

NOTAS DE FÍSICA

VOLUME VI

Nº 16

THE PRINCIPLE OF ELECTRONEGATIVITY EQUALIZATION

I- BOND MOMENTS

by

Ricardo Carvalho Ferreira

CENTRO BRASILEIRO DE PESQUISAS FÍSICAS

Av. Wenceslau Braz, 71

RIO DE JANEIRO

1960

THE PRINCIPLE OF ELECTRONEGATIVITY EQUALIZATION  
I- BOND MOMENTS \* †

Ricardo Carvalho Ferreira \*\*

Centro Brasileiro de Pesquisas Físicas

Rio de Janeiro - Brazil

(Received December 2, 1960)

INTRODUCTION

It has been increasingly recognised in the last ten years that the concept of electronegativity <sup>1,2</sup>, in spite of its considerable early successes, is in a crisis <sup>3</sup>. The concept of electronegativity has only a semi-quantitative significance, and, as the theory of the chemical bond becomes more refined that concept loses its importance. In this way, unless we try to refine

---

\* This work was done while the author was a Rockefeller Foundation Fellow at the California Institute of Technology, Pasadena, during the academic year 1959-1960.

† Submitted for publication in the Journal of Physical Chemistry.

\*\* On leave of absence from the University of Recife, Recife, Brazil.

the concept of electronegativity in order that its usefulness can be enhanced we may well have to agree with Mulliken <sup>4</sup> when he expressed his fears that the concept may some day outlive its usefulness.

To a large extent the limitations of the concept of electronegativity for describing bond properties are due to the fact that the effective electronegativity of an atom in a molecule is not equal to the electronegativity of the free atom,  $X(0)$ . This difference occurs because electronegativity is a function of the hybridization state of the atom (hybridization effect) and of the net charge of the atom (charge effect). It is our purpose to show that by taking into account these two effects it is possible to give to the concept of electronegativity a flexibility which permits improved quantitative uses, without introducing undeserved complications. More specifically, we will try to show how this can be accomplished by using the principle of electronegativity equalization. In this paper we ~~will~~ discuss the fundamentals of this principle and its application for the calculation of bond moments <sup>5</sup>, and in the subsequent papers of this series we will discuss force constants and bond dissociation energies.

The principle of electronegativity equalization is a generalization firstly proposed by Sanderson <sup>6</sup> and in its most general form it can be formulated thus: in a given atomic system the electronegativities of all bonded atoms at their equilibrium distances are equal. This generalization can be established from the LCAO-MO method and, in fact, it is as valid as this approximation.

Let us consider an atom B with a valence electron  $\underline{i}$  obeying the equation:

$$-\frac{h^2}{8\pi^2m} \nabla^2 \psi_B(i) + V_B \psi_B(i) = E_B \psi_B(i) \quad (1)$$

where  $V_B$  is the Coulomb potential acting on the  $\underline{i}$  electron and  $\psi_B(i)$  is its wave function. The potential  $V_B$  is given by  $Z_B^*e/r_B$ , where  $Z_B^*$  is the effective nuclear charge acting at the distance  $r_B$ . The ionization potential of the  $\underline{i}$  electron includes also the kinetic energy and the virial theorem permits one to write  $V_B = 2I_B(i)$ . If we add an electron  $\underline{j}$  to the atomic orbital  $\psi_B$  the potential acting on it is equal to  $2E_B(j)$ , where  $E_B(j)$  is the electron-affinity of atom B for the  $\underline{j}$  electron. According to Mulliken<sup>2</sup>, the electronegativity of atom B is given by  $1/2 (I_B(i) + E_B(j))$ : thus the electronegativity represents the average binding energy of the electron-pair by atom B.

In the same way the  $\underline{j}$  electron of an atom A obeys the equation:

$$-\frac{h^2}{8\pi^2m} \nabla^2 \psi_A(j) + V_A \psi_A(j) = E_A \psi_A(j) \quad (2)$$

where  $V_A = Z_A^*e/r_A$  is the Coulomb potential acting on the  $\underline{j}$  electron and equal to  $2I_A(j)$ . If we add an electron  $\underline{i}$  to the atomic  $\underline{j}$  to the atomic orbital  $\psi_A$  the potential acting on it is given by  $2E_A(i)$ , where  $E_A(i)$  is the electron-affinity of atom A for the  $\underline{i}$  electron. Mulliken's electronegativity is  $1/2 (I_A(j) + E_A(i))$ , that is, the average binding energy of the electron pair by atom A.

Now, let us suppose that atoms A and B combine to form a bond involving electrons  $\underline{i}$  and  $\underline{j}$ . These two electrons now occupy

the same molecular orbital  $\psi_n$  and are subject to the same molecular potential  $V_M$ . Let us suppose also that  $X_A(0) = X_B(0)$ ; in this case there will occur an overlap between the atomic orbital  $\psi_A$  and  $\psi_B$  but since the average binding energy of the electron pair by the two atoms are the same, no net charge transfer will occur. The situation can be visualized by the following diagram:

In general, however,  $X_A(0) \neq X_B(0)$ ; for example, suppose that  $X_A(0) > X_B(0)$ . In this case, and considering the continuous distribution of the electrons in the space, the system will not be in equilibrium. There will occur a partial charge transfer from B to A, increasing  $X_B$  and decreasing  $X_A$ , until the condition  $X_A = X_B$  attains; this is the equilibrium condition. In this way we obtain exactly the principle of electronegativity equalization. The bonding electrons  $\underline{i}$  and  $\underline{j}$  now obey the equation:

$$-\frac{h^2}{8\pi^2 m} \nabla^2 \psi_M + V_M \psi_M = E_M \psi_M \quad (3)$$

It is seen that since the electronegativities of the free atoms differ from element to element and since their values are equalized by a process of charge transfer, Sanderson's principle

permits, in principle, the calculation of the amount of charge transferred, hence of the primary bond moments. In practice, difficulties may arise: in the first place, the electronegativity is a function of the hybridization state of the atom <sup>7</sup> and there is no general criterion for establishing the actual hybridization state of an atom in a molecule, and, in the second place there is the difficulty in the choice of the proper screening-constants of the bonding electrons, that is, in the evaluation of the charge effect.

Let us discuss this last difficulty in the first place. In our previous note <sup>5</sup> we already pointed out that the electronegativity of an atom can be treated as a potential function, and proposed a modification of the linear dependence between electronegativity and charge suggested by Pauling <sup>8</sup>. The refinement takes into account the fact that the value of the screening-constant of an electron depends of its wave function. For a molecule  $B_n A_m$  our equations are:

$$X_B(+mq) = X_B(0) + q \sum_{i=1}^m \Delta X_i^+ \quad (4)$$

$$X_A(-nq) = X_A(0) - q \sum_{j=1}^n \Delta X_j^- \quad (5)$$

in which  $X_A(0)$  and  $X_B(0)$  are the electronegativities of atoms A and B in the uncombined state (with  $X_A(0) > X_B(0)$ ),  $n$  and  $m$  are the corresponding oxidation numbers,  $q$  is the fractional charge transferred when  $n = -1$  and  $m = +1$ , and  $\Delta X_i^+$  and  $\Delta X_j^-$  represent the variations in the value of  $X$  caused by the complete removal

of the  $i$  electron of atom B and the complete acceptance of the  $j$  electron by atom A, respectively. The principle of electronegativity equalization requires that  $X_A(-nq) = X_B(+mq)$ . Hence:

$$q = \frac{X_A(0) - X_B(0)}{\sum_{i=1}^m \Delta X_i^+ + \sum_{j=1}^n \Delta X_j^-} \quad (6)$$

The expressions for  $\Delta X_i^+$  and  $\Delta X_j^-$  are given by:

$$\Delta X_i^+ = \frac{\sigma_i}{1 - \sigma_k} \left\{ X_{B+1}(0) - X_B(0) \right\} \quad (7)$$

$$\Delta X_j^- = \frac{\sigma_j}{1 - \sigma_h} \left\{ X_A(0) - X_{A-1}(0) \right\} \quad (8)$$

where  $\sigma_i$  is the screening-constant of the  $i$  electron of atom B,  $\sigma_k$  is the screening-constant of the differentiating electron of element  $Z_{B+1}$ ,  $\sigma_j$  is the screening-constant of the  $j$  electron accepted<sup>9</sup> by atom A, and  $\sigma_h$  is the screening-constant of the differentiating electron of atom A.

It is well known that not only does the screening-constant of an electron depend of its wave function, but, as Sommerfeld<sup>10</sup> firstly pointed out, different screening-constant must be used for different properties. This introduces another difficulty because screening-constant for electronegativity are not known. In the simple treatment of the charge effect, Pauling<sup>8</sup> and also Haissinsky<sup>11</sup> chose for the electronegativity screening-constant of one valence electron for another the size screening-constant<sup>12</sup> of the  $1s$  electron of hydrogen. We prefer to use the values

established by Kohlrausch<sup>13</sup> from ionization potential data, and presently we will discuss the approximations involved in this procedure.

In this paper we will consistently use Mulliken's electronegativity scale. According to this scale, electronegativities are given  $X(O) = \frac{I(v) + E(v)}{6.3}$ , in which  $I(v)$  and  $E(v)$  are, respectively, the valence state ionization potential and the valence state electron-affinity of the free atom (the numerical coefficient 6.3 was introduced by Pritchard and Skinner<sup>3</sup> in order that when  $I(v)$  and  $E(v)$  are measured in electron-volts,  $X(O)$  as defined above be comparable with Pauling's values). Now, not only  $I(v)$  is not necessarily equal to the ground-state ionization potentials used by Kohlrausch, but, more important still, whereas  $I_0$  (the ground state ionization potential) does not increase monotonically with increasing values of  $Z$  along a given period of the Periodic System of the Elements, the sum  $I(v) + E(v)$ , that is  $X(O)$ , does increase monotonically along each period. The errors introduced by using Kohlrausch's values as the true electronegativity screening-constants are particularly large for the elements of groups IIIb and VIb, since these elements have abnormally low ground state ionization potentials, when compared with the elements immediately preceding them in the Periodic System<sup>14</sup>. This fact corresponds to large values of Kohlrausch screening-constants of the differentiating electrons of these elements of groups IIIb and VIb, but since the electronegativities are normal the corresponding screening-constants must be much smaller. For these elements, therefore, it is more reliable to use interpolated values for the electronegativity screening-constants. With these corrections,



Kohlrausch's values cannot differ from the true electronegativity screening-constants by more than a few percent, and can be confidently used within these limits.

The hybridization effect introduces difficulties of a more fundamental character. The electronegativity of an atom is a function of the hybridization state of the atom<sup>2,7,15</sup> and in particular the value of  $X(0)$  increases as the value of  $\underline{a}$  in the isovalent hybrid orbital of the form  $(a\underline{s} + b\underline{p})$  increases. This fact is shown in Table I, constructed from the data by Pritchard and Skinner<sup>3</sup> and Pritchard<sup>16</sup>; this Table also shows the values of the screening-constants of the differentiating electrons calculated from Kohlrausch's data<sup>13</sup>. Although no sure criterion exists for the establishment of the hybridization state of an atom in a molecule, the molecular geometry gives in many cases reliable informations for the correct utilization of the values shown in Table I<sup>17</sup>.

### THE EFFECTIVE ELECTRONEGATIVITIES

If we calculate from equation (6) the value of  $\underline{g}$  for a given molecule, and use this value in equations (4) and (5), then  $X_B(+mq)$  and  $X_A(-nq)$  are the effective electronegativities of atoms B and A in the compound  $B_n A_m$ . It should be pointed out that in the various treatments of the relations between electronegativity difference and ionic character of bonds<sup>8,18,19</sup>, the ionic fraction  $\underline{g}$  is uniquely determined by the value of the electronegativity difference,  $X_A(0) - X_B(0)$ , and it is possible

to draw a curve connecting the ionic character with this difference. According to equation (6), however,  $g$  is not a unique function of  $X_A(0) - X_B(0)$ , but depends also of the screening-constants of the bonding electrons. In other words,  $g$  is a property characteristic of each molecule as an independent entity, and a single curve connecting  $g$  with electronegativity difference has no meaning at all. This is, we believe, an important result of the principle of electronegativity equalization <sup>6,20</sup>.

#### THE CALCULATION OF BOND MOMENTS

Both the valence bond method and the molecular orbital method predict that the electric moment of a bond is the sum of four distinct contributions:

- i - the primary moment, due to the assymetry of charge in the bonding electrons, and equal to  $eqR_0$ ,  $R_0$  being the equilibrium internuclear distance;
- ii - the homopolar dipole or overlap dipole, due to the inequality of size of the bonding orbitals <sup>21</sup>. This contribution is zero only if the bonding orbitals are of the same size, or if the overlap integral is zero <sup>22</sup>;
- iii - the atomic moment or hybridization moment, which arises from the assymetry of the hybrid atomic orbitals in relation to the atomic nucleus; its value is zero for non-hybrid orbitals;
- iv - the electron-pair moment, due to the fact that as the bonding orbitals are hybridized the non-bonding electrons also

hybridize; this contribution is opposite to the atomic moment.

From the above considerations it is clear that we cannot expect that a calculation of the primary bond moment alone could give good results for the total moment. It seems, however, that the primary moment is the main component of the total dipole moment in the hydrogen halides. Table II gives, in the second column, the values of  $\underline{q}$  for these molecules, obtained from equation (6) and assuming that the halogen atoms use pure  $\underline{p}$  orbitals. The agreement between  $eqR_0$  and the experimental values of the gaseous dipole moments is surprising.

It is well known <sup>23</sup> that the dipole moment of a molecule like HCl is extremely sensitive to bond hybridization. If the chlorine atom uses a pure  $\underline{p}$  bonding orbital the homopolar moment puts a negative charge in the hydrogen atom, but this negative charge is reduced and even reserved by assuming an  $\underline{s}$ -contribution to the bonding orbital of the chlorine atom or by introducing ionic terms to the total wave function of the molecule <sup>24,25,26</sup>. This same entangled situation occurs in the interpretation of nuclear quadrupole coupling constants <sup>3,18,25</sup>. Now, we have seen that as we increase the  $\underline{s}$ -character of the bonding orbitals the electronegativity increases. This means that the value of  $\underline{q}$  increases with the amount of  $\underline{s}$ -character and a simple calculation shows that the experimental values of the dipole moments are obtained from equation (6) by assuming an  $\underline{s}$ -contribution to the halogen wave function of 4% in HF, 2% in HCl, 3% in HBr, and 0% in HI. It is seen that any increase in the  $\underline{s}$ -character of the bonding orbitals leads to an increase in the ionic fraction, so that the two effects are not mutually independent.

A test for the reliability of the values of  $q$  given by equation (6) could be made only if it is possible to find molecules obeying the following conditions:

- a) The hybridization state of the atoms is known from a sure criterion;
- b) Electron-pair dipoles do not exist;
- c) Atomic dipoles exactly counterbalance one another;
- d) Homopolar dipoles also obey condition (c) or are vanishingly small.

These conditions occur within a good approximation in certain carbon compounds in which the hybridization state of the various carbon atoms can be known from the differing spatial arrangements of the bonds <sup>27</sup>. For example, in the case of toluene, propene, butene-1, methylacetylene, and butyne-1, all the restrictive conditions (a-d) prevail, and the electric moments of the gaseous molecules should be given by the vectorial sum of all primary bond moments. Table III shows in the second column the values of  $q$  calculated from (6) for the bonds  $C(sp^3) - C(sp^2)$  and  $C(sp^3) - C(sp)$ . Columns 4 and 5 show the calculated primary moments of these bonds and the experimental gaseous dipole moments for these molecules, respectively. It is seen that the calculated values are within the limits of the experimental error for toluene, propene, and butene-1, and about 15% larger than the experimental values for the substituted acetylenes.

Since the total moment of the molecules is given by the sum of all primary moments, the good results obtained for the first

three compounds are justified only if the  $C(sp^3) - H$  primary moment is equal to the  $C(sp^2) - H$  primary moment <sup>28</sup>. Now, the  $\overleftarrow{C-H}$  primary moment in ethane is 0.21 D, whereas the  $\overleftarrow{C-H}$  primary moment in ethylene is 0.41 D. However, the primary moment of the C-H bond in the methyl group of toluene, propene, and butene-1 is certainly larger than 0.21 D, because the positive charge in the  $sp^3$  carbons of these molecules, due to the charge transfer to the  $sp^2$  carbons, increase their electronegativities. In the same way, the primary moment of the C-H bonds of the methylene group of propene and butene-1 (and the  $C(sp^2) - H$  primary bond moment of toluene) is less than 0.41 D. Calculations by an iterative process show that, in fact, the primary moments of the two types of C-H bonds cannot differ by more than 0.05 D.

For the substituted acetylenes there is a similar situation but since the primary  $\overleftarrow{C-H}$  bond moment in acetylene (0.98 D) is much larger than the primary  $\overleftarrow{C-H}$  moment in ethane, it is not completely counterbalanced by the  $C(sp^3) - H$  bond moment; an iterative calculation shows that the difference  $\mu_{C(sp)-H} - \mu_{C(sp^3)-H}$  is about 0.2 D, in the opposite sense of the primary  $C(sp^3) - C(sp)$  bond, again in excellent agreement with the experimental values (Table III).

We have applied the method also to two alicyclic hydrocarbons, 1,3-cyclopentadiene and cyclohexene. The experimental values for the dipole moments of these substances are 0.53 D and 0.55 D, respectively (see references given in Table III). The sum of the  $C(sp^3) - C(sp^2)$  bond moments, calculated from the known configuration of these substances are 0.45 D for 1,3-cyclopentadiene and 0.58 D for cyclohexene.

An interesting consequence of these results is that they tend to disprove the dipole moment evidences put forward in support of the existence of hyperconjugation <sup>29</sup>. In a recent discussion Dewar and Schmeising <sup>30</sup> have pointed out that since  $sp^2$  carbon is more electronegative than  $sp^3$  carbon, the bonds between a trigonal carbon and a tetrahedral carbon must be polar, and they stated that "unless the magnitude of the  $C(sp^3) - C(sp^2)$  dipole can be estimated and shown to be less than the observed moments of propene and toluene, one cannot conclude from the polarity of these hydrocarbons that the bonds to methyl are not single". Our results are definitely in favour of the view that hyperconjugation does not contribute to the ground states of these molecules <sup>30a</sup>.

#### THE ELECTRONEGATIVITY OF DIAGONAL CARBON

The large value for the electronegativity of sp carbon used in this paper, 3.37, may be questioned. This value is obtained from spectroscopic data <sup>3</sup> and it is further supported from a study of the dipole moments of mono-halogenated acetylenes and of the polarity and ionization potential of carbonyl groups.

Table IV shows the values of calculated  $C(sp) - Hal$  primary moments in monochloro-acetylene and monobromo-acetylene, obtained from equation (6) and assuming an sp electronegativity for carbon of 3.37 and a pure p electronegativity for chlorine (3.00) and bromine (2.76) <sup>31</sup>. The results are particularly impressive and it must be pointed out that the zero dipole moment of  $CH \equiv CBr$  had never before been interpreted. The fact that the

halogen atoms of these molecules do have a positive charge is indeed entirely in agreement with the chemical behaviour of these substances.

Walsh <sup>7</sup>, noting that the ionization potential of the carbonyl group of various compounds changes from 14.55 eV in CO to 10.2 eV in acetone (Table V), tried to relate this variation with the polarity of the C = O group. Price <sup>32</sup> had shown that the ionization potential of the carbonyl group refers to the non-bonding p electrons of the oxygen atom, and should be compared with the ground-state ionization potential of atomic oxygen, which corresponds to the transition  $(0, ^3P_2) \longrightarrow (0^+, ^4S_{3/2})$ . On the assumption that  $X_O(0)$  is always larger than  $X_C(0)$ , Walsh attributed the decreasing ionization potential in the series CO, CO<sub>2</sub>, HCOOH, H<sub>2</sub>CO, CH<sub>3</sub>-CO-CH<sub>3</sub>, to an increasing negative charge in the oxygen atom. However, it is impossible in this way to explain why it is that the ionization potential of the oxygen atom in CO and CO<sub>2</sub> is larger than  $I_O$  for oxygen. Walsh also noted that the decrease in the ionization potential is accompanied by an increase in the C-O bond distance, which means a decrease in the C-O bond strength.

We think that these facts can be interpreted in the following way: in CO and CO<sub>2</sub> the carbon atom is in the sp state <sup>33</sup>, and its electronegativity is larger than the p electronegativity of oxygen ( $X_C(sp) = 3.37$ ;  $X_O(p) = 3.17$ ). Hence, both in CO and CO<sub>2</sub> the oxygen atoms have a positive charge which results from  $\sigma$ -bonding electron transfer to the carbon atom. The charge calculated from equation (6) is however reduced by the atomic dipole of the sp carbon <sup>34</sup>. In the organic carbonyl compounds, on the other hand

the carbon atom is in the trigonal state and the electronegativity difference is reversed, with the oxygen atom negatively charged. We have calculated by our method the charge transferred by  $\sigma$ -bonding alone, and the results are shown in Table V. For formaldehyde and formic acid monomer the results were obtained by a simple iterative process. We did not compute the charge in the oxygen atom of acetone because the atomic dipoles of the  $C(sp^3) - C(sp^2)$  bonds reduce the electronegativity of the trigonal carbon by an unknown amount.

The increase in the C-O bond distance observed in passing from CO and CO<sub>2</sub> to the organic carbonyl compounds is clearly associated with the change in hybridization of the carbon atom <sup>35</sup>.

A positive charge in the oxygen atom of CO is substantiated by some recent work on this molecule. Thus, Burrus <sup>36</sup> has shown that the dipole moment of CO is 0.112 D, and Rosenblum, Nethercot Jr., and Townes <sup>37</sup> have conclusively shown, in what is probable the first absolute determination of the sign of a dipole moment, that the positive end of the dipole of the CO molecule is in the oxygen atom. Theoretical calculations by Ransil <sup>38</sup> tends to confirm this.

#### THE ALKALI-METAL HALIDE MOLECULES

Another class of compounds which partially obeys the restrictive conditions discussed on page 9 are the alkali-metal halides. In these compounds the overlap integral is small, so that the homopolar dipole is practically zero, and we can further



assume that the halogen atoms use pure p bonding orbitals. Unfortunately, only for a small number of compounds we can make a comparison between the calculated and the experimental dipole moments. Thus, although the electric moment of gaseous KF, KCl and KI are known<sup>39,40</sup> there is not in the literature electron-affinity data for calcium, and this prevents us from calculating  $\Delta X_i^+$  for potassium. As for the lithium and sodium halides, reliable values of the dipole moments exist only for LiF, LiCl, and NaI, and these are shown in the last column of Table VI. For comparison the fourth column of Table VI shows the values of  $eqR_0$  for these molecules, calculated from equation (6).

An interesting result of our calculation is that the lithium halides are apparently more ionic than the corresponding sodium compounds, although the differences  $X_{\text{Hal}}(0) - X_{\text{Na}}(0)$  are larger than the corresponding differences  $X_{\text{Hal}}(0) - X_{\text{Li}}(0)$ . The explanation of this fact resides in that the screening-constant of the 3s electron of sodium is larger than the screening-constant of the 2s electron of lithium.

#### WATER AND HYDROGEN SULPHIDE

If we assume that the oxygen atom in water uses pure p bonding orbitals<sup>41</sup>, we obtain from equation (6) the value  $q = 0.114$  e. u., which means that each hydrogen atom has a positive charge of 0.114 e. u., and the oxygen atom a negative charge of - 0.228 e. u. This corresponds to a dipole moment of only 0.64 D and furthermore there could be no electron-pair contribution. The

experimental value of the dipole moment of gaseous  $\text{H}_2\text{O}$  is 1.85 D (reference given in Table II). On this ground we must reject this electronic structure for water, and we must admit that in this molecule the oxygen atom uses  $\text{sp}^3$  bonding orbitals<sup>42</sup>. Using the  $\text{sp}^3$  electronegativity of oxygen we obtain  $q = 0.24$ , and this corresponds to a primary dipole moment of 1.36 D, which would be further increased by the resultant of the two electron-pair dipoles.

For the molecule  $\text{H}_2\text{S}$  the situation is different, since we know from valence angle data<sup>43</sup> that the S-H bond involves almost pure  $p$  bonding orbitals, with perhaps a few percent s-character. Our calculations tend to support this view: if we use the  $\text{sp}^3$  electronegativity of sulfur, 3.52, we obtain  $q = 0.21$ , which gives a resultant primary dipole moment of 1.86 D for the molecule  $\text{H}_2\text{S}$ , and to which we must add the electron-pair dipoles. The experimental value of the dipole moment of gaseous  $\text{H}_2\text{S}$  is only 0.92 D; this value can be obtained as the resultant primary moment only by assuming that the sulfur bonding orbitals in  $\text{H}_2\text{S}$  involve 10% s-character ( $q = 0.083$ ). In fact, this value (10% s-character) is an upper limit for s-hybridization, since we did not take into account the electron-pair dipoles.

An important conclusion of the principle of electronegativity equalization is that the polarity of, let us say, the two O-H bonds in water is the same, without simultaneously implying that the polarity of adjacent bonds are mutually independent. In other words, the polarity of the O-H bond in the free radical OH is different<sup>44</sup> from the polarity of the O-H bonds in the molecule  $\text{H}_2\text{O}$ , but the fact that the electronegativities of all the three

atoms in this last molecule are equal means that the polarity of the two O-H bonds in water is the same. It is perhaps interesting to note that this conclusion is not reached by the conventional ionic-covalent resonance theory. The inconsistency of the resonance approach is well illustrated by the following remarks due to Coulson <sup>15</sup>: "as soon as one O-H bond is ionic, the flow of charge to the oxygen atom neutralizes the excess electronegativity and renders the probability that the second bond should be simultaneously ionic, much smaller than before".

### COMPLEX IONS

The extension of this method to more complicated systems, such as molecules with multiple bonds, coordination compounds, ionic crystals, etc., presents many difficulties. For example, the charge distribution calculated for the alkali-metal halides (Table VI) refers to the gaseous molecules. In the crystal the charge distribution is different, since each atom (ion) is under the influence of the total crystal field.

For the complex ions we need first obtain reliable data on the valence state ionization potentials of the central ions (involving outer s and p orbitals). It is possible, however, to extend our method in a rough way, provided we know the (approximate) electronegativity of the central metallic atom and restricting ourselves to ligands without vacant orbitals to form  $\pi$ -bonds. As an illustrative example, let us consider the hexamine-cobalt-(III) ion,  $[\text{Co}(\text{NH}_3)_6]^{+3}$ . Let us suppose that Sidgwick's dative bond

structure applies initially to this ion. We can visualize it as formed by the species  $\text{Co}^{-3}$  linked by normal covalent bonds with six species  $\text{H}_3\text{N}^{+1}$ . The electronegativity of cobalt is 1.8 according to Bellugue and Daudel <sup>45</sup>, and assuming an average  $\Delta X^-$  of 3.0 we obtain  $X_{\text{Co}}(-3) = -7.2$ . In the same way we can calculate that the electronegativity of  $\text{N}^{+1}$  is 7.6. It is seen that the electronegativity of  $\text{Co}^{-3}$  is very low and the electronegativity of  $\text{N}^{+1}$  is extremely high; there will be a large charge transfer from  $\text{Co}^{-3}$  to the ligands. Using equation (6) one gets  $q = \frac{7.6 - (-7.2)}{4 + (6 \times 3)} = 0.66$ . Hence the net charge in the cobalt atom will be  $(-3 + (6 \times 0.66)) = +0.96$  e. u., and the net charge in the nitrogen atom of ammonia will be  $(1 - 0.66) = +0.34$  e. u. This charge in the nitrogen atom is further reduced by the electron transfer in the N-H bonds, but our data is so rough that we think that a refinement in the calculation by an iterative process is not worth while. The interesting conclusion, however, is that even such a crude procedure indicates that the charge in a complex ion is uniformly distributed over the various atoms, in accordance with the "postulate of electric neutrality" <sup>46</sup>.

This simple result compare well with the charge in the central atoms of similar complexes determined from paramagnetic resonance spectroscopy by Owen <sup>47</sup>.

:\*:\*:\*:\*:\*:

#### ACKNOWLEDGMENTS

We wish to thank the Rockefeller Foundation for a generous fellowship. Appreciation is expressed to Dr. R. S. Mulliken, Dr. N. Davidson and Dr. T. Yamane for encouragement.

APPENDIX

Referring to the diagram on page 3 we wish to point out the following: in the LCAO-MO method there appears integrals of the type:  $H_{AA} = \int \psi_A H \psi_A d\tau$ . These integrals are the so called Coulomb integrals and it is generally recognised that they measure the total energy of the bonding electron (in our case, the  $j$  electron of atom A) in the molecule AB, the Hamiltonian referring to the whole molecule. From the diagram on page 3 it is clear that the potential energy of the  $j$  electron is given by  $2I_A + 2E_B$  (note that  $2E_B$  is essentially the attraction of  $Z_B^* e$  for the  $j$  electron less the  $e_j, e_i$  repulsion). By the virial theorem the total energy is half the potential energy, hence:

$$H_{AA} = I_A + E_B$$

In the same way we must have:

$$H_{BB} = \int \psi_B H \psi_B d\tau = I_B + E_A$$

We think that the identification of the Coulomb integrals  $H_{AA}$ ,  $H_{BB}$ , etc., with the sums  $I_A + E_B$ ,  $I_B + E_A$ , etc., may be extremely useful for the calculation of molecular energy levels by the LCAO-MO method.

BIBLIOGRAPHY AND NOTES

1. L. PAULING, J. Am. Chem. Soc., 54, 3570 (1932).
2. R. S. MULLIKEN, J. Chem. Phys., 2, 782 (1934).
3. See the general discussion held in the Royal Society, as reported in Proc. Roy. Soc., A-207 (1951); H. O. PRITCHARD, and H. A. SKINNER, Chem. Revs., 55, 745 (1955).
4. R. S. MULLIKEN, J. Phys. Chem., 41, 318 (1937).
5. R. C. FERREIRA, J. Phys. Chem., 63, 745 (1959).
6. R. T. SANDERSON, Science, 114, 670 (1951); J. Am. Chem. Soc., 74, 272, 4798 (1952); J. Chem. Educ., 29, 539 (1952).
7. A. D. WALSH, J. Am. Chem. Soc., 68, 2408 (1946); Disc. Faraday Soc., 2 18 (1947); W. MOFFITT, Proc. Roy. Soc., A-202, 534, 548 (1950).
8. L. PAULING, "The Nature of the Chemical Bond", Cornell University Press, 2nd. Edition, 1940, p. 65.
9. The electrons successively accepted by atom A are the differentiating electrons of elements  $Z_{A+1}$ ,  $Z_{A+2}$ , etc., except for the small corrections due to the correlation effects, which will be neglected in this treatment. The small variations in the screening-constant of an electron with hybridization will be also neglected.
10. A. SOMMERFELD, Ann. Physik, 51, 125 (1916).
11. M. HAISSINSKY, J. de Physique, 7, 7 (1946); see also P. DAUDEL and R. DAUDEL, Ibid., 7, 12 (1946).
12. L. PAULING, and J. SHERMAN, Z. Krist., 81, 1 (1932).
13. K. W. F. KOHLRAUSCH, Acta Phys. Austriaca, 3, 452 (1949).
14. For example:  $I_0 = 14.51$  eV for nitrogen and  $I_0 = 13.57$  eV for oxygen.

15. C. A. ~~Coulson~~ COULSON, Proc. Roy. Soc., A-207, 63 (1951).
16. H. O. PRITCHARD, Chem. Revs., 52, 529 (1953).
17. The hybrid wave functions may include d orbitals and f orbitals; these orbitals, however, contribute little to the total wave function and will be neglected in this paper, although they can eventually be included in a refined treatment.
18. C. H. TOWNES, and B. P. DAILEY, J. Chem. Phys., 17, 782 (1949); Ibid., 23, 118 (1955).
19. W. Gordy, Disc. Faraday Soc., 19, 14 (1955).
20. B. LAKATOS, Z. Elektrochemie, 61, 944 (1957); B. LAKATOS, J. BOHUS and G. MEDGYESI, Acta Chim. Hung., 20, 1 (1959); this important conclusion results also from the definition of ionicity proposed by J. K. WILMSHURST, J. Chem. Phys., 30, 561 (1959) and by G. M. Barrow, Ibid., 28, 485 (1958).
21. R. S. MULLIKEN, J. Chem. Phys., 3, 573 (1935).
22. Recently Pritchard questioned the existence of this contribution (Disc. Faraday Soc., 19, 276 (1955); but see also C. A. Coulson, Ibid., 19, 277 (1955).
23. D. Z. ROBINSON, J. Chem. Phys., 17, 1022 (1949).
24. P. N. SCHATZ, Ibid., 22, 695 (1954).
25. W. GORDY, Ibid., 22, 1740 (1954).
26. R. A. BALLINGER, Mol. Phys., 2, 139 (1959).
27. We are making the assumption that the carbon orbitals are definitely either tetrahedral, trigonal, or diagonal. The actual situation may be more complicated (R. S. MULLIKEN, Tetrahedron, 6, 68 (1959)).
28. Since  $2 \times \cos 60^\circ = 3 \times \cos (180^\circ - 109^\circ 28')$ .

29. G. W. WHELAND, "Resonance in Organic Chemistry", John Wiley Sons, New York, 1955, pp. 226, 230.
30. M. J. S. DEWAR, and A. N. SCHMEISING, *Tetrahedron*, 5, 166 (1959).
- 30a. R. C. FERREIRA, *Nature* (in press).
31. This may be questioned: in the methyl halides and vinyl halides the observed dipoles cannot be explained unless we assume that the halogen atoms use hybrid orbitals with a few percent s-character. We will show in the third paper of this series that the conditions for s hybridization of the chlorine and bromine atoms are more favourable in a  $C(sp^3)-X$  bond than in a  $C(sp)-X$  bond (the  $C(sp^2)-X$  bond is in an intermediate position).
32. W. C. PRICE, *Proc. Roy. Soc.*, A-167, 216 (1938).
33. L. H. LONG, and A. D. WALSH, *Trans. Faraday Soc.*, 43, 342 (1947); W. MOFFITT, *Proc. Roy. Soc.*, A-196, 524 (1949); A-199, 487 (1950).
34. The problem of charge distribution of  $\pi$ -bonds cannot be treated by this method. However, since the electronegativity of a p-carbon is only 1.78, against the p-electronegativity of 3.17 for oxygen, it is probable that  $\pi$ -bonding puts a negative charge in the oxygen.
35. M. G. BROWN, *Trans. Faraday Soc.*, 45, 694 (1959); G. R. SOMAYAJULU, *J. Chem. Phys.*, 31, 919 (1959).
36. C. A. BURRUS, *J. Chem. Phys.*, 28, 427 (1958).
37. B. ROSENBLUM, A. H. NETHERCOT JR., and C. H. TOWNES, *Phys. Rev.*, 109, 400 (1958).
38. B. H. RANSIL, *J. Chem. Phys.*, 30, 1113 (1959).



39. L. GRABNER, and V. HUGHES, Phys. Revs., 79, 819 (1950).
40. H. SCHEFFERS, Physik Z., 35, 425 (1934).
41. L. PAULING, reference 8, p. 78.
42. D. F. HEATH, and J. W. LINNET (Trans. Faraday Soc., 44, 556 (1948)), have shown that the electrostatic repulsion between the two hydrogen atoms cannot account for the observed bond angle increase in the molecule  $H_2O$ , relatively of the theoretical bond angle of  $90^\circ$ .
43. L. PAULING, Proc. Nat. Acad. Sci., 35, 495 (1949).
44. If the oxygen atom in the OH radical is in the  $sp^3$  state,  $q = 0.39$ ; if, as it is more probable, it uses a pure p bonding orbital,  $q = 0.17$ .
45. J. BELLUGUE, and R. DAUDEL, Rev. Scient., 84, 541 (1946).
46. L. PAULING, J. Chem. Soc., 1948, 1461.
47. J. OWEN, Disc. Faraday Soc., 19, 127 (1955). This author found  $q = + 0.78$  e. u. for  $Ni(H_2O)_6^{++}$ ,  $q = +1.11$  e. u. for  $Cr(H_2O)_6^{+++}$ . For the hexa-aquo-nickel-(II) ion our method gives  $q = + 1.2$  e. u. See also T. M. Dunn, J. Chem. Soc. 1959, 623.

:\*:\*:\*:\*:\*:

T A B L E I

Element	Electronegativity					Screening-constant of differentiating electron
H	2.28(s)					(0.625) <sup>a</sup>
He	3.82(s)					0.625
Li	0.94(s)					(0.59) <sup>a</sup>
Be	0.91(p)	2.01(s)	1.46(sp)			0.59
B	1.37(p)	3.29(s)	2.33(sp)	2.01(sp <sup>2</sup> )	1.85(sp <sup>3</sup> )	(0.66) <sup>b</sup>
C	1.78(p)	4.83(s)	3.37(sp)	2.88(sp <sup>2</sup> )	2.63(sp <sup>3</sup> )	0.73
N	2.33(p)	6.55(s)	4.55(sp)	3.88(sp <sup>2</sup> )	3.55(sp <sup>3</sup> )	0.75
O	3.17(p)	8.75(s)	-	-	4.88(sp <sup>3</sup> )	(0.755) <sup>b</sup>
F	3.91(p)	10.77(s)				0.76
Ne						0.78
Na	0.93(s)					(0.67) <sup>a</sup>
Mg	0.78(p)	1.87(s)	1.32(sp)			0.67
Al	1.29(p)	2.84(s)		1.81(sp <sup>3</sup> )		(0.69) <sup>b</sup>
Si	1.38(p)	2.84(s)			2.44(sp <sup>3</sup> )	0.71
P	1.81(p)	5.17(s)			3.00(sp <sup>3</sup> )	0.74
S	2.41(p)	6.85(s)			3.52(sp <sup>3</sup> )	(0.75) <sup>b</sup>
Cl	3.00(p)	6.59(s)				0.76
A						0.78
As	1.75(p)	5.14(s)			2.98(sp <sup>3</sup> )	0.81
Se	2.23(p)					(0.815) <sup>b</sup>
Br	2.76(p)	5.98(s) <sup>c</sup>				0.82
Kr						0.83
Te	2.10(p)					(0.83) <sup>b</sup>
I	2.56(p)	5.40(s) <sup>c</sup>				0.84
Xe						0.84

a Values obtained by assuming that in virtue of the spherical symmetry of the g electrons, two electrons with the same ng number have the same screening-constant.

b Interpolated values.

c Extrapolated values.

T A B L E II


Molecule	q(e.u.)	R <sub>o</sub> (A)	eqR <sub>o</sub> (D)	μ <sub>exp</sub> (D)
HF	0.33	0.92	1.45	1.91 - 1.74 <sup>a</sup>
HCl	0.16	1.275	0.99	1.05
HBr	0.10	1.414	0.68	0.80
Hi	0.056	1.604	0.42	0.42

Experimental gaseous dipole moments of HCl, HBr, and HI from: A. A. Maryott, and F. Buckley, "Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State", National Bureau of Standard Circular # 537, Washington, D. C., 1953.

Bond distances from "Tables of Interatomic Distances and Configurations in Molecules and Ions", Special Publication # 11, The Chemical Society, London, 1958.

a Until recently the accepted value for the dipole moment of HF(g) has been 1.91 D, found by N. B. Hannay, and G. P. Smyth (J. Am. Chem. Soc., 68, 171 (1946) but a new absolute value of 1.74 D has been reported by G. A. Kuipers (Quart. Progr. Rep. Solid -State Molec. Theory Gp., M. I. T., 15 January 1958, p. 42).

T A B L E III

Molecule	q(e.u.)	R <sub>o</sub> (A) <sup>a</sup>	eqR <sub>o</sub> (D)	μ <sub>exp</sub> (D)
CH <sub>3</sub> - 	0.049	1.52	0.357	0.36 ± 0.02
CH <sub>3</sub> -CH=CH <sub>2</sub>	0.049	1.53	0.359	0.35 ± 0.01
CH <sub>3</sub> -CH <sub>2</sub> -CH=CH <sub>2</sub>	0.049	1.54	0.362	0.30 0.38
CH <sub>3</sub> -C≡CH	0.13	1.46	0.92	0.75 ± 0.01
CH <sub>3</sub> -CH <sub>2</sub> -C≡CH	0.13	1.47	0.92	0.80

Dipole moments and bond distances from the same sources as in Table II.

a The bond distances refer to the C(sp<sup>3</sup>) - C(sp<sup>2</sup>) and C(sp<sup>3</sup>) - C(sp) bonds.

T A B L E IV

Molecule	$q_{C-X}$ (e.u.)	$R_o$ (Å)	$eqR_o$ (D)	$\mu_{C-H}$ (D)	$\mu_{calc}$ (D)	$\mu_{exp}$ (D)
$HC \equiv C-Cl$	0.076	1.63	-0.59 <sup>a</sup>	0.98	0.39	0.44
$H-C \equiv C-Br$	0.114	1.80	-0.98 <sup>a</sup>	0.98	0.00	0.0

Bond distances and dipole moments from the same sources as in Table II.

a The minus sign means that the positive end of the dipole is in the halogen atom.

T A B L E V

Molecule	I.P. (eV)	Hybridization state of C	$R_o$ (Å)	Charge in the oxygen atom (e.u.)
CO	14.55	sp	1.128	+ 0.038
CO <sub>2</sub>	13.73	sp	1.160	+ 0.024
O	13.57			0.000
H-COOH	11.3	sp <sup>2</sup>	1.23	- 0.095
H <sub>2</sub> -C=O	10.83	sp <sup>2</sup>	1.23	- 0.13
CH <sub>3</sub> -CO-CH <sub>3</sub>	10.2	sp <sup>2</sup>	1.23	

T A B L E VI

Molecule	$q$ (e.u)	$R_o$ (Å)	$eqR_o$ (D)	$\mu_{obs}$ (D)
LiF	0.75	1.51	5.5	5.04 <sup>a</sup> 6.6-0.3 <sup>b</sup>
LiCl	0.59	2.0	5.8	5.9±1.3 <sup>c</sup>
NaF	0.69			
NaCl	0.54	2.36	6.1	-
NaI	0.38	2.71	4.9	4.9 <sup>d</sup>

a E.S. Rittner, J. Chem. Phys., 19, 1030 (1951).

b R. Braunstein, and J.W. Trischka, Phys. Rev., 98, 1092 (1955).

c D.T.F. Marple, and J.W. Trischka, Phys. Rev., 103, 597 (1956).

d H. Scheffers, Physik Z., 35, 425 (1934).