Theoret. chim. Acta (Berl.) 23, 203—207 (1971)

Relationes

Properties of Atoms in Molecules

III. Atomic Charges and Centers of Electronic Charge in Some Heteronuclear Diatomic Molecules

Peter Politzer
Department of Chemistry, Louisiana State University in New Orleans,
New Orleans, Louisiana 70122, USA

Received June 29, 1971

The electronic charges and the positions of the centers of these charges have been calculated for the atoms of a number of second- and third-row heteronuclear diatomic molecules. For both the oxygen and the fluorine atoms, the charge associated with one of these atoms can be correlated, within a series of molecules containing that atom, with both the orbital energy of the atom's 1*s* electrons and also with the difference in electronegativities of the atoms that comprise the molecule. The centers of electronic charge are outside of the internuclear regions, except for the positive atoms in the more ionic molecules and in HF.

The first two papers in this series have dealt with two different properties of atoms in molecules. In Part I, a method was presented for determining the quantity of electronic charge associated with an atom in a molecule [1], while Part II was concerned with the calculation of the position of the center of this charge [2].

The basis of the proposed procedure is the partitioning of the space of the molecule into regions "belonging" to the individual atoms [1]. The electronic charge associated with a given atom A is then given by

$$Q_A = \int_A \varrho(\boldsymbol{r})\, d\boldsymbol{r}$$

where $\varrho(\boldsymbol{r})$ is the molecular electronic density function and the integration is carried out only over the region belonging to atom A. Once Q_A is known, the net charge associated with atom A is simply $(Z_A - Q_A)$, where Z_A is the nuclear charge of A. The position of the center of the charge Q_A is

$$\boldsymbol{r}_A = \frac{1}{Q_A} \int_A \boldsymbol{r}\varrho(\boldsymbol{r})\, d\boldsymbol{r}$$

$\boldsymbol{r}_A$ and $\boldsymbol{r}$ being measured from some convenient origin. The regions of space belonging to the individual atoms are defined in terms of the superposed electronic densities of the corresponding free atoms, placed at the same positions as they occupy in the molecule. The requirement is imposed that each region must contain the same amount of electronic charge (as determined by integrating over the sum of the superposed free atom densities) as belongs to that particular atom in the free state.

Table 1. *Summary of calculated results*[a]

Molecule, *AB*	$0.5R$[b]	Net atomic charges *A*	Net atomic charges *B*	Centers of electronic charge[c] *A*	Centers of electronic charge[c] *B*
HF	0.866	+0.27	−0.27	−0.90	+0.90
LiF	1.444	+0.52	−0.52	−1.24	+1.49
BeO	1.219	+0.59	−0.59	−0.99	+1.30
BF	1.196	+0.10	−0.10	−1.41	+1.25
CO	1.066	+0.14	−0.14	−1.19	+1.13
NO	1.087	+0.11	−0.11	−1.17	+1.15
NaF	1.814	+0.62	−0.62	−1.76	+1.86
NaCl	2.230	+0.60	−0.60	−2.17	+2.25
MgO	1.653	+0.69	−0.69	−1.58	+1.72
AlF	1.563	+0.31	−0.31	−1.64	+1.62
SiO	1.375	+0.42	−0.42	−1.41	+1.46
PN	1.335	+0.25	−0.25	−1.35	+1.45

[a] Distances are in atomic units and electronic charges are in electron units.

[b] R is the calculated bond length [3].

[c] The positions of the centers of electronic charge are measured from the midpoint of the molecule. The position of nucleus A is $-0.5R$, and that of nucleus B is $+0.5R$.

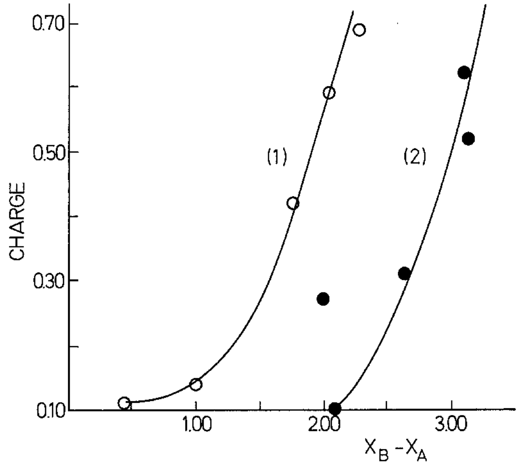

Fig. 1. Relationships between net atomic charges and electronegativity differences for oxygen-containing molecules (1) and fluorine-containing molecules (2). The electronegativities are from [5]

The quantities $(Z_A - Q_A)$ and r_A have now been computed for the atoms in a group of second- and third-row heteronuclear diatomic molecules. Extended-basis-set self-consistent field wave functions were used for both the molecules [3] and the atoms[1]. The results are presented in the Table 1.

---

[1] The atomic wave functions used were those of Clementi [4] and those of Bagus and Gilbert (see [3]), the choice in each case depending upon which was more consistent with the basis set of the particular molecular wave function. The NO wave function was computed by G. Malli and P. E. Cade, and was very kindly sent to the author by Dr. Cade.

The polarities indicated by the calculated net atomic charges are in all cases in agreement with what would be expected on the basis of the electronegativities of the atoms involved. When the magnitudes of the charges are considered, however, the correlation with electronegativities becomes more limited. In Fig. 1, the net charge $(Z_A - Q_A)$ is plotted against the difference in electronegativities, $(X_B - X_A)$, for the oxygen-containing molecules and the fluorine-containing molecules. The overall result is a complete scatter of points. But if the two types of molecules are considered separately, good correlations are found[2]. This is consistent with the usual conclusion that electronegativities are most meaningful when used in studying groups of closely-related molecules.

While the calculated polarities are, in all cases, consistent with the relative electronegativities of the atoms involved, they differ, in two noteworthy instances, from the polarities which might be inferred from the signs of the molecular dipole moments. The available evidence [6, 7] indicates that the signs of the dipole moments of CO and BF are such as would imply the polarities C^-O^+ and B^-F^+. These are the opposite of what would be anticipated from electronegativity considerations, and they are also the opposite of the polarities calculated for these molecules in the present work. It is suggested that these apparent anomalies are simply illustrations of the fact that the magnitude and the sign of the dipole moment of a molecule reflect a number of other factors (e.g., the sizes of the atoms, the types of hybridization, the effects of "lone pairs", etc.) besides the transfer of charge between the atoms [8, 9]. The present results for CO and BF demonstrate the important roles which these other factors can play.

When two free atoms combine to form a molecule, the accompanying rearrangement of electronic charge results in a change of the potential in the vicinity of each nucleus [10]. This should affect the binding energies of the core electrons of each atom. It has been shown that for a series of molecules involving a given atom, an approximate relationship may exist between the net charge associated with the atom and the binding energies of its core electrons [10–12]. In the present work, the existence of such a relationship has been investigated for the oxygen atom in the molecules CO, BeO, MgO, NO, and SiO, and for the fluorine atom in BF, LiF, HF, NaF, AlF, and HC_2F. For each of these two atoms, the binding energy of its 1*s* electrons, approximated by the computed energy of the appropriate self-consistent-field molecular orbital [3], was plotted against its net charge, taken from the Table[3]. The results are shown in Fig. 2. It is seen that a good linear correlation is obtained in each case. An interesting feature of Fig. 2 is the fact that the two lines have quite similar slopes, as determined by the method of least squares; the slope of line (1) is -0.45 a.u./electron unit, while that of line (2) is -0.59[4].

In Part II, it was shown that the centers of electronic charge of the atoms in N_2, O_2, and F_2 are located *outside* of the internuclear regions [2]. This rather surprising fact was interpreted as arising from the effects of the "lone pair"

---

[2] Either BF or HF, depending upon how one chooses to draw the curve, does not fit curve (2). As this curve is drawn in Fig. 1, HF is the deviant molecule.

[3] The value for the charge associated with the fluorine atom in HC_2F is taken from [1].

[4] This feature has previously been observed by Basch and Snyder for the carbon, nitrogen, fluorine, and oxygen atoms in a variety of polyatomic molecules [11].

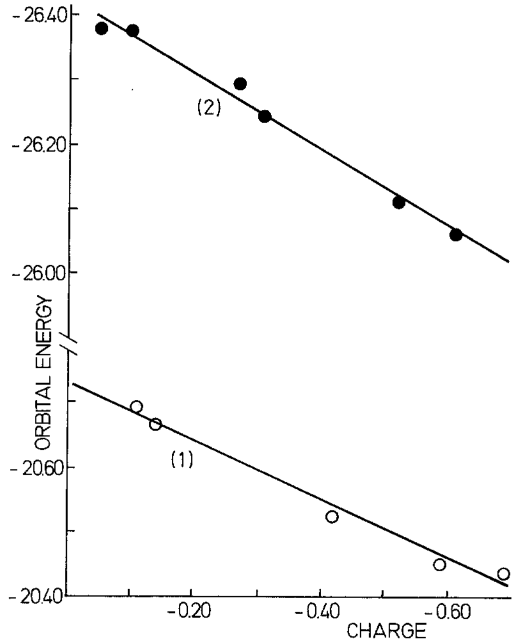

Fig. 2. Relationships between 1*s* electron binding energies (approximated by calculated molecular orbital energies) and net charges on oxygen atoms (1) and fluorine atoms (2). The energies are in atomic units (1 a.u. = 27.21 eV)

electrons on each atom. Again in the present work, the centers of electronic charge of one or both atoms in many of the molecules studied were found to be outside of the internuclear region, and in most cases this can again be attributed to fairly localized molecular orbitals which can loosely be described as representing lone pairs. The only molecules in the Table in which the center of charge of one of the atoms is between the nuclei are those which are commonly classed as highly ionic: LiF, BeO, NaF, MgO, and NaCl. In each of these, the center of charge of the positive atom is in the region between the nuclei. None of these positive atoms have lone pairs, in the five molecules considered. It must be noted, however, that the position of the center of the electronic charge of an atom cannot be correlated exclusively with the presence or absence of lone pairs, as can be seen from the results for the hydrogen atom in HF (Table) and in H_2 [2].

Acknowledgements. The author wishes to thank Mr. R. R. Harris, Dr. R. L. Matcha, and Mr. M. Milleur for assistance and advice concerning the computations. He also wishes to express his appreciation for the financial support of the L.S.U.N.O. Computer Research Center.

References

1. Politzer, P., Harris, R. R.: J. Amer. chem. Soc. **92**, 6451 (1970).
2. — Stout, Jr., E. W.: Chem. Physics Letters **8**, 519 (1971).
3. McLean, A. D., Yoshimine, M.: Tables of linear molecule wave functions, San Jose, Calif.: International Business Machines Corp. 1967.
4. Clementi, E.: Tables of atomic wave functions, San Jose, Calif.: International Business Machines Corp. 1965.

5. Little, E., Jones, M.: J. chem. Educat. **37**, 231 (1960).
6. Ozier, I., Yi, P., Khosla, A., Ramsey, N. F.: J. chem. Physics **46**, 1530 (1967).
7. Yoshimine, M., McLean, A. D.: Int. J. quant. Chemistry **1 S**, 313 (1967).
8. Sanderson, R. T.: Chemical periodicity, p. 45. New York: Reinhold Publishing Corp. 1960.
9. Coulson, C. A., Rogers, M. T.: J. chem. Physics **35**, 593 (1961), and references cited therein.
10. Siegbahn, K., Nordling, C., Johansson, G., Hedman, J., Heden, P. F., Hamrin, K., Gelius, U., Bergmark, T., Werme, L. O., Manne, R., Baer, Y.: ESCA applied to free molecules, Amsterdam: North-Holland Publishing Co. 1969.
11. Basch, H., Snyder, L. C.: Chem. Physics Letters **3**, 333 (1969).
12. Peyerimhoff, S. D., Buenker, R. J.: Theoret. chim. Acta (Berl.) **19**, 1 (1970).

Prof. Dr. P. Politzer
Department of Chemistry
Louisiana State University in New Orleans
New Orleans, Louisiana 70122, USA