_B may even be *radical* orbitals, i.e., belong to radicals A or B (cf. earlier papers of this series). Or one or both may belong to a *group* of atoms; e.g., ϕ_A may belong to a carbon atom, ϕ_B to the group Cl_4 , in the building up of a nonlocalized bonding orbital of CCl_4 . The discussion can, however, also equally well be applied to localized orbitals corresponding to the separate C—Cl bonds in CCl_4 (cf. XII of this series).

Corresponding to the two independent orbitals ϕ_A and ϕ_B with which we start, the perturbation problem must of course yield two solutions, say

$$\begin{aligned}\phi_{AB} &= a^\times \phi_A + b^\times \phi_B, & \text{with energy } W^\times \\ \phi_{AB}^* &= a^* \phi_A + b^* \phi_B, & \text{with energy } W^*.\end{aligned}\quad (7)$$

We assume ϕ_A and ϕ_B each normalized, but note that they are not orthogonal (except for $r = \infty$). They are made both positive in the region where they overlap. Proceeding in the usual way, the secular equation

$$(H_{AA} - W)(H_{BB} - W) - (H_{AB} - SW)^2 = 0 \quad (8)$$

is found. Here

$$\begin{aligned}H_{AA} &= \int \phi_A H \phi_A dv, & H_{AB} &= \int \phi_A H \phi_B dv, \\ H_{BB} &= \int \phi_B H \phi_B dv, & S &= \int \phi_A \phi_B dv.\end{aligned}\quad (9)$$

Introducing the abbreviations

$$X = (H_{AA} + H_{BB})/2, \quad V = (H_{AA} - H_{BB})/2, \quad (10)$$

the solutions of (8) can be written in the form

$$W(1 - S^2) = X - SH_{AB} \pm [(H_{AB} - SX)^2 + V^2(1 - S^2)]^{1/2}. \quad (11)$$

If atoms A and B are identical, V is zero and (11) reduces to the well-known expression (valid, e.g., for H_2^+)

$$W = (X \pm H_{AB})/(1 \pm S). \quad (12)$$

In this case we have

$$a^\times = b^\times = (2 + 2S)^{-1}, \quad a^* = -b^* = -(2 - 2S)^{-1}; \quad (13)$$

the upper sign in (12) here belongs to W^\times , the lower to W^* . Thus ϕ_{AB}^* is the antibonding orbital complementary to the bonding orbital ϕ_{AB} . The quantities $W, X = H_{AA}, H_{AB}$ are all negative and S is positive, at least for the case of ordinary stable molecules and ions in their respective equilibrium states. It should be noted that $X = H_{AA} = H_{BB}$ is considerably lower than the energy of ϕ_A or ϕ_B at $r = \infty$ (all are negative):

$$H_{AA} = (H_{AA})_{r=\infty} < (H_{AA})_{r=0} \equiv W(\phi_A).$$

If atoms A and B are not identical, but the molecule AB (or more accurately, the orbital ϕ_{AB}) is known to be slightly or moderately polar, (12) and (13) should still be roughly true. We may then expand (11) in terms of the quantity V which vanishes when $A \equiv B$. Similarly, the quantities $a^\times - b^\times$ and $a^* + b^*$, or $(a^\times/b^\times) - 1$ and $(-a^*/b^*) - 1$, may be expanded in powers of V . For the energy, one gets

$$W = (X \pm H_{AB})/(1 \pm S) \pm V^2/2Y \mp V^4(1 - S^2)/8Y^3 + \dots, \quad (14)$$

$$\text{where} \quad Y = H_{AB} - SX. \quad (15)$$

From the perturbation theory equations, one finds

$$\begin{aligned}a/b &= (W - H_{BB})/(H_{AB} - SW) \\ &= (W - X + V)/(H_{AB} - SW).\end{aligned}\quad (16)$$

Substituting for W according to Eq. (14), expanding again, and making use of the normalization condition

$$a^2 \pm 2Sab + b^2 = 1, \quad (17)$$

and with the upper signs in Eqs. (14), (17), (18)

for a^\times , b^\times , the lower for a^* , b^* , one finally arrives at

$$\begin{aligned} a(2 \pm 2S)^{\frac{1}{2}} &= \pm 1 + (1 \pm S)R/2 \pm (S^2 - 1)R^2/8 \\ &\quad - 3(1 \pm S)(1 - S^2)R^3/16 + \dots, \\ b(2 \pm 2S)^{\frac{1}{2}} &= 1 \mp (1 \pm S)R/2 + (S^2 - 1)R^2/8 \\ &\quad \pm 3(1 \pm S)(1 - S^2)R^3/16 + \dots, \end{aligned} \quad (18)$$

$$\text{where} \quad R = V/Y = V/(H_{AB} - SX). \quad (19)$$

In particular, the coefficients a^\times , b^\times of ϕ_{AB} are

$$\begin{aligned} a^\times(2 + 2S)^{\frac{1}{2}} &= 1 + (1 + S)R + \dots, \\ b^\times(2 + 2S)^{\frac{1}{2}} &= 1 - (1 + S)R + \dots, \end{aligned} \quad (20)$$

and

$$\begin{aligned} a^\times - b^\times &= [(1 - S)/2]^{\frac{1}{2}} R \{1 - 3(1 - S^2)R^2/8 + \dots\} \\ a^\times - b^\times &= R \{1 - (1 - S^2)R^2/2 + \dots\}. \end{aligned} \quad (21) \quad (22)$$

Since we have taken $a^\times = b^\times$ or $a^{\times 2} = b^{\times 2}$ as a criterion of equality of electroaffinity of atoms A and B (or more strictly, of ϕ_A and ϕ_B), we see from Eqs. (21), (22) that the quantity R , of which the vital factor is V , is some sort of measure of the difference in electroaffinity of atoms A and B. Let N represent "absolute electroaffinity." It will be shown below that, although no unique definition can be given, any quantity such as $-V$, $-V(-Y)^{\frac{1}{2}}$, or $-V/-Y \equiv R$, usually may reasonably be identified with $(N_A - N_B)$, because of the usual rough constancy in practice of Y . At any rate, the *sign* of $(N_A - N_B)$ is determined by that of $-V$.

At this point it may be noted that Y in Eq. (19) is negative in practice; H_{AA} and H_{BB} are also negative; hence $V (\equiv (H_{AA} - H_{BB})/2)$ is negative when R is positive, and *vice versa*. Now N is by definition positive, and larger for a more electronegative atom. Hence finally, positive $(N_A - N_B)$ must correspond to positive R and negative V .

Before going further with the discussion of the "normal" case in which Y is fairly constant, it may be noted that if for any reason $-Y$ should be unusually small, R and so the difference between a and b (cf. Eq. (21)) will tend to be increased. That is, for a given difference in electronegativity, or at any rate for a given V , the polarity of a molecule tends to be greater if the strength of the bond (measured approximately by $-Y$) is weaker. Also, when Eqs.

(18)–(22) are applied to the polyatomic case, and when we use nonlocalized molecular orbitals for the latter, the quantity Y is found to depend not only on bond strength but also on bond angles. This introduces an additional factor tending to affect the values of a and b (cf. discussion of H_2O in XII of this series).

It may be well at this point to dispose of the question as to whether our results will lack significance because of the roughness of the LCAO approximation for molecular orbitals. It is important to note that even though the LCAO form may be greatly distorted as compared with the real orbital, the degree of polarity should apparently be correctly represented (especially if we are guided by empirical electroaffinity scales rather than theoretically calculated R 's) in either of two limiting cases, namely $a^2 = b^2$ (homopolar) and $a = 1$, $b = 0$ or $a = 0$, $b = 1$ (extreme heteropolar). In intermediate cases, the sign of the polarity should always be correct, and even its magnitude should be less in error than are other characteristics of the LCAO form.

5. THEORETICAL BASIS OF PAULING'S ELECTRONEGATIVITY SCALE

Before going farther with a consideration of the a 's and b 's, it will first be shown that Eq. (14) affords a theoretical explanation of the basis of Pauling's electronegativity scale. Let $P_A - P_B$ be the relative electronegativity of atoms A and B on this scale. The latter is based on the empirical relation⁵

$$(P_A - P_B)^2 + \dots = \Delta_{AB}, \quad (23)$$

$$\text{where} \quad \Delta_{AB} = D_{AB} - \frac{1}{2}(D_{A_2} + D_{B_2}). \quad (24)$$

Here D is the energy of dissociation, in electron volts, of a molecule or bond. Insofar as the theorem⁵ of the "additivity of normal covalent [i.e., homopolar] bond energies" holds good, Δ_{AB} should, as Pauling showed, always be positive and should be a measure of the departure of the A–B bond from the pure homopolar type. In practice, the Δ 's proved to be indeed positive in the cases cited,⁵ and proved amenable to interpretation in terms of a linear scale of electronegativities P in accordance with the empirical Eq. (23).

A theoretical explanation of the form of Eq.

(23) has not been given hitherto, but may be obtained as follows. The total energy of a molecule AB in its normal state can be expressed by $W^i = W^i + 2W$ with W given by Eq. (14), using the upper signs in this equation. $2W$ then refers to the pair of bonding electrons, and W^i to the remaining energy. It is now readily seen that

$$\Delta_{AB} = -W'_{AB} + \frac{1}{2}(W'_{A_1} + W'_{B_1}). \quad (25)$$

We note that in Eq. (14) as applied to a molecule A_2 or B_2 , $V = 0$. Putting $[(X + H_{AB})/(1 + S)] = K$ in Eq. (14), and $W^i + 2K = L$, Eq. (25) now yields

$$\Delta_{AB} = \{-L_{AB} + \frac{1}{2}(L_{A_1} + L_{B_1})\} + V^2/-Y - V^4(1 - S^2)/(-4Y^3) + \dots \quad (26)$$

Now if Pauling's theorem of the additivity of homopolar bond energies is valid, the expression in braces must be equal to zero, and we get

$$\Delta_{AB} = aV^2 - bV^4 + \dots, \quad (27)$$

with $a = -1/Y$, $b = (1 - S^2)/(-4Y^3)$, the coefficients a and b being positive. The argument leading to Eq. (27) can be extended to show that the latter should hold also for polyatomic molecules.

Eq. (27) is in complete agreement with Pauling's empirical Eq. (23), and the foregoing discussion gives a theoretical derivation of the form of Eq. (23), and also shows that

$$(P_A - P_B) = (-Y)^{-1}(-V) = -\frac{1}{2}(-Y)^{-1} \times (H_{AA} - H_{BB}). \quad (28)$$

This permits the following definition of the "absolute electroaffinity" P on Pauling's scale, a quantity not considered by Pauling:

$$P_A = \frac{1}{2}(-Y)^{-1}(-H_{AA}). \quad (29)$$

All these results depend of course on the validity of the theorem of the additivity of homopolar bond energies. This theorem is an empirical one, and is undoubtedly not exact.⁵ The best evidence for its correctness is really the approximate empirical validity of Eq. (23) in most cases.*

The exact validity of Eqs. (27)–(29) with a

* A case where Eq. (23) apparently fails completely is that of diatomic LiH, where Δ_{AB} is apparently negative, although it should have a large positive value as judged by $N_H - N_{Li}$ on the writer's electroaffinity scale, where $N_H - N_{Li}$ is comparable with $N_F - N_H$. To be sure, the value of D for LiH is not very sure, yet the error in it can hardly be large enough to make LiH conform to Eq. (23).

definite constant P value for each atom would imply that the quantity $-Y$, which depends on both the atoms A and B, must be a universal constant. Since this is certainly not exactly true, it is clear that the P values are inherently incapable of representing exactly definable properties of atoms, but must be rough averages based on an average value of $(-Y)^{-1}$. The lack of definiteness of P scale values is also affected by the fact that H_{AA} in Eq. (29) is far from being independent of the second atom B.

The success of Eq. (23) suggests that Y is in practice fairly constant in ordinary cases. This is understandable so long as we deal with molecules not differing too greatly in bond strength, since $-Y$ should generally be roughly proportional to the latter. The effects of Y variation are also diminished because P depends on $(-Y)^{\frac{1}{2}}$.

For large values of $(P_A - P_B)$, Eq. (27) predicts that Δ_{AB} should be less than aV^2 . This is in accordance with findings of Pauling on strongly polar molecules: for H_2O there is an appreciable deviation from Eq. (23) in the sense of Eq. (27), and in HF there is a large deviation. For really heteropolar molecules (diatomic NaCl, etc.) it is clear that the approximations involved in Eqs. (14), (27), (29), etc. break down completely. Thus the whole basis of Pauling's (also of the writer's) N scale breaks down in such cases. Nevertheless, it so happens that polarities and Δ 's usually tend still to increase monotonically with $(N_A - N_B)$ even when Eqs. (27), (29) no longer hold, so that the N scales can still usually be used empirically in a qualitative way. This is true, for example, for ordinary diatomic salt molecules like NaCl, but apparently not, as regards Δ , for certain less polar salt molecules like LiH where apparently the additivity theorem for homopolar bond energies fails completely.*

Some readers may be dissatisfied with the foregoing analysis, in particular with the theoretical justification of the form of Eq. (23), on the ground that the use of LCAO molecular orbitals gives too poor an approximation. The writer has therefore carried through the analysis again using atomic orbitals (HLPs wave functions combined with ionic functions),^{5, 6} and finds in place of Eq. (27) a similar equation in which Δ_{AB} again comes out approximately proportional to the square of

a quantity which must be identified with $(P_A - P_B)$ of Eq. (23). The details of the analysis will not be given here, since they are considerably more complicated than those of the analysis above, but lead to essentially the same result.

6. ELECTROAFFINITY SCALES AND LCAO COEFFICIENTS

By referring to Eqs. (27), (19), (21), (22) it will now be seen that all of the quantities Δ^\dagger , $(a^\times - b^\times)$, and $(a^{\times^2} - b^{\times^2})$ can be expressed in the form

$$k(P_A - P_B) - l(P_A - P_B)^3,$$

where k and l are different for each of the three quantities, but should be fairly constant for any one insofar as Y and S are constant. (S should be fairly constant if Y is.) Our discussion does not show for which of the three quantities the k and l will be the more nearly constant. The equations for the three cases are as follows:

$$\Delta^\dagger = (P_A - P_B) - [(1 - S^2)/(-8Y)] \times (P_A - P_B)^3 + \dots, \quad (30)$$

$$(a^\times - b^\times) = (b^* + a^*) = [(1 + S)/(-2Y)]^\dagger \times (P_A - P_B) - (3/-8Y)(1 - S^2)[(1 + S)/(-2Y)]^\dagger \times (P_A - P_B)^3 + \dots, \quad (31)$$

$$(a^{\times^2} - b^{\times^2}) = (b^{*2} - a^{*2}) = (-Y)^{-1}(P_A - P_B) - \frac{1}{2}(1 - S^2)(-Y)^{-1}(P_A - P_B)^3 + \dots \quad (32)$$

It may be well to point out that, because of the roughness of the LCAO approximation used in deriving Eqs. (30)–(32) and other equations, one can hardly hope to attach quantitative significance to their coefficients. The forms of these do, however, possess at least suggestive value.

It will be seen that, instead of defining $N = P$ as in Eq. (29), which makes $k = 1$ for Δ^\dagger , we might have defined N so as to make $k = 1$ for $(a^\times - b^\times)$, or for $(a^{\times^2} - b^{\times^2})$. Such definitions of N would be those naturally suggested by Eqs. (21), (22). It will be simpler, however, to keep to the Eqs. (28)–(29) definition, since then we can use Pauling's scale values directly, also because P involves Y only as $(-Y)^{-1}$, while for the other definitions, N would involve $(-Y)^{-1}$.

One wonders, however, whether it might not be possible to find an N scale on which the scale value for an atom A could be made more nearly

independent of atom B than is the case for the P or other scales suggested above. Quite possibly such an improved scale could be found, but until the nature of the dependence of H_{AA} and Y on atom B has been more carefully investigated, we can hardly expect to set it up with confidence. Besides, our above analysis of possible N scales makes it fairly clear that it is inherently impossible to consider the electroaffinity N of an atom as an exact atomic property; even at best, N must be admitted to vary somewhat with the nature of other atoms in the molecule.

Nevertheless, the writer has in a previous paper⁶ set up a scale of "absolute electroaffinity" in which N , which may here be called M to distinguish it from P or other possible N definitions, is given by

$$M = (I + E)/2 \quad (33)$$

for any atom. Although Eq. (33) gives a means of assigning a definite number M for the electroaffinity of each atom, its theoretical justification as a measure of electroaffinity can apparently be given only very roughly (reference 6; section 2 above; and below). Its best justification so far is perhaps its empirical agreement in certain simple cases with Pauling's empirical approximate scale of P 's relative to P_H , the numerical relation between the two scales⁶ being, empirically,

$$(M_A - M_B) = 2.78(P_A - P_B), \quad (34)$$

with P in (volt electrons)¹, M in volt electrons.

It is possible, in the case of neutral diatomic molecules with one electron-pair bond, to establish a rather illuminating connection between the quantity $(M_A - M_B)$ and the quantity $-V$ of Eqs. (19), (21), and so with $(P_A - P_B)$ of Eq. (28). Recalling that $-V = -(H_{AA} - H_{BB})/2$, we note that H_{AA} and H_{BB} are energies of ϕ_A and ϕ_B as calculated when atoms A and B are close together and in each other's fields ($r = r_c$). If taken for $r = \infty$, $-(H_{AA} - H_{BB})/2$ (let us call this $-V_\infty$) would be equal to half of $T_A - T_B$, the difference between the term values of ϕ_A and ϕ_B each calculated for a separate central field.

Referring to the last paragraph of section 2, it will be seen that T_A and T_B here refer not to force centers with equal net charges $+\frac{1}{2}e$ (let T_A, T_B for the latter case be called T_A^0, T_B^0), but to centers in which a net charge, say Q , has been

displaced from A to B. If, roughly, we put

$$T = RZ^{*2}/n^2, \text{ then } dT/dZ^* = 2T/Z^*.$$

Now the effect of charge Q , approximately, is to alter Z^* by an amount $dZ^*_B = aQ/e = -dZ^*_A$, where $a = 0.35$ approximately (Slater), noting that Q goes into the outer shell. From this we find, approximately,

$$T_A = T^0_A(1 - 2a_A Q/eZ^*_A); \\ T_B = T^0_B(1 + 2a_B Q/eZ^*_B).$$

As will be shown in the next section, $Q/e = (a^\times - b^\times)$ for an electron-pair (cf. Eq. (39)), or *half* this in our case where are interested in the Hartree field corresponding to one electron of the pair. Hence, using Eqs. (22), (19), (10),

$$Q/e = (T_A - T_B)/-4Y + \dots$$

Combining this with the equations just given for T_A and T_B , one finds

$$T_A - T_B = C(T^0_A - T^0_B), \quad (35)$$

$$\text{where } C = \{1 + [(a_A T^0_A/Z^*_A) + (a_B T^0_B/Z^*_B)]/-2Y\}^{-1}. \quad (36)$$

In practice, C is less than, but probably in rough approximation equal to, unity.

From Eq. (35), it will be seen that $T_A - T_B$, hence $-V_\infty$, is proportional to $T^0_A - T^0_B$, insofar as C is constant. Further, it is plausible that $-V$ of Eq. (19) ($r = r_e$) is approximately proportional to $-V_\infty$ under ordinary circumstances. (Note that for $A \equiv B$, $I_{AA} - I_{BB}$ vanishes simultaneously at all values of r .) Now as we have seen in section 2, T^0_A and T^0_B are approximately equal or proportional to the quantities $(I + E)/2$ of neutral atoms A and B. Hence $-V$ may plausibly be expected to be approximately proportional to $M_A - M_B$. Now, however, according to Eq. (28), $-V$ is also approximately proportional to $(P_A - P_B)$. Thus it is shown by theoretical considerations, although not rigorously, to be at least plausible that $(M_A - M_B)$ should be proportional to $(P_A - P_B)$, in agreement with the empirical Eq. (34).

The above justification of the M scale refers to neutral molecules composed of uniunivalent atoms A, B. Complications arise when one extends the argument to polyatomic molecules (cf. also the discussion in reference 6). Although

it is likely that the use of the M scale could be justified also in such cases, we shall for the present use the P scale for these. The theoretical basis given for the P scale in section 5 appears to be equally valid if A and/or B is polyvalent. Empirically also, the P scale has been established for several polyvalent atoms, in the case of single bonds.

In concluding this section, some qualitative applications of Eq. (31) will be mentioned. Consider for example the σ bonding orbital (cf. Eqs. (7)) of a molecule XY (X, Y = halogen atoms)⁸:

$$\sigma = a^\times(3p\sigma)_{Cl} + b^\times(5p\sigma)_I + \dots; \\ \sigma^* = a'(5p\sigma)_I - b'(3p\sigma)_{Cl} + \dots. \quad (37)$$

Here the a 's and b 's can all be chosen positive. If $YX = \text{ClI}$, ClBr , BrI , etc., then from the P scale, $a^\times > b^\times$ and $a' > b'$ in each case, and the quantities a/b are greater for ClI than for ClBr . Similarly, if $AB = \text{XH}$, we see that $a/b > 1$ throughout, increasing in the order IH , BrH , ClH , FH .

7. CHARGE DISTRIBUTIONS AND RELATIVE ELECTRONEGATIVITIES

Given two electrons occupying a bonding orbital ϕ_{AB} (Eqs. (1) or (7)), the corresponding mean charge density is given by $-2e(\phi_{AB})^2$, a function in space. By drawing a boundary surface somewhere between the two atoms (obviously a mid-plane if $A \equiv B$) one might seek to find how much of the total charge $-e$ belongs to each atom, and from this to determine a net charge for each. Incidentally, one might define the difference in electronegativity of two atoms as proportional to the above-determined net mean charge transferred from the one to the other. This definition is essentially equivalent, for *small* or moderate $(N_A - N_B)$ values, to those discussed in section 6.

Unfortunately no rule free from arbitrariness can be set up for drawing a boundary surface between A and B, except in the case $A \equiv B$. The difficulty appears in enhanced form in more complex molecules, e.g., when one tries to allocate net charges to the various atoms in ClO_4^- . This difficulty is an example of the essential impossibility of giving exact definitions without arbitrariness for any atomic property, e.g.,

electroaffinity or atomic or ionic radius, for an atom in combination.

In the diatomic case, a fairly natural even though arbitrary procedure for dividing the bonding electrons' charge can be set up. Consider the following equation, obtained by using Eqs. (7), (9) and (17):

$$-2e = -2e \int (\phi_{AB})^2 dv = -2e(a^{x^2} + 2a \times b \times S + b^{x^2}). \quad (38)$$

A reasonable procedure would be to assign the amount of bonding electron charge $q_A = -2e(a^{x^2} + a \times b \times S)$ to atom A, $q_B = -2e(a \times b \times S + b^{x^2})$ to atom B. Since the net charge on each atom is $+e$ if the two bonding electrons are omitted, the actual net charges Q are obtained by taking $Q = q + e$. With the help of Eq. (17), one then gets

$$Q_A = -e(a^{x^2} - b^{x^2}) = -Q_B. \quad (39)$$

One notes that Eq. (39) gives $Q_A = 0$ for $a^x = b^x$, $Q_A = \mp e$ for $a^x = 1$, $b^x = 0$ or $a^x = 0$, $b^x = 1$, as it should. Incidentally, it may be mentioned that the ideal heteropolar case $a^x/b^x = 0$ or $b^x/a^x = 0$ cannot be realized unless ϕ_A and ϕ_B are orthogonal, i.e., $S = 0$, which in practice is not likely to be more than approximately true for a stable molecule. (Cf. Eq. (16) for a/b or b/a , noting that H_{AB} in general vanishes if and only if S does.)

Combining Eq. (32) with Eq. (39) one gets

$$-Q_A/e = k'(P_A - P_B) - l'(P_A - P_B)^3 + \dots, \quad (40)$$

where k' and l' are both positive, with $k' = (-Y)^{-1}$, $l' = \frac{1}{2}(1 - S^2)(-Y)^{-1}$, and $l'/k' = (1 - S^2)/(-2Y)$. Eq. (40), which is based on the expansions Eqs. (18), is valid only if $|Q/e|$ is not too large (say $|Q/e| < \frac{1}{2}$). For heteropolar molecules (say $\frac{1}{2} < |Q/e| < 1$), Eq. (40) could be replaced by another expression based on expansion of Eq. (16) about the case $a = 1$ or $b = 1$. This range of cases will, however, not be considered here.

As can be seen from the discussion in section 6, we may expect k' and l' to be roughly constant in ordinary cases. If we could estimate their values, Eq. (40) should give interesting information as to the Q 's of various bonds, and might also be helpful in interpreting dipole moment data.

In estimating k' and l' , we might try to make use of Pauling's conclusion¹⁰ that HF is about

half-way between the homopolar and the ideal heteropolar case. Half-way would mean a^{x^2} half-way between $1/(2+2S)$ and 1, b^{x^2} half-way between $1/(2+2S)$ and 0 (cf. Eqs. (20)). This gives $a^{x^2} - b^{x^2} = \frac{1}{2}$, hence $Q_F = -\frac{1}{2}e = -Q_H$ according to Eq. (39). At the same time, $(P_F - P_H)$ is about 2.00 according to Pauling.⁵

Unfortunately, the polarity of HF is so strong that the term in $(P_A - P_B)^3$ in Eq. (40) can hardly be ignored. If, however, we do neglect it for the moment, we find $k' = 0.25$. Actually this gives only a lower limit for k' , since the term in $(P_A - P_B)^3$ is negative. For a guess (to be tested later), suppose $l' = 1/48$; then to get $Q_F = -0.50e$ for HF with $P_F - P_H = 2.00$, $k' = 1/3$ is required. That is,

$$Q_B/e = -Q_A/e = (P_A - P_B)/3 - (P_A - P_B)^3/48. \quad (41)$$

Instead of making a guess, however, we might try to estimate the ratio l'/k' , with the help of Eq. (30), from the experimental Δ value⁵ ($\Delta^1 = 1.66$) for HF. Substituting this, also $(P_F - P_H) = 2.00$, in Eq. (30), one gets $(1 - S^2)/(-8Y) = 0.34/8$ for HF. But now l'/k' in Eq. (40)—see above,—should be $(1 - S^2)/(-2Y)$. Hence $l'/k' = 0.17$. We now have sufficient information to determine both k' and l' , and get

$$Q_B/e = 0.76(P_A - P_B) - 0.13(P_A - P_B)^3. \quad (41a)$$

Unfortunately this equation cannot be correct, since it gives absurd results (Q larger for the NH and OH bonds than for HF). This may be attributed partly to uncertainty in the P scale value for F, but is perhaps mainly a result of the roughness of the LCAO approximation; in particular, it is probable that the ratios l'/k' calculated using Eqs. (30), (32), (40) are badly in error because of the inadequacy of the approximation. It is of interest to note that if Eq. (41a) were correct, the quantities Y and S could be calculated from its coefficients (see text near Eq. (40)). Eq. (41a) thus gives $-Y = 1.72$ volts, which is probably far too small; it also gives $S^2 = 0.42$, a not unreasonable value.

Since l'/k' should be constant, it should be possible to calculate it again, in the same manner as above, using Pauling's data on the O-H bond, where $\Delta^1 = 1.326$, $(P_O - P_H) = 1.40$. Combining the l'/k' ratio so obtained ($l'/k' = 0.11$, which it

¹⁰ L. Pauling, J. Am. Chem. Soc. **54**, 988 (1932).

will be noted is *not* the same as before) with the HF data $Q_H/e = \frac{1}{2}$ and $P_F - P_H = 2.00$, one gets

$$Q_B/e = 0.44(P_A - P_B) - 0.0475(P_A - P_B)^2. \quad (41b)$$

This gives much more reasonable Q 's for the NH and OH bonds, but still too large. Also, it gives $-Y = 5.2$ volts, better than before, but it gives $S^2 = -0.11$, which is impossible.

It appears necessary to abandon any attempt to estimate l'/k' theoretically by the use of Eqs. (30) or otherwise. We may, however, with some confidence rely on the theoretical derivation of the *form* of Eq. (40), and on the rough constancy of k' and l' , which is related theoretically to the existence of the P scale.

If the result $Q/e = \frac{1}{2}$ for HF can be approximately trusted, and if k' and l' are approximately constant, we now know that the correct Eq. (40) must lie somewhere between Eq. (43), where l' is surely too large, and the equation

$$Q/e = 0.25(P_A - P_B),$$

obtained by setting $l' = 0$. We are thus led by a trial and error process back to an equation with coefficients about as given in the "guess" Eq. (41). We may now seek to test the correctness of the coefficients in Eq. (41) by seeing, if possible, whether it gives correct Q 's for other cases than HF. Our main difficulty is that at present we have no source of accurate Q 's, either empirical or theoretical.

8. DIPOLE MOMENTS AND RELATIVE ELECTRONEGATIVITIES

If used with caution, electric moment data for simple molecules (HCl, H₂O, NH₃ etc.) should help us by giving *lower limits* for Q 's. For a diatomic molecule in which only the bonding-electron pair contributes to the electric moment, the latter should be readily calculable in LCAO approximation. The mean distribution of electricity as given by Eq. (38) for the two bonding electrons comprises (a) a charge $-2ea \times^2$ centered around atom A; (b) a charge $-4ea \times b \times S$ centered around a point between A and B; (c) a charge $-2eb \times^2$ centered around B. If the distance between the centers A and B is r_e , and the distance of the electric center of item (b) from the midpoint (to be taken as origin) of the line A \longleftrightarrow B

is z , then the net electric moment of AB corresponding to items (a), (b), (c) plus a charge $+e$ on each atom, is

$$\mu = er_e(a \times^2 - b \times^2) - 4eza \times b \times S. \quad (42)$$

Positive μ is taken as corresponding to polarity A-B⁺, which exists if $a \times^2 > b \times^2$. The positive z direction is taken as the direction A \rightarrow B.

To the *primary* (bonding-pair) dipole moment given by Eq. (42) must be added the secondary moment induced in the nonbonding electrons, say μ_s . Including this and also substituting from Eq. (39), we get

$$\mu_{AB} = Q_B r_e - (4eza \times b \times S - \mu_s). \quad (43)$$

Of considerable interest is the "homopolar dipole" term $4eza \times b \times S$, whose presence discloses the hitherto perhaps unsuspected fact that molecules which fulfill the criterion of homopolar bonding ($a \times = b \times$) may still have a dipole moment. This of course does not apply to strictly homopolar molecules (A \equiv B), where $z = 0$, but in all other cases the homopolar dipole term must be present and may be fairly large. Its magnitude increases with inequality in *size* of the two atoms, which is measured by z . Its sign is such that its positive pole is always directed toward the larger atom. Thus it may either assist or oppose the main dipole term $Q_B r_e$. For instance in the hydrogen halides, with the barely possible exception of HF, it opposes the main dipole term. In turn, however, it may often be opposed by μ_s ; examination of the μ data on the hydrogen halides indicates that μ_s there opposes and partially cancels $4eza \times b \times S$ (see below).

It may perhaps be well to state at this point that an equation similar to Eq. (39), but more complicated, can be developed using atomic orbitals^{5, 6} (HLPS method) for describing the electronic structure of AB; the equation includes a term in $(\alpha^2 - \beta^2)$, corresponding to $(a \times^2 - b \times^2)$ in Eq. (39). Likewise equations identical in form with Eqs. (40) and (41) can be obtained. Further, equations for μ corresponding to Eqs. (42), (43) can be obtained, but are considerably more complicated. It is especially to be noted that a homopolar dipole term again appears in these, and is of the same order of magnitude as in Eqs. (42), (43). Thus even though our approximation based on LCAO molecular orbitals may be

poorer than one using atomic orbitals, there is no reason to doubt that the conclusions reached here as to Q 's and μ 's are qualitatively sound.

Returning to Eq. (43), we shall wish to apply this to simple polyatomic molecules like H_2O and NH_3 . It is probably safe, as an approximation, to use Eq. (43) for each bond separately in such a molecule. Also it is probably safe to say, in the cases of H_2O and NH_3 , that if we take μ_{AB}/r_e for a bond (OH or NH), this will give a *lower limit* for Q_B . For there is little doubt that H is effectively smaller in size than O or N (e.g., Pauling¹¹ gives 0.29Å for the radius of H, 0.66Å and 0.70Å for O and N respectively), so that the homopolar dipole will oppose the main dipole; while μ_s , even if opposed to the homopolar dipole and so assisting $Q_B r_e$, is doubtless smaller than the homopolar dipole.

In Table I a comparison is made between the

TABLE I. *Effective charge on H atom.*

Molecule	$\mu \times 10^{18}$	Bond angle	$\mu_{AH} = \mu$ per bond ($\times 10^{18}$)	Q_H/e	
				μ_{AH}/er_e	Eq. (30)
HF	—	—	—	—	0.50
H_2O	1.85	105°	1.53	0.33	0.41
NH_3	1.49	107°	1.33	0.27	0.30
HCl	1.03	—	1.03	0.17	0.30

Notes. Cf. reference 6, Table I. In the case of NH_3 , the H—N—H bond angle is revised, the new value being based on calculations from band spectrum data, giving, respectively, 0.38Å and 1.02Å as the height and length of the NH_3 pyramid (cf. M. F. Manning, J. Chem. Phys. 3, 136 (1935) and references there given).

values of Q_H/e calculated from Eq. (41) for the A—H bonds in NH_3 , H_2O and HCl, and the lower-limit values of Q_H/e obtained in accordance with the foregoing discussion by taking μ_{AH}/er_e . Although we can do little more than guess how much the true values of Q_H should exceed the lower-limit values, it would seem from Table I that the values obtained from Eq. (41) are fairly reasonable. At any rate, it appears probable that we shall commit no gross error in using Eq. (41) to roughly estimate Q 's, also a' 's and b' 's (cf. Eq. (39)) in following papers of this series. If anything, it seems likely that k' in Eq. (43) should be increased, so as to give somewhat larger Q_H 's;

thus Q/e for HF may well be as large as 0.55 or even 0.60 instead of the 0.50 assumed above.

Digressing for a moment from the main object of the present paper, it may be remarked that the extension of Table I to HBr, HI, and various other molecules seems to offer some possibility of throwing new light on dipole moments, although further study and refinement of the method are first needed. It might be better to use the Q expressions obtained from approximations using HLPs electronic structures (atomic orbitals only).

It is easy to estimate the homopolar dipole term in Eq. (43) or in the corresponding equation based on atomic orbitals, by using Pauling's empirical atomic radii¹¹ to estimate z , and estimating S from Heitler-London calculations. This homopolar term is often found to be larger than the main term Qr_e (using Eq. (41)), e.g., in HI (by both molecular and atomic orbital methods). Since its sign in, e.g., HI is opposite to that of Qr_e , one must assume that μ_s of Eq. (43) comes to the rescue and largely cancels the homopolar term, leaving, however, for μ a net observable result which is still much less than Qr_e .

In the molecules HX, this net deficit of μ compared with Qr_e apparently increases steadily from HF to HI. This makes it qualitatively possible that the actual μ can be approximately proportional to Q , hence by Eq. (41) to $(P_A - P_B)$. Such a situation would afford an explanation of the parallelism of μ_{AH} to $(P_A - P_H)$ noted by Malone and used by him as a basis for the electric-moment scale¹² of relative electronegativities. The present analysis indicates that this parallelism is somewhat fortuitous, and that it probably would not hold in general; hence that the electric-moment scale of electronegativities is less significant than the other scales. As a matter of fact, the agreement between Pauling's scale and the electric moment scale is much less good for O and especially N than Malone supposed, when the band spectrum values of the HOH and HNH angles are used (cf. Table I of reference 6, note f, in regard to μ_{OH} , and cf. the revised value for μ_{NH} in the present Table I).

¹¹ L. Pauling, Proc. Nat. Acad. Sci. 18, 293 (1932).

¹² J. G. Malone, J. Chem. Phys. 1, 197 (1933).