

## Electronic Structures of Molecules XII. Electroaffinity and Molecular Orbitals, Polyatomic Applications

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## Electronic Structures of Molecules

## XII. Electroaffinity and Molecular Orbitals, Polyatomic Applications

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The use of electroaffinity data in the approximate estimation of the polarity coefficients of molecular orbitals and of the effective charges on atoms in polyatomic molecules is illustrated by application and extension of the results of XI of this series. Applications are made especially to  $\text{CH}_4$ ,  $\text{CX}_4$  and  $\text{H}_2\text{O}$ , also to  $\text{CH}_3\text{X}$ ,  $\text{NH}_4^+$ ,  $\text{ClO}_4^-$ , etc. Electronic structures are given first using localized, later using nonlocalized molecular orbitals. Comparisons are also made with Slater-Pauling electron

configurations. Among tetrahedral molecules  $\text{RA}_4$ , the homopolar part of the valence is shown to be in some cases nearly all  $s$ , in others nearly all  $p$  valence; in others both; and a varying part of the valence is heteropolar. Consideration of these facts suggests that the special stability of the tetrahedral type  $\text{RA}_4$  should be attributed rather to close packing associated with coordination number four than to special properties of the mixture of  $s$  and  $p$  valence.

## 1. LOCALIZED MOLECULAR ORBITALS

The treatment given in XI of this series<sup>1</sup> was there applied primarily to diatomic molecules AB. It can be extended to polyatomic molecules in either of two ways, namely, (a) by assigning the two electrons of each chemical bond to a diatomic type molecular orbital localized in the region of the bond (Hund method<sup>2</sup>), or (b) using nonlocalized molecular orbitals (present method). The former method is considered in this section, the latter in the next.

Insofar as we can consider the several bonds going out from a single atom as independent, the methods and equations of XI can be directly applied in determining  $a$ 's and  $b$ 's and  $Q$ 's for the localized orbitals of the Hund method. Since Pauling's relative electronegativity values ( $P_A - P_B$ ) for polyvalent atoms refer to these atoms while exerting their full valence, these values should be suitable for use in Eq. (41) of XI, i.e., the mutual influences of the several valence bonds going out from any atom have already been discounted. Naturally this discounting can represent only a rough average. More exactly, the electronegativities of atoms, and the  $Q$ 's developed at the ends of bonds, cannot be entirely independent of the nature of the other atoms and bonds present in the same molecule.

Further, if one should deal with the same atoms in varying valence stages, one would in general expect a different electroaffinity for each

stage. There are indications, however, that these differences are not great so long as 'only the number, but not the type ( $s$ ,  $p$ , etc.) of the valence is altered. If the type is altered, the electroaffinity may change considerably.<sup>3</sup>

The discussion of polarity coefficients and  $Q$ 's for localized orbitals in this section is of interest not only in itself but also as a preparation for the somewhat more complicated case of non-localized orbitals in the next section. At the same time, it affords an opportunity of making comparisons, in respect to the description of polarity, between molecular wave functions constructed using molecular orbitals, and molecular wave functions based on atomic orbitals alone. In making these comparisons, a few simple molecular types  $\text{RA}_n$ , in particular  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{CX}_4$ , will be used as examples.

Using atomic orbitals (Slater-Pauling method) the normal state of  $\text{H}_2\text{O}$  (symmetry  $C_{2v}$ ) appears as

$$1s_o^2 2s_o^2 (2p_{y'})_o \cdot (1s_H) (2p_{z'})_o \cdot (1s_H) (2p_z)_o^2, {}^1A_1. \quad (1)$$

The bonds are formed between  $(2p_{y'})_o$  and  $1s$  of one H, and  $(2p_{y'})_o$  and  $1s$  of the other H. The pair  $(2p_z)_o^2$  are nonbonding electrons. The axes  $y'$  and  $z'$  are taken so that the bisector of the  $90^\circ$  angle between them coincides with the bisector of the actual  $105^\circ$  angle of  $\text{H}-\text{O}-\text{H}$ . The fact that the total electron state can belong to a representation (here  $A_1$ ) of the symmetry group of the molecule, even though the atomic orbitals do not belong to such a representation,

<sup>1</sup> R. S. Mulliken, J. Chem. Phys. this issue: XI of this series.

<sup>2</sup> F. Hund, Zeits. f. Physik **73**, 565; **74**, 1, 429 (1932).

<sup>3</sup> R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934).

has been discussed in IV of this series,<sup>4</sup> section 2. Similar remarks apply to configuration (2) and others similarly expressed below.

Using Hund molecular orbitals for the bonding electrons, we have

$$1s_O^2 2s_O^2 [(2p_{y'})_O + (1s_H)]^2 [(2p_{z'})_O + (1s_H)]^2 (2p_z)_O^2, {}^1A_1. \quad (2)$$

Here  $[(2p_{y'})_O + (1s_H)]$  may be considered as an abbreviation for  $a(2p_{y'})_O + b(1s_H)$ , an LCAO approximation to an H—O bonding molecular orbital; or better as a brief suggestive symbol for a “real” molecular orbital<sup>5</sup> whose exact details are not yet known. From the relative electronegativities of H and O, it is clear that  $a$  very considerably exceeds  $b$ . The same values of  $a$  and  $b$  hold for the  $z'$  orbital, which is geometrically and physically equivalent to the  $y'$ .

The degree of polarity of the bonds can be roughly expressed in terms of the amount of negative charge displaced from H to O. According to Eq. (41) of XI, with  $P_O - P_H = 1.40$ ,<sup>6</sup> we get  $Q_H = +0.41e$ . Considering both bonds, the total polarity may be expressed roughly by writing  $(H^{+0.4})_2O^{-0.8}$ .

The electron configuration (2) has a great advantage over (1), at least conceptually, in that it can be made to correspond to the actual strong polarity in the O—H bonds, whereas (1) corresponds to pure homopolar bonds. This disadvantage of (1) can be overcome only by writing additional electron configurations involving ionic binding, of which the most important are

$$(1s)_O^2 (2s)_O^2 (2p_{y'})_O^2 (2p_{z'})_O \cdot (1s_H) (2p_z)_O^2, {}^1A_1, \quad (3)$$

$$(1s)_O^2 (2s)_O^2 (2p_{y'})_O \cdot (1s_H) (2p_{z'})_O^2 (2p_z)_O^2, {}^1A_1,$$

belonging to  $HO-H^+$ . Then the actual wave function for the normal state of  $H_2O$  must be taken as a linear combination of wave functions corresponding to (1) and (3) (and others), with coefficients to be determined, say, by minimizing the calculated energy. Our estimate, based on a electronegativity data, that  $H_2O$  is roughly of polarity like  $(H^{+0.4})_2O^{-0.8}$ , indicates that the two terms (3) should greatly predominate over (1) in this linear combination.

As Coolidge has shown,<sup>7</sup> accurate calculations corresponding to (1) give results which disagree very badly with experiment. He obtains a much better, although still poor, result, by using an admixture of (1) with (3). It is to be noted, however, that contrary to our estimate of polarity  $(H^{+0.4})_2(O^{-0.8})$  based on Eq. (41) of XI, Coolidge finds that the calculated energy is minimized with a wave function in which (1) still strongly predominates over (3). However, as we have seen near the end of XI, the observed electric moment of  $H_2O$  supports our estimate of the polarity, and thus indicates that the calculations made using atomic orbitals, with a minimizing condition for the energy, are not accurate enough to give a good estimate of the polarity. It seems probable, in view of the work of James and Coolidge,<sup>8</sup> that the use of molecular orbitals (either localized ones as in (2) or non-localized ones) could give better quantitative results than Coolidge's combination of (1) and (3).

For molecules like  $CH_4$  and  $CCl_4$ , Pauling and Slater have used, for the carbon atom, atomic orbitals which are hybrids (mixtures) of the “natural” atomic orbitals  $2s$  and  $2p$ . From  $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$  they construct four equivalent hybrid atomic orbitals, which may be called tetrahedral orbitals and designated  $2t$ . Omitting Cl atom inner electrons, the Pauling-Slater electron configurations for the respective normal states of  $CH_4$  and  $CCl_4$  (symmetry  $T_d$ ) may be written

$$(1s_C)^2 \{ (2t_C) \cdot (1s_H) \}^4, {}^1A_1;$$

$$(1s_C)^2 \{ (2t_C) \cdot (3p\sigma_{Cl}) \}^4 (3p\pi_{Cl})^4 \times 4, {}^1A_1. \quad (4)$$

Each of the four C—H or C—Cl bonds is represented by one  $2t_C$  and one  $1s_H$  or  $3p\sigma_{Cl}$  electron, with the axis of the  $2t_C$  orbital along the C—H or C—Cl line (cf. IV of this series,<sup>4</sup> section 2, for a fuller description). Electron configuration (4) corresponds to homopolar C—H or C—Cl bonds; the actual, partially polar, nature of the bonds can be represented only by assuming resonance (mixing) of several other partially ionic electron configurations with (4).

In the Hund method, each bond is represented by a pair of electrons assigned to a localized

<sup>4</sup> R. S. Mulliken, Phys. Rev. **43**, 279 (1933): IV.

<sup>5</sup> R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935): VI.

<sup>6</sup> L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

<sup>7</sup> A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

molecular orbital whose form can be indicated in LCAO approximation as  $(a2t_C + b1s_H)$  or  $(a3p\sigma_{C1} + b2t_C)$ , with  $a > b$  corresponding to the electronegativity order  $Cl > C > H^6$ . Thus the electron configurations (omitting Cl inner electrons) may be written symbolically as

$$(1s_C)^2(2t_C + 1s_H)^{2 \times 4}, {}^1A_1; \\ (1s_C)^2(3p\sigma_{C1} + 2t_C)^{2 \times 4}(3p\pi_{C1})^{4 \times 4}, {}^1A_1. \quad (5)$$

Configurations (5) have the advantage over (4) that they can take care of any existing degree of polarity. In the writer's method, discussed for  $CH_4$  in the next section, the rather "unnatural" mixing of  $2s$  and  $2p$  required in both (4) and (5) is avoided, but the advantages of (5) in regard to the description of polarity are retained. At the same time, the nonlocalized description is well adapted,—more "natural,"—for the discussion of excited and ionized states.

It is of interest to try to determine roughly the polarities of the bonds in  $CH_4$  and  $CX_4$  by the method already used for  $H_2O$ , based on the rough Eq. (41) of XI. Using Pauling's relative electronegativity values for C, H, I, Br, Cl and F, we get from Eq. (41) the following results for the net charge on each outer atom, in units of  $e$ :  $Q_H = +0.18$ ,  $Q_I = +0.05$ ,  $Q_{Br} = -0.07$ ,  $Q_{Cl} = -0.13$ ,  $Q_F = -0.42$ . The estimated internal polarities of the various molecules may then be expressed by  $C^{-0.72}(H^{+0.18})_4$ ;  $C^{-0.2}(I^{+0.05})_4$ ;  $C^{+0.28}(Br^{-0.07})_4$ ;  $C^{+0.52}(Cl^{-0.13})_4$ ;  $C^{+1.68}(F^{-0.42})_4$ . Of course these estimates are very rough.

Tentatively accepting the foregoing estimates, however, one concludes that (4) can represent a fairly good approximation only for  $Cl_4$  and  $CBr_4$ . For  $CH_4$ , four equivalent electron configurations of type  $C^{-1}H_3H^+$  would need to be given greatest weight in the necessary linear combination of wave functions. For  $CF_4$ , six wave functions of type  $C^{+2}F_2(F^-)_2$  would be most important. If, however, we use (5), a fairly good approximation can be secured in every case with a single electron configuration.

Although a detailed discussion of molecules like  $CH_3X$ ,  $CH_2X_2$ ,  $CHX_3$  will not be given here, it seems appropriate to give one or two examples of the charge distributions obtained for such molecules using Eq. (41) of XI. We apply Eq. (41) to each bond separately, and add the resulting charges at the carbon ends of the various

bonds, just as we did for  $CH_4$  and  $CX_4$ . In this way are obtained  $H^{+0.18}C^{+0.03}(Br^{-0.07})_3$ ;  $(H^{+0.18})_2C^{-0.10}(Cl^{-0.13})_2$ ;  $(H^{+0.18})_3C^{-0.12}F^{-0.42}$ . Interesting conclusions result, e.g., that in  $CH_3F$  the rather strong net negative charge on the F atom is drawn from the H atoms. Results such as these have a bearing on the interpretation of electric moment data, although, of course, one must not neglect various other factors which are or may be of comparable importance.

## 2. NONLOCALIZED MOLECULAR ORBITALS

We turn now to the method using nonlocalized molecular orbitals for shared electrons. Consider, for example, the  $CH_4$  or  $CX_4$  molecule (cf. V of this series<sup>8</sup>), with electron configuration

$$(1s_C)^2[s a_1]^2[p t_2]^6, {}^1A_1 \\ \text{or} \\ (1s_C)^2[s a_1]^2[p t_2]^6(n p \pi_X)^{4 \times 4}, {}^1A_1. \quad (6)$$

In LCAO approximation, the bonding molecular orbitals  $[s]$  and  $[p_x]$ ,— $[p_y]$  and  $[p_z]$  are similar,—are given (cf. V of this series,<sup>8</sup> Eqs. (5)) by

$$[s] = a(2s_C) + b\{(\alpha + \beta + \gamma + \delta)/N\}, \quad (7)$$

$$[p_x] = c(2p_x)_C + d\{(\alpha - \beta - \gamma + \delta)/N'\}, \quad (8)$$

where  $\alpha, \beta, \gamma, \delta$  refer to  $1s$  orbitals of the four H atoms, or to  $n p \sigma$  of the four X atoms.

First let us consider  $CH_4$ . According to Pauling's scale,<sup>6</sup> the carbon atom is about 0.55 units more electronegative than the hydrogen atom. This, however, refers to the *average* behavior of the four valence electrons (one  $2s$ , three  $2p$ ). The writer<sup>3</sup> has pointed out that separate electroaffinities can be given for the  $2s$  and the  $2p$  electrons, and these are obviously needed when we use whole-molecule orbitals like the  $[s]$  and  $[p]$  of  $CH_4$  given above. The writer has estimated (reference 3, Table I) that for  $2s$ , carbon is 3.04 units more electronegative than hydrogen on Pauling's scale; for  $2p$ , 0.28 unit less electronegative than hydrogen.

In (7), the orbital  $[s]$  may be regarded as of the type  $\phi_{AB}$  of Eq. (1) or (7) of XI if we treat  $(\alpha + \beta + \gamma + \delta)/N$  as a single orbital of  $H_4$  ( $N$ =normalization factor),  $H_4$  thus being regarded as B in AB. The results and equations

<sup>8</sup> R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933): V.

of XI then apply. Since  $a=b$  is the criterion of equal electronegativity, we may say that if  $2s$  of C and  $(\alpha+\beta+\gamma+\delta)/N$  of  $H_4$  had equal electronegativity, then  $a=b$  should be true. In a similar way, we should have  $c=d$  in Eq. (8) if  $2p$  of C had the same electroaffinity as  $(\alpha-\beta-\gamma+\delta)$  of  $H_4$ .

In the actual case, we shall not have  $a=b$  or  $c=d$ . Departures from these equalities will depend on differences in electroaffinity, also somewhat on  $Y$  values (cf. Eq. (19) of XI), as discussed in section 4 of XI. It is not difficult to see that the order of magnitude of  $H_{AB}$  and  $Y$  should be the same here as when a localized orbital of Hund's type is used for each bond. It appears likely, however, that  $Y$  here may be larger for the  $[s]$  than for the  $[p]$  orbitals, the  $Y$  for the localized orbitals then being intermediate in value.

As for the electroaffinities of  $(\alpha+\beta+\gamma+\delta)/N$  and  $(\alpha-\beta-\gamma+\delta)/N$  of  $H_4$ , we may use the value for the H atom as a rough approximation. The actual value is probably greater in the case of  $(\alpha+\beta+\gamma+\delta)$  because of H-H bonding, and somewhat less than for free H in the case of  $(\alpha-\beta-\gamma+\delta)$ , where antibonding actions between H's predominate over bonding actions.

Using the electronegativity difference ( $P_{C2s} - P_H = 3.04$ ) estimated above for carbon  $2s$  relative to hydrogen (1s), there can be no doubt that there is a strong inequality  $a > b$ , even allowing for the H-H bondings. Thus the  $[s]$  orbitals must have strong polarity of  $C-H^+$  type, with an  $a/b$  ratio probably greater than in HF ( $P_F - P_H = 2.00$ ). From the carbon  $2p$  electronegativity ( $-0.28$  compared with H), we conclude that  $c/d$  is not far from unity. That is, the  $[p]$  orbitals are nearly homopolar. If the value  $-0.28$  is approximately correct, there is a slight  $C^+H^-$  polarity ( $c/d$  slightly less than 1).

In terms of homopolar strength, the bonding per electron is then probably stronger for the  $[p]$  than for the  $[s]$  electrons. Nevertheless, especially if  $Y$  is considerably larger for  $[s]$  than for  $[p]$ , the former may give rather strong homopolar bonding. There is also more or less heteropolar bonding. One might think to divide the latter between the  $[s]$  and  $[p]$  orbitals, but such a division would probably be meaningless. In fact in the last analysis the energy of forma-

tion of a molecule from its atoms cannot be assigned exclusively, nor even more than in a very rough way, to the "bonding electrons" alone, no matter what type of electron configuration is used. Nevertheless the presence of the "bonding electrons" or of the heteropolar character is decisive for the stability of the molecule.

If we make use of electroaffinity and other data in studying the  $[s]$  and  $[p]$  orbitals of  $CX_4$  and other similar molecules  $RA_4$  (e.g.,  $SiH_4$ ,  $SiX_4$ ,  $NH_4^+$ ,  $BF_4^-$ ,  $SO_4^{2-}$ ,  $ClO_4^-$ ), we find interesting variations in the polarity and in the relative bonding effects of  $[s]$  and  $[p]$ . At one extreme is the case where the  $[s]$  orbitals have very strong  $R^+A^-$  polarity and so are practically unshared  $ns$  electrons of the central atom  $R$ , while the  $[p]$  orbitals are nearly homopolar and strongly bonding (probable example  $ClO_4^-$ , and to a less complete extent  $Cl_4$  (cf. I of this series<sup>9</sup>)). In such a case the *four* C-H bonds of classical chemical valence theory are provided almost entirely by *three* pairs of  $[p]$  electrons, the total bonding of the group  $[p]^6$  being directed, however, equally toward all four A's (cf. I of this series).

At the other extreme, which occurs when A is very electronegative relative to R, we have  $a$  and  $b$  nearly equal so that the  $[s]$  orbitals give strong homopolar bonding. At the same time the  $[p]$  orbitals have very strong  $R^+A^-$  polarity ( $c \ll d$ ) and so belong predominantly to the outer atoms A and contribute only a little to the homopolar part of the R-A bonding (example,  $SiF_4$ ). In such a case the total bonding is about as much heteropolar as homopolar, or in other words is about half-way between these two ideal cases.

The foregoing discussion tends to indicate that, contrary to a suggestion of Pauling and Slater, the high stability of tetrahedral molecules and ions  $RA_4$  is not due particularly to an ability of  $s-p$  mixed (tetrahedral) atomic orbitals to form especially strong homopolar bonds. For as we have just seen, the types  $RA_4$  range over a variety of cases from one where there is strong homopolar  $p$  binding but hardly any homopolar  $s$  binding to one where the roles of  $s$  and  $p$  are

<sup>9</sup> R. S. Mulliken, Phys. Rev. **40**, 55 (1932): I.

reversed; at the same time the heteropolar contribution to the binding varies greatly. Approximate calculations of Van Vleck,<sup>10</sup> using various types of electron configurations (Slater-Pauling, LCAO molecular orbital, and ionic), also indicate that the stability of the tetrahedral arrangement is not specially connected with the simultaneous presence and mixing of  $s$  and  $p$  atomic orbitals.

Instead of this, the foregoing discussion strongly suggests, as has been pointed out without the present detailed justification in earlier papers (I, II, and especially V, p. 501 of this series<sup>8</sup>), that the exceptional chemical stability of tetrahedral  $RA_4$  types is due to an unusually favorable close packing of positive charges and negative electricity which is possible for this rather high type of symmetry. In crystal structure the great importance of coordination number in relation to stability is well recognized. A similar effect may well operate here. It appears that the form  $RA_4$  (neutral or charged) is favored whenever it can be attained without sacrificing the even more important stability criterion (cf. II of this series, sections 3 and 7)<sup>11</sup> that the electrons surrounding each nucleus constitute from the latter's point of view a set of closed shells of relatively low energy.

We return now to a consideration of degrees of heteropolarity in molecules  $RA_4$ . The total strength of the  $R-A$  bonds can, at least roughly, be divided into a homopolar and a heteropolar part. The homopolar strength is approximately proportional to the quantity  $H_{AB}$  or  $Y$  of Eq. (19) of XI, which is usually approximately proportional to the "overlapping integral"  $S = \int \phi_A \phi_B dv$ . The heteropolar strength can be roughly gauged from a knowledge of  $R-A$  distances and of the net charges  $Q$  assignable to the atoms  $R$  and  $A$ . These charges can most conveniently be determined by the method of section 1, based on Eq. (41) of XI, with the use of localized molecular orbitals for each bond.

The same net charges should, however, presumably be obtainable by applying Eq. (41) of XI using nonlocalized molecular orbitals and summing the effective atomic charges corre-

sponding to all the electrons assigned to such orbitals. Let us consider  $CCl_4$  and  $CF_4$  as examples. In order to get  $Q_C$ , we should obviously take

$$Q_C = (Q_C \text{ for } [s]) \text{ plus } 3 \times (Q_C \text{ for } [p]),$$

since  $Q_A$  of Eq. (41) of XI gives the net charge on atom  $A$  due to *one pair* of electrons distributed between  $A$  and another atom, or group of atoms in the present application, called  $B$ . With the usual reservations, somewhat enhanced here because the quantity  $Y$  may differ very considerably for  $[s]$  and  $[p]$ , we may use Eq. (41).

From Eq. (41), we find

$$CCl_4: Q_C = -0.51 + 3 \times 0.37 = +0.60;$$

$$CF_4: Q_C = -0.32 + 3 \times 0.51 = +1.21.$$

Thus we get net polarities  $(C^{+0.60})(Cl^{-0.15})_4$  and  $(C^{+1.21})(F^{-0.30})_4$  as compared with the results  $(C^{+0.52})(Cl^{-0.13})_4$  and  $(C^{+1.68})(F^{-0.42})_4$  obtained in section 1. The lack of exact agreement is probably not due entirely to our use of different approximate wave functions in the two cases, but partly if not largely to the rough form in which we have developed the theory. At least part of the discrepancy is obviously due to our use of the two-term Eq. (41) with constant coefficients. It seems hardly worth while to consider the matter here in more detail. Besides, it seems clear that the results obtained by the method of section 1 should be at least approximately applicable here, and they are probably more accurate than those calculated here by applying Eq. (41) to  $[s]$  and  $[p]$  separately and summing.

We turn now to another problem often encountered in studying the forms of nonlocalized molecular orbitals. As was mentioned in section 4 of XI, coefficient ratios such as  $a/b$  in any  $\phi_{AB}$  depend, except in the case  $a=b$ , not only on relative electronegativities, but also on bond angles in case these are not fixed by the assumed symmetry. In the tetrahedral type  $RA_4$  discussed above, the bond angles are fixed by the symmetry so that we did not need to consider them.

In some cases the  $H_{AB}$ 's and  $Y$ 's of different molecular orbitals depend on bond angles in a way which is important for our qualitative treatment. As an example, we may consider the

<sup>10</sup> J. H. Van Vleck, J. Chem. Phys. **1**, 177, 219 (1933); **2**, 20, 297 (1934).

<sup>11</sup> R. S. Mulliken, Phys. Rev. **41**, 49 (1932): II.

bonding orbitals of  $\text{H}_2\text{O}$ . The normal state electron configuration<sup>12</sup> is

$$1s^2(2sa_1)^2[yb_2]^2[za_1]^2(2p_zb_1)^2, {}^1A_1, \quad (9)$$

all the orbitals being essentially nonbonding O atom orbitals except the two O–H bonding orbitals  $[y]$  and  $[z]$ . These may be approximated (cf. IV of this series,<sup>4</sup> Eqs. (8)) by

$$[y] = a(2p_y)_O + b\{(\alpha - \beta)/N\}, \quad (10)$$

$$[z] = c(2p_z)_O + d(\alpha + \beta)/N'; \quad (11)$$

the  $z$  axis bisects the HOH angle, the  $y$  axis lies in the HOH plane, and  $\alpha$  and  $\beta$  refer to  $1s$  orbitals of the two H atoms, with the  $\alpha$  nucleus located in the region of positive  $y$ .

Now if O and H had equal electroaffinity (more rigorously, if  $2p$  of O had the same electroaffinity as  $\alpha - \beta$  and  $\alpha + \beta$  of H–H), then we should have  $a = b$  and  $c = d$ . Since actually O is much more electronegative than H, we have  $a/b > 1$  and  $c/d > 1$ . We do not, however, in general have  $a/b = c/d$ . This can easily be seen qualitatively by considering extreme values  $180^\circ$  and  $0^\circ$  for the HOH angle  $\phi$ .

For  $\phi = 180^\circ$ , the directions  $x$  and  $z$  become equivalent, both being perpendicular to the line HOH which is now the  $y$  axis; the symmetry now becomes  $D_{\infty d}$ . Here  $[z]$  becomes pure  $2p_z$  of O, i.e.,  $c = 1$ ,  $d = 0$  in (11), and  $2p_z$  and  $2p_x$  become a degenerate pair of nonbonding orbitals which may be called  $2p_{\pi u}$ . The result  $c = 1$ ,  $d = 0$ , i.e.,  $c/d = \infty$ , shows (cf. Eq. (16) of XI) that  $(H_{AB} - SW) = 0$  for  $[z]$  when  $\phi = \pi$ . At  $\phi = \pi$ ,  $H_{AB}$  and  $S$  both vanish together, as is easily seen from symmetry considerations. The quantity  $Y = H_{AB} - SX$ , which is nearly the same as  $H_{AB} - SW$ , also approaches zero as  $\phi \rightarrow \pi$ . At the same time that  $-H_{AB}$ ,  $S$ , and  $-Y$  approach zero for  $[z]$ , they can be shown to approach a maximum value for  $[y]$ , which becomes a double-bonded bonding orbital of  $\sigma_u$  type. The energy is

then very considerably lower ( $I$  greater) for  $[y]$  than for  $[z]$ .

For  $\phi = 0$  the roles of  $[y]$  and  $[z]$  are reversed. The symmetry is  $C_{\infty v}$ . Here  $[y]$  becomes pure  $2p_y$  ( $a = 1$ ,  $b = 0$ ) and is degenerate with  $2p_x$ , the two being classifiable as  $2p_{\pi}$ , while  $[z]$  has maximum bonding and maximum  $I$ , and is of type  $\sigma$ . It is easily seen that as  $\phi$  goes from 0 to  $\pi$ ,  $b/a$  goes up from zero to a maximum value, while  $d/c$  descends from a maximum value to zero, each varying roughly in proportion to  $Y$  of  $[y]$  or  $[z]$ , respectively. It is evident that for some angle between zero and  $\pi$ ,  $a/b = c/d$  must hold; also somewhere  $H_{AB}$ ,  $S$ , and  $Y$  must be equal for  $[y]$  and  $[z]$ ; and somewhere  $I$  must be the same for  $[y]$  as for  $[z]$ .

These relations, it can be shown,<sup>13</sup> would all nearly hold for  $\pi/2$  if we could entirely neglect all terms in  $W$  of Eq. (11) of XI which in any way involve both H atoms (either their orbitals, or their potentials) simultaneously. In this case we should have  $b/a > d/c$  for the actual H–O–H angle of about  $105^\circ$ , and  $-H_{AB}$ ,  $S$ ,  $-Y$ , and  $I$  would be somewhat larger for  $[y]$  than for  $[z]$ , as was estimated (in the case of  $I$ ) in V of this series.<sup>8</sup> Allowance must, however, be made for the H–H interactions, which tend to lower the energy of  $[z]$  considerably relative to  $[y]$ , since the former involves H–H bonding, the latter H→H antibonding. Hence actually for  $\pi/2$ ,  $[z]$  should be lower in energy than  $[y]$ , and the critical angle at which the  $[y]$  and  $[z]$  curves of  $I$  against  $\phi$  cross must exceed  $\pi/2$ . Quite possibly  $[y]$  and  $[z]$  are nearly degenerate for the actual angle of about  $105^\circ$ .

The methods exemplified in this paper for qualitatively or semiquantitatively determining polarities in molecular orbitals will be used continually, explicitly or implicitly, in the papers of this series.

<sup>13</sup> The writer is indebted to Professor Van Vleck for calling his attention to this point. The proof is easily obtained using Eq. (11) of XI; cf. also F. Hund, *Zeits. f. Physik* 73, 1 (1931).

<sup>12</sup> R. S. Mulliken, *J. Chem. Phys.* 3, 506 (1935): VII.