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# On the Relation Between the Formal Atomic Charges and Total Molecular Energies

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It is shown that the total SCF molecular energies are fairly well reproduced by the sum of electrostatic potentials exerted on the nuclei calculated in the point-charge approximation. Hence, there is a very simple relation between the total energies and formal atomic charges in molecules. The semiempirical SCC-MO charges have the same performance as the *ab initio* DZ ones.

**Key words:** Charges of atoms in molecules – Hybrid orbitals.

Considerable attention has been focused on approximate expressions of total molecular energy in last few years [1–5]. Ruedenberg showed that there is linear, albeit approximate, relation between the total SCF energy and the sum of orbital energies [1]. This observation has been further elaborated by a number other researchers [2]. Another interesting relation between the total energy, the sum of electrostatic potentials exerted at the nuclei and their derivatives was proposed by Politzer and Parr [3]. Politzer has subsequently shown that the approximate relationship

$$E_t = \sum_A k_A Z_A V_A \qquad (1)$$

is capable to reproduce total molecular energy within an error of 0.5% [4, 5]. Here, $k_A$ is the adjustable weighting factor which depends only on the nature of the atom $A$, $Z_A$ is the atomic number and $V_A$ is the electrostatic potential at the site of the nucleus $A$. It is the aim of this work to show that Eq. (1) can be further simplified by expressing the potential $V_A$ in the point-charge approximation yielding an explicit relation between the total molecular energy and formal

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atomic charges. Retaining only monopole terms in the Taylor expansion of $V_A$ one straightforwardly obtains

$$V_A = -\sum_{\mu}^{A} (\xi_{A\mu} Q_{\mu}^{A} / n_{A\mu}) + \sum_{B}' (Z_B - Q_B)/R_{AB} \tag{2}$$

where $Q_{\mu}^{A}$ and $Q_B$ are gross electron populations of the atomic orbital $\phi_{A\mu}$ and atom $B$, respectively, and $\xi_{A\mu}$ is the effective nuclear charge $\xi_{A\mu} = Z_A - S_{A\mu}$ "felt" by the electron placed in the orbital $\phi_{A\mu}$. The principal quantum number of the latter is denoted by $n_{A\mu}$. The best way to check the validity of the formula (2) is to use total energies obtained by some *ab initio* scheme for a set of characteristic molecules and the gross orbital and atomic populations calculated within the same level of approximation. Then both sides of the approximate formula (2) are treated in the same footing. We have chosen for this purpose *ab initio* results of Snyder and Basch [6] which are of DZ quality. Thus the total energy in (2) is SCF in nature. The weighting factors $k_A$ are easily obtained by the least-squares fitting procedure of the energy expectation values. Perusal of the data presented in Table 1 shows that *ab initio* formal atomic charges reproduce $\langle 0|\hat{H}|0\rangle$ values

**Table 1.** Comparison of the total molecular energy computed as the Hartree-Fock expectation value by using DZ basis set and the corresponding entities obtained in the point-charge approximation employing the same DZ set and the semiempirical SCC-MO formal atomic charges (in a.u.)

| | Point-charge approximation | | *ab initio* DZ |
|---|---|---|---|
| Molecule | SCC-MO | *ab initiio* DZ | Average energy |
| $H_2O$ | −76.086 | −75.940 | −76.004 |
| $NH_3$ | −56.129 | −56.009 | −56.171 |
| $N_2H_4$ | −111.238 | −111.226 | −111.126 |
| $H_2O_2$ | −150.848 | −150.694 | −150.737 |
| $CH_3OH$ | −115.201 | −115.239 | −115.006 |
| CHOOH | −188.771 | −188.882 | −188.689 |
| HCN | −93.005 | −92.769 | −92.829 |
| $C_2H_4$ | −78.047 | −77.969 | −78.005 |
| $N_2H_2$ | −110.073 | −110.127 | −109.942 |
| $H_2$ | −0.992 | −0.858 | −1.127 |
| $CH_4$ | −39.963 | −39.989 | −40.182 |
| $C_2H_2$ | −76.964 | −76.842 | −76.792 |
| $H_2CO$ | −114.001 | −113.906 | −113.821 |
| $C_2H_6$ | −78.921 | −79.189 | −79.198 |
| $CO_2$ | −187.221 | −187.304 | −187.538 |
| CO | −112.705 | −112.641 | −112.676 |
| NNO | −183.334 | −183.521 | −183.576 |
| $N_2$ | −108.799 | −108.749 | −108.870 |
| Weighting factors | $k_H = 0.4150$ | 0.3679 | |
| | $k_C = 0.4317$ | 0.4309 | |
| | $k_N = 0.4252$ | 0.4266 | |
| | $k_O = 0.4191$ | 0.4233 | |

fairly well, the standard deviation being 0.1 a.u. This is by no means negligible, but it is highly encouraging because only Coulomb interactions are taken into account in semiempirical formulae (1) and (2). Since the *ab initio* point-charge approach in calculating total molecular SCF energy works reasonably well, we examined performance of the semiempirical self-consistent charge (SCC-MO) method. It proved very useful in discussing the electronic charge distribution in molecules as evidenced by successful calculations of molecular quadrupole moments [7], ESCA chemical shifts [8] and diamagnetic shieldings of the nuclei [9]. The SCC-MO atomic charges in conjunction with the expression (2) yield total molecular energies with a standard deviation which is virtually the same as for the *ab initio* ones (0.1 a.u.). This is very important because the SCC-MO wavefunctions are not obtained by the strict application of the variation theorem on the molecular hamiltonian. Instead, the idea of the effective model hamiltonian is used. Therefore present calculations represent a stringent test of the form of the adopted model hamiltonian. It is gratifying that the results are in satisfactory accordance with *ab initio* expectation $\langle \hat{H} \rangle$ values.

Good performance of the formula (2) sheds also some light on the close relation between the formal atomic charges and molecular energetics discussed earlier by several workers [10, 11]. Even better results could be anticipated by the inclusion of the exchange term in the expression (2). Since the exchange energy is very well reproduced by the overlap integrals (or squares thereof) of the local hybrid orbitals [12], present analysis indicates that hybrids coupled with the concept of point charges (not necessarily coinciding with nuclei) could provide a very simple physical model able to give reliable estimates of molecular energy. This work is in progress.

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