On the Calculation of the Electrostatic Potentials at the Nuclei in the Point-charge Approximation

Z. B. Maksić * and K. Rupnik

Theoretical Chemistry Group, The "Rudjer Bošković" Institute, Zagreb, Yugoslavia

Z. Naturforsch. **38 a,** 308–312 (1983); received September 14, 1982

It is shown that the concept of atomic charge in molecules is a useful tool in studying electrostatic potentials at the nuclei which in turn are closely related to a number of molecular properties. Calculations executed on a selected set of widely different compounds provide extensive evidence that the semiempirical SCC-MO (self-consistent charge) atomic charges are equally successful in this respect as the ab initio DZ ones.

1. Introduction

The electrostatic potentials exerted at the nuclei in molecules involve high content of chemical information [1]. They are closely related to inner-shell binding energy shifts revealed by the XPS (or ESCA) technique [2–6], diamagnetic shielding of the nuclei [7] and to the total molecular energies [8, 9]. Consequently, it is desirable to have at the disposal an efficient, inexpensive and reliable method of calculating the intramolecular electrostatic potentials. It is the purpose of this work to show that the semiempirical self-consistent charge MO (SCC-MO) method provides such a simple tool. This is not surprising because the SCC-MO method proved very useful in discussing properties of the ground-state charge distribution in molecules as evidenced by the calculation of molecular dipoles [10], quadrupole moments [11] and ESCA chemical shifts [6]. Conclusive evidence will be given here which shows that the electrostatic potentials at the sites of the nuclei can be satisfactorily accounted for by using the simple and transparent point-charge concept.

2. The Calculations

The expectation value of the $1/r_A$ operator is given by

$$-\langle 0|\, 1/r_A \,|0\rangle = -\sum_{\mu,\nu} P_{\mu\nu} \langle \Phi_\mu |\, 1/r_A \,| \Phi_\nu \rangle\,, \quad (1)$$

where the sums are extended over all AOs Φ_μ of the basis set. Employing the Mulliken approximation $\Phi_\mu \Phi_\nu = (1/2)\, S_{\mu\nu}(\Phi_\mu^2 + \Phi_\nu^2)$ and Taylor-expansion of the operator $1/r_A$ terminating after the first term, one obtains straighthforwardly the following approximate formula

$$-\langle 0|\, 1/r_A \,|0\rangle = -\sum_{\mu}^{A} Q_\mu \langle \Phi_\mu |\, 1/r_A \,| \Phi_\mu \rangle - \sum_{B}{}' Q_B / R_{AB}\,, \quad (2)$$

where $Q_\mu = P_{\mu\mu} + \sum_B \sum_\nu{}' P_{\mu\nu} S_{\mu\nu}$ and $Q_B = \sum_\mu^B Q_\mu$ are gross orbital and atom populations, respectively. Here, the provision is taken for the difference in screening of s- and p-type of AOs. The second term in (2) is customarily called the Madelung potential in analogy with the term appearing in solid state theory. Taking into account the influence of the nuclei ($B \neq A$), the electrostatic potential at the site of the atom A reads

$$V_A = -\sum_{\mu}^{A} Q_\mu \langle \Phi_\mu |\, 1/r_A \,| \Phi_\mu \rangle + \sum_{B}{}' (Z_B - Q_B)/r_{AB}\,. \quad (3)$$

Thus the potential is expressed in terms of formal atomic charges which combine the computational and conceptual advantages. The most direct way to check the point-charge approach is to compare the results for both sides of (3) calculated within the same set of approximations. We shall use for this purpose the ab initio DZ results of Snyder and Basch [13] for two reasons. It is the largest compendium of ab initio calculations performed on the medium size molecules obtained at the same level of sophistication. Secondly, DZ quality of the wave-

---

* Also at the Faculty of Natural Sciences and Mathematics, University of Zagreb, Marulićev trg 19, 4100 Zagreb, Yugoslavia.

Reprint requests should be sent to Prof. Dr. Z. B. Maksić, Theoretical Chemistry Group, the "Rudjer Bošković" Institute, Bijenička c. 54, 41001 Zagreb, Yugoslavia.

0340-4811 / 83 / 0300-0308 $ 01.3 0/0. – Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung") beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

functions ensures that the $\langle 0 | 1/r_A | 0 \rangle$ expectation values are close to the true ones because this one-electron property is little affected by electron correlation and use of the larger basis sets involving polarization funcions etc. [14]. However, before we employ (3) a short analysis of the Mulliken approximation is in place. It is known that it works very well for two-center $1/r_A$ integrals. The DZ Gaussian basis set, however, has two primitive Gauss-type functions per AO which are strongly coupled, i.e. have large one-center overlap integrals. The accuracy of the Mulliken one-center approximation will be measured by the entity $\Delta_{\mu\nu}$

$$\begin{aligned}\Delta_{\mu\nu} = {} & \langle \Phi_{A\mu} | 1/r_A | \Phi_{A\nu} \rangle \\ & - (1/2)\, S_{\mu\nu} (\langle \Phi_{A\mu} | 1/r_A | \Phi_{A\mu} \rangle \\ & + \langle \Phi_{A\nu} | 1/r_A | \Phi_{A\nu} \rangle)\,. \end{aligned} \tag{4}$$

The integrals appearing in (4) are rigorously computed by using Snyder-Basch basis set functions, which in turn are denoted in pairs by: s1, s2; s3, s4; x1, x2; y1, y2; z1, z2. It should be pointed out that $\Delta_{\mu\nu} = 0$ if the overlap integral between $\Phi_{A\mu}$ and $\Phi_{A\nu}$ vanishes due to the difference in symmetry properties since the $1/r_A$ operator is totaly symmetry. The first two functions describe "1s" orbital, the second pair belongs to the "2s" type orbital and the rest corresponds to three "2p" type orbitals. The rigorous treatment of the one-center term in (1) yields the slightly more involved expression for the electrostatic potential than (3)

$$V_A = -\sum_{\mu,\nu}^{A} P_{\mu\nu} \langle \Phi_{A\mu} | 1/r_A | \Phi_{A\nu} \rangle + \sum_{B}{}' (Z_B - Q_B)/R_{AB}\,. \tag{5}$$

Inspection of the (3) and (5) shows that an error introduced by the Mulliken approximation for the basis functions $\Phi_{A\mu}$ and $\Phi_{A\nu}$ residing on the nucleus A are given by

$$\Delta\,(\Phi_{A\mu}, \Phi_{A\nu}) = 2\, P_{\mu\nu}\, \Delta_{\mu\nu}\,. \tag{6}$$

They are examined for the carbon potentials in a series CH_4, C_2H_2 and CHOOH (Table 1). Perusal of the displayed data shows that the largest correction is comming from the appreciable overlapping of s1 and s2 Gaussians. It is, however, constant along the series. The second largest error is related to Δ (s2, s3) but it varies very slowly. The corrections arising due to overlapping of valence one-center orbitals are small while all others, e.g. s1 and s4 coupling, are negligible and left out of the Table 1. It is noteworthy that "1s" contribution (in Mulliken approximation) is practically constant. It is roughly three times larger than the one-center contribution of the complete carbon valence shell. The latter varies because there are significant differences in populations of the valence AOs between the members of the series. The rigorous (DZ) one-center contributions of the inner-shell given by "1s" + Δ (s1, s2) + (Δ (s2, s3) are compared with the numbers obtained by the Slater and Clementi-Raimondi [15] 1s orbitals assuming that 1s shell is perfectly localized and populated by 2 electrons. One observes that ab initio DZ inner-shell contributions are constant in the first approximation indicating that treatment of closed shells as highly localized unpolarizable cores in semiempirical methods is a resonable one. Closer look, however, reveals that "1s" + Δ (s1, s2) + Δ (s2, s3) contributions do de-

Table 1. One-center $1/r_C$ integrals over Snyder-Basch basis functions calculated in the Mulliken approximation and their corrections (in a. u.).

Molecule	"1s"	"2s" + "2p"	Δ (s1, s2)	Δ (s2, s3)	3Δ (x1, x2) + Δ (s3, s4)
CH_4	−11.236	−3.876	−0.125	−0.071	0.
C_2H_2	−11.238	−3.538	−0.125	−0.079	0.007
CHOOH	−11.236	−3.253	−0.124	−0.088	0.005

Table 2. Contributions of the $1s_A$ inner-shell electrons to the $\langle 1/r_C \rangle$ electrostatic potentials by using various AOs (in a. u.).

Molecule	"1s"	"1s" + Δ (s1, s2) + Δ (s2, s3)	Slater 1s	Clementi-Raimondi 1s
CH_4	−11.236	−11.434	−11.4	−11.345
C_2H_2	−11.238	−11.442	−11.4	−11.345
CHOOH	−11.236	−11.448	−11.4	−11.345

Table 3. Comparison of the potentials at the nuclei calculated in the point-charge approximation by using ab initio DZ and semiempirical SCC-MO wavefunctions (in a. u.).

Compound	Point-charge approximation				Ab initio DZ expectation value[c]
	ab initio[a]	ab initio[b]	SCC-MO[a]	SCC-MO[b]	
H_2O					
H	-1.194	-0.985	-1.130	-0.960	-0.9727
O	-22.166	-22.313	-22.327	-22.303	-22.3409
NH_3					
H	-1.248	-1.085	-1.182	-1.062	-1.0463
N	-18.293	-18.389	-18.292	-18.349	-18.3709
N_2H_4					
H_1	-1.216	-1.052	-1.172	-1.059	-1.0428
H_2	-1.223	-1.086	-1.166	-1.053	-1.0353
N	-18.322	-18.345	-18.288	-18.335	-18.3431
H_2O_2					
H	-1.144	-0.934	-1.079	-0.898	-0.9361
O	-22.127	-22.251	-22.275	-22.233	-22.2740
CH_3OH					
H_1	-1.185	-1.072	-1.137	-1.037	-1.0992
H_2	-1.186	-1.091	-1.131	-1.032	-1.1030
H_3	-1.218	-1.020	-1.191	-1.049	-0.9832
C	-14.734	-14.708	-14.542	-14.647	-14.6800
O	-22.263	-22.397	-22.428	-22.370	-22.3515
CHOOH					
H_1	-1.069	-0.958	-1.076	-0.966	-1.0235
H_2	-1.116	-0.890	-1.077	-0.913	-0.9067
C	-14.657	-14.611	-14.504	-14.563	-14.5401
O_1	-22.182	-22.302	-22.377	-22.332	-22.3201
O_2	-22.170	-22.298	-22.238	-22.226	-22.2735
HCN					
H	-1.089	-0.911	-1.111	-0.986	-0.9490
C	-14.672	-14.675	-14.564	-14.682	-14.6686
N	-18.228	-18.360	-18.299	-18.350	-18.3110
CH_4					
H	-1.252	-1.131	-1.199	-1.106	-1.114
C	-14.755	-14.760	-14.607	-14.754	-14.7545
C_2H_6					
H	-1.236	-1.133	-1.199	-1.119	-1.1223
C	-14.787	-14.764	-14.604	-14.740	-14.7453
C_2H_4					
H	-1.210	-1.099	-1.195	-1.105	-1.0950
C	-14.735	-14.728	-14.607	-14.738	-14.7271
C_2H_2					
H	-1.141	-0.981	-1.178	-1.073	-1.0158
C	-14.698	-14.708	-14.614	-14.758	-14.7152
N_2H_2					
H	-1.167	-1.011	-1.140	-1.007	-1.0078
N	-18.294	-18.356	-18.270	-18.313	-18.2961
H_2CO					
H	-1.117	-1.016	-1.101	-0.986	-1.0508
C	-14.665	-14.657	-14.520	-14.611	-14.6096
O	-22.199	-22.323	-22.382	-22.351	-22.3181

Table 3. (continued)

Compound	Point-charge approximation				Ab initio DZ expectation value[c]
	ab initio[a]	ab initio[b]	SCC-MO[a]	SCC-MO[b]	
CO_2					
C	−14.591	−14.561	−14.459	−14.500	−14.4675
O	−22.086	−22.207	−22.228	−22.230	−22.2335
CO					
C	−14.554	−14.574	−14.536	−14.636	−14.5945
O	−22.153	−22.277	−22.256	−22.273	−22.2262
NNO					
N_1	−18.107	−18.165	−18.148	−18.178	−18.2000
N_2	−18.239	−18.228	−18.082	−18.083	−18.0722
O	−22.141	−22.260	−22.303	−22.290	−22.2494
N_2					
N	−18.207	−18.322	−18.205	−18.239	−18.2326
H_2					
H	− 1.166	− 1.098	− 1.200	− 1.092	− 1.0981

Atoms		Weighting factors			Standard deviation
		k_1	k_2	k_3	
H	SCC−MO	−1.474	−1.009	0.684	0.046
	DZ[c]	−1.606	−1.006	0.779	0.032
C	SCC−MO	−1.253	−0.994	0.672	0.033
	DZ[c]	−0.933	−0.979	−0.298	0.029
N	SCC−MO	−1.106	−0.997	0.475	0.022
	DZ[c]	−0.843	−0.949	−1.024	0.056
O	SCC−MO	−0.719	−0.993	−2.003	0.032
	DZ[c]	−1.049	−0.995	0.210	0.031

[a] Unscaled point-charge values.
[b] Correlated point-charge values.
[c] Double-zeta ab initio values of Snyder and Basch, Ref. [13].

crease along the series by ~ 0.008 a.u. showing clearly that some empirical adjustants in the final point-charge formulae for the intramolecular potentials are necessary. Consequently, we shall use the weighted point-charge formula

$$V_A = -k_{A1}\sum_{\mu}^{A} Q_\mu \langle \Phi_\mu | 1/r_A | \Phi_\mu \rangle + k_{A2}\sum_{B}{}' (Z_B - Q_B)/r_{AB} + k_{A3}\,, \qquad (7)$$

where adjustable constants $k_{Ai}\,(i = 1, 2, 3)$ depend only on the nature of the atom A. They are determined by the least-squares method fitting the rigorous $\langle 1/r_A \rangle$ expectation values of Snyder and Basch [13].

The concept of point-charge is more useful within the framework of the ab initio theory for interpretative purposes than for the actual computation of one-electron properties. In contrast, its role is much more important in semiempirical description of chemical bonding. Therefore we examined the performance of the SCC-MO method in the calculation of the potentials at the nuclei. A discussion of this semiempirical method was given previously [11] and is not to be repeated here. It should be only pointed out that Clementi-Raimondi AOs [15] were employed in the calculations.

3. Results and Discussion

The intramolecular electrostatic potentials calculated by using SCC-MO and ab initio formal atomic charges for a selected set of widely different molecules are compared with $\langle 1/r_A \rangle$ expectation values in Table 3. Both formulas, scaled (7) and unscaled (3), were utilized. The agreement with ab initio DZ results is quite satisfactory particularly for the weighted point-charge approach. This is evidenced by the averaged absolute errors which drop from the 0.11 (unscaled) to 0.03 (scaled) for ab initio DZ atomic charges (in au). The corresponding values for the SCC-MO calculations read 0.08 and 0.03, respectively. Thus, the simple SCC-MO method has on average the same performance as the ab initio DZ one within the limits of the point-charge approximation. It is interesting to examine the quality of the results for particular nuclei. Ab initio values are better for H and C whereas SCC-MO results are superior for nitrogen. Both approaches have about equal performance for oxygen. Another point of interest are k_{A2} constants which are in absolute value very close to unity irrespective of the atom A. This shows conclusively that the Madelung term describes quite accurately the many-center contributions to the $\langle 1/r_A \rangle$ expectation values. It also supports our contention that widely different weighting factors of the Madelung terms in the semi-empirical treatments of ESCA chemical shifts describe in fact a part of the relaxation process taking place upon photoionization [6]. It should be mentioned in this connection that ESCA shifts are reproduced by the SCC-MO method much better than the absolute values of the potentials at the nuclei [6]. The standard deviations of the former are smaller by at least 50%. This is a consequence of the substantial cancellation of errors since the ESCA shifts are measured for to the same nucleus in different chemical environments and relative to a particular bonding situation taken as a standard.

Although the results of the SCC-MO method are satisfactory, there is still room for improvement. It would be probably advantageous to avoid equipartitioning of the mixed charge inherent in the Mulliken population analysis and to distinguish between the atom and bond charges. The latter were found to be useful in considering stretching force constants [16] and were placed between the bonded atoms.

Since the intramolecular electrostatic potentials are fairly well reproduced by the SCC-MO atomic charges, even better results by this simple approach can be expected in the calculation of extramolecular equipotential curves particularly at medium and large distances. This is of some importance because extramolecular potentials provide a very useful index of chemical reactivity especially in determining regions of the molecule that are susceptible to electrophilic attack [17].

[1] P. Politzer, Isr. J. Chem. **19,** 224 (1980).
[2] M. E. Schwartz, Chem. Phys. Letters **6,** 631 (1970).
[3] M. E. Schwartz, J. D. Switalski, and R. E. Stronski, Electron Spectroscopy, D. A. Shirley, ed., North Holland, Amsterdam 1972, p. 605.
[4] W. L. Jolly and D. N. Hendrickson, J. Amer. Chem. Soc. **92,** 1863 (1970); W. B. Perry and W. L. Jolly, Inorg. Chem. **13,** 1211 (1974) and the references cited therein.
[5] D. W. Davis and D. A. Shirley, Chem. Phys. Lett. **15,** 185 (1972); J. El. Spectry. Rel. Phenom. **3,** 137 (1974).
[6] Z. B. Maksić and K. Rupnik, Croat. Chem. Acta **50,** 307 (1977); Theoret. Chim. Acta **54,** 145 (1980); Z. Naturforsch. **35a,** 988 (1980); Croat. Chem. Acta **53,** 413 (1980); Nouv. J. Chim. **5,** 515 (1981); J. Organomet. Chem. **219,** 21 (1981).
[7] N. F. Ramsey, Phys. Rev. **78,** 699 (1950); **86,** 243 (1952).
[8] P. Politzer and R. G. Parr, J. Chem. Phys. **61,** 4258 (1974).
[9] P. Politzer, J. Chem. Phys. **64,** 4239 (1976); **69,** 491 (1978); **70,** 1067 (1979).
[10] J. E. Bloor, B. R. Gilson, and F. P. Bellingsley, Theoret. Chim. Acta **12,** 360 (1968).
[11] J. E. Bloor and Z. B. Maksić, Mol. Phys. **22,** 351 (1971); Mol. Phys. **26,** 397 (1973); Z. B. Maksić and J. E. Bloor, Croat. Chem. Acta **44,** 435 (1972).
[12] A. Graovac, Z. B. Maksić, K. Rupnik, and A. Veseli, Croat. Chem. Acta **49,** 695 (1977).
[13] L. C. Snyder and H. Basch, Molecular Wave Functions and Properties, John Wiley and Sons, New York 1972.
[14] H. F. Schäfer, The Electronic Structure of Atoms and Molecules, Addison-Wesley, Reading 1972.
[15] E. Clementi and D. L. Raimondi, J. Chem. Phys. **38,** 2686 (1963).
[16] R. G. Parr and R. F. Borkman, J. Chem. Phys. **49,** 1055 (1968); R. G. Parr and J. E. Brown, J. Chem. Phys. **49,** 4849 (1968).
[17] E. Scrocco and J. Tomasi, Top. Curr. Chem. **42,** 95 (1973); E. Scrocco and J. Tomasi, Adv. Quant. Chem. **11,** 116 (1978).