Theoret. Chim. Acta (Berl.) 38, 101—107 (1975)

Properties of Atoms in Molecules

VI. Atomic Charges Computed for Some Semi-Empirical Wave Functions

Peter Politzer, Katherine C. Leung, James D. Elliott, Shirley K. Peters
Department of Chemistry, University of New Orleans

Received July 29, 1974/January 24, 1975

Atomic charges calculated by the population analysis method for three types of semi-empirical wave functions have been compared with charges obtained by integrating the corresponding electronic density functions over individual atomic regions. It was found that the two sets of charges compare quite well for CNDO wave functions and for extended-Hückel functions which are in terms of orthogonalized basis orbitals. However only the CNDO charges are reasonably close to those obtained by integrating near-Hartree-Fock electronic density functions.

Key words: Atoms in molecules

1. Introduction

It has been shown that a physically-meaningful estimate of the charges on the atoms in a molecule can be obtained by integrating the molecular electronic density function over previously-determined regions of space associated with the various atoms [1–4]. A large number of diatomic and linear polyatomic molecules have been studied in this manner, using extended-basis-set self-consistent-field wave functions of near-Hartree-Fock accuracy. Since it has been found that the charges computed from the electronic density function may differ significantly from those calculated by the widely-used population analysis procedure [5], a considerable amount of chemical and physical evidence has been gathered in support of the validity and meaningfulness of the former [1–4, 6].

For non-linear molecules, the integration procedure becomes somewhat more complicated. Fortunately, it is possible to obtain very good estimates of the charges in many such cases by using simple linear correlations between the charges and the calculated (near-Hartree-Fock) $1s$ orbital energies of the atoms in the molecules [6].

For most molecules of chemical and biological interest, extended-basis-set SCF wave functions are not presently available; semi-empirical techniques, such as the CNDO [7] or extended-Hückel [8] methods must be used. Two questions may then be posed: First, how do atomic charges obtained by applying the population analysis procedure to these semi-empirical wave functions compare with those determined by integrating the corresponding semi-empirical electronic density functions? Second, how do both of these sets of results compare with the charges calculated by the integration method from near-Hartree-Fock electronic densities? It was the purpose of this investigation to provide at least partial answers to these two questions.

2. Procedure and Results

Semi-empirical wave functions were computed by both the CNDO and the iterative-extended-Hückel method for the following molecules: HCN, FCN, NNO, FC≡CH, LiC≡CH, and HC≡CCN. These molecules represent a wide range of bond types and polarities.

In the iterative-extended-Hückel method [8], the elements of the *H* matrix are written as functions of the atomic charges. An iteration procedure is then carried out, until self-consistency in these charges is achieved[1]. The final wave function will of course depend upon the definition of atomic charge that is being used [9, 10]. In the present work, two different procedures for computing atomic charges were used in conjunction with this iteration scheme: One was the standard population analysis, in which the overlap charge is divided equally between the atoms involved [5]; the other was a modified version of this, in which the basis orbitals are first orthogonalized [11], so that the problem of apportioning overlap charge does not arise [9, 10]. In the CNDO procedure, the atomic charges are also calculated by a population analysis, but the overlap integrals (and hence the overlap charges) are defined to be zero [7].

Thus, for each of the above molecules, one CNDO and two extended-Hückel wave functions were computed. In order to permit valid comparisons, identical minimum basis sets of Slater orbitals [12], representing only the valence electrons, were used (for lithium, a $2p$ basis orbital was included). The bond lengths were the calculated equilibrium values of McLean and Yoshimine [13].

In Table 1 are presented the various population analysis charges for the atoms in each of these molecules, and also the charges determined by integrating the electronic densities obtained from these semi-empirical wave functions[2]. In establishing the atomic regions over which these integrations were carried out, the free atom electronic density functions were expressed in terms of the same atomic orbitals as made up the basis sets for the molecular computations, so as to ensure consistency. For the purpose of comparison, Table 1 also includes the atomic charges previously calculated by the integration method from near-Hartree-Fock molecular wave functions [1, 4, 13].

Besides indicating the differences in the atomic charges obtained by the various procedures, the data in Table 1 also allow quantitative comparisons of the electronic density distributions predicted for a given molecule by the three different semi-empirical wave functions. This is possible because the three semi-empirical density functions for each molecule were integrated over identical atomic regions, the latter having been established in terms of the same set of free atom orbitals. Thus, the amounts of electronic charge computed for a given atomic region provide a valid comparison of the charge distributions corresponding to the three types of wave functions. In fact, meaningful comparisons can even be made with the near-Hartree-Fock electronic charge distributions, although the atomic regions in these cases were defined in terms of near-Hartree-Fock free

---

[1] Self-consistency was considered to have been achieved when input and output charges differed by not more than ± 0.0005.

[2] Before obtaining the electronic density from the CNDO wave function, the basis set was "deorthogonalized" [14–16].

Table 1. Calculated atomic charges

Molecule	Extended-Huckel (non-orthog. basis)		Extended-Huckel (orthog. basis)		CNDO		Near-Hartree-Fock
	Pop. anal.	Integration	Pop. anal.	Integration	Pop. anal.	Integration	Integration
HCN:							
H	+0.009	+0.004	+0.007	+0.011	+0.065	+0.066	+0.18
C	+0.343	+0.285	+0.317	+0.339	+0.037	+0.055	0.00
N	-0.352	-0.289	-0.324	-0.350	-0.102	-0.120	-0.18
NNO:							
N	-0.209	-0.241	-0.227	-0.193	-0.148	-0.095	-0.08
N	+0.514	+0.540	+0.535	+0.505	+0.472	+0.401	+0.33
O	-0.306	-0.299	-0.308	-0.310	-0.323	-0.305	-0.25
FCN:							
F	-0.283	-0.170	-0.222	-0.227	-0.114	-0.116	-0.02
C	+0.659	+0.527	+0.592	+0.606	+0.294	+0.291	+0.23
N	-0.376	-0.358	-0.370	-0.378	-0.180	-0.175	-0.21
LiCCH:							
Li	+0.911	+0.573	+0.788	+0.553	+0.224	+0.395	+0.49
C	-1.951	-1.497	-1.555	-1.242	-0.241	-0.355	-0.36
C	+1.118	+0.953	+0.853	+0.752	-0.017	-0.066	-0.23
H	-0.078	-0.030	-0.086	-0.064	+0.034	+0.025	+0.10
FCCH:							
F	-0.340	-0.224	-0.275	-0.278	-0.132	-0.139	-0.05
C	+0.525	+0.408	+0.458	+0.406	+0.204	+0.177	+0.09
C	-0.314	-0.253	-0.287	-0.211	-0.163	-0.120	-0.19
H	+0.129	+0.069	+0.104	+0.083	+0.091	+0.082	+0.15
NCCCH:							
N	-0.387	-0.340	-0.359	-0.390	-0.133	-0.149	-0.16
C	+0.363	+0.295	+0.330	+0.343	+0.108	+0.114	+0.09
C	-0.081	-0.029	-0.066	-0.027	+0.007	+0.018	-0.05
C	+0.058	+0.052	+0.057	+0.044	-0.055	-0.050	-0.06
H	+0.046	+0.023	+0.039	+0.030	+0.074	+0.067	+0.18

atom wave functions[3]. This is because of the quite remarkable similarity between these regions and those established using just single Slater orbitals to represent the various electrons. Some examples are given in Table 2.

3. Discussion

An examination of the data in Table 1 shows that for both the CNDO and the EH-orth (extended-Hückel, orthogonalized basis set) wave functions, the population analysis charges are generally very similar to those obtained by integrating over the corresponding electronic density functions. In the case of the CNDO charges, the difference is 0.02 or less for 15 of the 22 atoms being considered, and it is greater than 0.05 for only 3 of the 22. For the EH-orth charges, the corresponding figures are 12 and 4. The EH-nonorth charges, however, show

---

[3] The free atom wave functions used were those which correspond as closely as possible to the basis sets of the near-Hartree-Fock molecular wave functions. These have been described in detail by McLean and Yoshimine [13].

Table 2. Some examples of atomic boundary positions

Molecule, ABCDE	Atomic wave functions	Boundary points on molecular axis[a]			
		A-B	B-C	C-D	D-E
NCCCH	min. basis, Slater	48.03%	49.95%	50.00%	74.79%
	near-Hartree-Fock	48.30	49.88	50.02	75.98
FCN	min. basis, Slater	43.11	51.97		
	near-Hartree-Fock	44.90	51.59		
NNO	min. basis, Slater	50.01	52.24		
	near-Hartree-Fock	49.93	51.55		
HCN	min. basis, Slater	24.31	51.85		
	near-Hartree-Fock	23.05	51.54		

[a] The boundary point between any two atoms X and Y is given as a percentage of the bond distance between X and Y, $X-Y$, measured from X.

significantly greater deviations. The population analysis charges are within 0.02 of those obtained by integration for only 5 atoms, and in 12 instances (more than half of the total number) the difference is greater than 0.05.

On the whole, therefore, the population analysis and the integration procedures give very similar results for the CNDO and the EH-orth wave functions. In both cases, the major deviations occur for LiC≡CH, especially for the Li–C portion of the molecule. This may reflect, at least in part, the considerable degree of polarity of the Li–C bond, and perhaps also the very large and diffuse natures of the lithium 2*s* and 2*p* orbitals[4].

The comparison of the population analysis charges with those determined by integrating the near-Hartree-Fock electronic density functions shows the CNDO results to be by far the closest to the latter. The difference is 0.08 or less for 14 of the 22 atoms, and it is greater than 0.12 in only 3 instances. Both the EH-orth and the EH-nonorth charges, on the other hand, are within 0.08 of the integrated near-Hartree-Fock values for only 3 of the 22 atoms, and the difference is greater than 0.12 in 17 cases!

These last results appear to be primarily an indication that the extended-Hückel wave functions give relatively poor charge distributions. This can be seen from the general lack of agreement between the charges obtained by integrating these extended-Hückel charge distributions and those computed from the near-Hartree-Fock density functions. It has been pointed out previously that the non-iterative extended-Hückel method seems to produce an

---

[4] For example, the calculated radius of the principal maximum in the charge-density distribution function for the 2*s* orbital of the free lithium atom is 1.586 Å [17], which is fully 84% of the Li–C bond length in LiC≡CH, 1.88 Å [13].

"exaggerated" shifting and separation of charge [18, 19]. The present results suggest that the iterative approach has a similar weakness[5]. The EH-orth charges (and even more so the EH-nonorth) are almost always larger in magnitude, frequently by a considerable amount, than the CNDO charges. The CNDO technique results in less rearrangement of electronic charge, and this is clearly a better representation of the near-Hartree-Fock charge distributions[6].

---

[5] Note the particularly poor representation of the carbons in $LiC\equiv CH$ by the extended-Hückel charge distributions.

[6] Near-Hartree-Fock electronic densities are, in turn, known to be good approximations (of first-order accuracy) to the true electronic charge distributions [20, 21].

Table 3. Comparison of some proposed procedures for calculating atomic charges

Molecule		Calculated atomic charges				
		Politzer-Harris[a]	Jolly-Perry[b]	Evans-Huheey[c]	Bader-Beddall-Cade[d]	Jug[e]
CO:						
	C	+0.14	+0.17	-----	+0.92	+0.28
	O	-0.14	-0.17	-----	-0.92	-0.28
HF:						
	H	+0.27.	+0.15	+0.29	-----	+0.20
	F	-0.27	-0.15	-0.29	-----	-0.20
FCN:						
	F	-0.02	-0.10	-----	-0.71	-----
	C	+0.23	+0.17	-----	+1.72	-----
	N	-0.21	-0.07	-----	-1.02	-----
HCN:						
	H	+0.18	+0.07	-----	-0.05	-----
	C	0.00	+0.08	-----	+1.04	-----
	N	-0.18	-0.15	-----	-0.99	-----
NNO:						
	N	-0.08	-0.06	-----	+0.39	-----
	N	+0.33	+0.12	-----	-0.07	-----
	O	-0.25	-0.05	-----	-0.32	-----
HCCH:						
	H	+0.14	+0.06	+0.14	-0.08	+0.17
	C	-0.14	-0.06	-0.14	+0.07	-0.17
FCCH:						
	F	-0.05	-----	-0.07	-0.75	-0.02
	C	+0.09	-----	+0.11	+0.26	-0.01
	C	-0.19	-----	-0.17	+0.57	-0.16
	H	+0.15	-----	+0.14	-0.07	+0.19
LiCCH:						
	Li	+0.49	-----	+0.46	+0.79	+0.33
	C	-0.36	-----	-0.32	-0.18	-0.17
	C	-0.23	-----	-0.17	-0.47	-0.29
	H	+0.10	-----	+0.03	-0.14	+0.13

[a] Refs. [1], [2], and [4].
[b] Ref. [22].
[c] Refs. [23] and [24].
[d] Refs. [25] and [26].
[e] Refs. [27] and [28].

The two questions which were raised earlier in this paper may now be given tentative answers as follows: Atomic charges calculated with the population analysis procedure for CNDO and EH-orth (but not EH-nonorth) wave functions compare, on the whole, quite well with those obtained by integrating the electronic densities corresponding to these semi-empirical wave functions. Only the CNDO results, however, are reasonably good approximations to the charges determined by integrating near-Hartree-Fock electronic density functions.

Since the atomic charges calculated by applying the integration method to near-Hartree-Fock electronic densities are being used as a standard, it is of interest to compare them to the results obtained by some other recently-proposed procedures for computing atomic charges. Such a comparison is presented in Table 3 for a group of eight molecules, five of which are also included in Table 1. The following procedures are represented in Table 3:

Politzer-Harris [1]: This is the integration method that has been discussed in the present paper; the values in Table 3 were computed using near-Hartree-Fock electronic density functions.

Jolly-Perry [22]: This is an electronegativity equalization procedure, which has been parametrized in terms of experimental core-electron binding energies.

Evans-Huheey [23, 24]: The charges are obtained by minimizing a semi-empirical expression for the molecular energy as a function of the atomic charges.

Bader-Beddall-Cade [25, 26]: The charges are again determined by integration of the electronic density, but the atomic regions are defined differently than in the Politzer-Harris method.

Jug [27, 28]: A modified population analysis procedure is used, in which the overlap charge is divided in a manner which conserves its dipole moment.

The high degree of similarity, both qualitative and quantitative, between the Politzer-Harris charges and those obtained by the two semi-empirical methods is very gratifying, especially in view of the very different approaches that are involved; the latter two procedures, for example, use no molecular wave functions. The Bader-Beddall-Cade (BBC) charges, on the other hand, appear to have rather exaggerated magnitudes in many instances, and are often even qualitatively different from those calculated by the other methods. For example, the BBC procedure predicts negative charges for the hydrogen atoms in HC≡CH, FC≡CH, LiC≡CH, and even in HCN. The Jug charges are again quite similar to the Politzer-Harris values, although this conclusion is qualified by the fact that Jug used minimum-basis-set SCF molecular wave functions.

Acknowledgements. The authors wish to express their appreciation for the generous support of the Kimberly-Clark Foundation. They are also grateful for the financial assistance provided by the U.N.O. Computer Research Center.

References

1. Politzer, P., Harris, R. R.: J. Am. Chem. Soc. **92**, 6451 (1970)
2. Politzer, P.: Theoret. Chim. Acta (Berl.) **23**, 203 (1971)
3. Politzer, P., Mulliken, R. S.: J. Chem. Phys. **55**, 5135 (1971)
4. Politzer, P., Reggio, P.H.: J. Am. Chem. Soc. **94**, 8308 (1972)

5. Mulliken, R. S.: J. Chem. Phys. **23**, 1833 (1955)
6. Politzer, P., Politzer, A.: J. Am. Chem. Soc. **95**, 5450 (1973)
7. Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory. New York: McGraw-Hill 1970
8. McGlynn, S. P., Vanquickenborne, L. G., Kinoshita, M., Carroll, D. G.: Introduction to applied quantum chemistry. New York: Holt, Rinehart and Winston 1972
9. Cusachs, L. C., Politzer, P.: Chem. Phys. Letters **1**, 529 (1968)
10. Stout, Jr., E. W., Politzer, P.: Theoret. Chim. Acta (Berl.) **12**, 379 (1968)
11. Löwdin, P.-O.: J. Chem. Phys. **18**, 365 (1950)
12. Slater, J. C.: Phys. Rev. **36**, 57 (1930)
13. McLean, A. D., Yoshimine, M.: Tables of linear molecule wave functions. San Jose, Calif.: International Business Machines Corp. 1967
14. Pople, J. A., Segal, G. A.: J. Chem. Phys. **43**, S 136 (1965)
15. Giessner-Prettre, C., Pullman, A.: Theoret. Chim. Acta (Berl.) **11**, 159 (1968)
16. Shillady, D. D., Billingsley, II, F. P., Bloor, J. E.: Theoret. Chim. Acta (Berl.) **21**, 1 (1971)
17. Waber, J. T., Cromer, D. T.: J. Chem. Phys. **42**, 4116 (1965)
18. Pullman, A.: Intern. J. Quantum Chem. **2** S, 187 (1968)
19. Boyd, D. B.: Theoret. Chim. Acta (Berl.) **23**, 383 (1972)
20. Hall, G. G.: Phil. Mag. **6**, 249 (1961)
21. Kern, C. W., Karplus, M.: J. Chem. Phys. **40**, 1374 (1964)
22. Jolly, W. L., Perry, W. B.: J. Am. Chem. Soc. **95**, 5442 (1973)
23. Evans, R. S., Huheey, J. E.: J. Inorg. Nucl. Chem. **32**, 777 (1970)
24. Evans, R. S., Huheey, J. E.: Chem. Phys. Letters **19**, 114 (1973)
25. Bader, R. F. W., Beddall, P. M.: Chem. Phys. Letters **8**, 29 (1971)
26. Bader, R. F. W., Beddall, P. M., Cade, P. E.: J. Am. Chem. Soc. **93**, 3095 (1971)
27. Jug, K.: Theoret. Chim. Acta (Berl.) **29**, 9 (1973)
28. Jug, K.: Theoret. Chim. Acta (Berl.) **31**, 63 (1973)

Prof. Dr. P. Politzer
Department of Chemistry
University of New Orleans
Lake Front
New Orleans, Louisiana 70122, USA