On the Approximate Relation Between the Sum of Semiempirical Molecular Orbital Energies and the Total Energy of a Molecule

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The Ruedenberg type formula relating the total molecular energy to the sum of orbital energies is examined by using SCC-MO and ab initio DZ MO eigenvalues. Comparison with rigorous ab initio DZ energy expectation values indicates that Ruedenberg's formula in its original form can not provide semiquantitative information on molecular energetics. Much more promissing in this respect is the electrostatic potential at the nuclei approach of Politzer and Parr.

1. Introduction

An intimate relation between the total molecular energy and a sum of SCF orbital energies was observed more than two decades ago for atoms [1, 2] and simple diatomics [2, 3]. However, Ruedenberg's suggestion [4] that there is a direct proportionality between the total energy and sum of orbital energies of electrons

$$E_t = 1.55 \sum_i n_i \varepsilon_i \tag{1}$$

aroused tremendous interest and gave strong impetus for investigations of approximate expressions for molecular energies. March has given some justification of the simple formula (1) by using statistical Thomas-Fermi theory [5]. Additional support was offered by Plindov and Pogrebnya [6] who derived (1) with some more terms on the right side which provide useful corrections. Ruedenberg's formula is strictly speaking valid for the equilibrium geometries and its inapplicability to other nuclear configurations was discussed by Anno and Sakai [7]. Limits of the accuracy of the expression (1) was critically examined by Sannigrahi et al. [8] and Sen [9]. An interesting generalization of the relation (1) holding for any geometries was suggested by Schaad et al. [10]. It was hoped that this type of analyses might provide some rationale for the Extended Hückel semiempirical schemes, Walsh rules and Woodward-Hoffmann correlation diagrams. The purpose of this work is to examine the performance of the semiempirical self-consistent charge (SCC-MO) MO method in calculating total molecular energies by using Ruedenberg type of formula (1). This is of some importance because the SCC-MO approach is one of the most successful semiempirical theories in describing the ground state charge distributions as evidenced by the calculations of molecular quadrupole moments [11, 12], diamagnetic contributions to magnetic susceptibilities [11, 12], ESCA chemical shifts [13] and diamagnetic shielding of the nuclei [14]. These results were superior to the ones obtained by the semiempirical methods involving the ZDO approximation. On the other hand, the SCC-MO method is not based on the variation theorem applied to some approximate hamiltonian. Instead, the idea of the effective hamiltonian is employed and the Coulomb interactions between the particles are not explicitly treated. The excessive intramolecular charge migration of the EHT approach is amended by the iterative-self-consistent charge procedure. This is accomplished in a satisfactory manner because the aforementioned properties are reproduced to a good accuracy. Since the SCC-MO method is very efficient and easily feasible on very large compounds, it would be advantageous to have at disposal some approximate formula(e) for estimating total molecular energies.

2. The Method

A discussion of the SCC-MO method is given elsewhere [11] and needs not to be repeated here. It is noteworthy that Clementi-Raimondi [15] AOs are

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used as a basis set. The SCC-MO orbital energies are checked against the ab initio SCF energy expectation values of Snyder and Basch [16], because this book represents the largest compendium of ab initio results for small and medium size molecules calculated in a uniform manner at the same level of approximation (DZ quality of the Gaussian basis set), being thus directly comparable. As it is usual in most semiempirical theories of chemical bonding, inner-shell electrons are considered in the SCC-MO method as highly localised unpolarisable cores possessing fixed integer populations. It is tacitly assumed that closed inner-shells are chemically inert and they are not explicitly treated in the computational procedure. This is fully justified as far as the ground state charge distributions of molecules are concerned. However, if the molecular energetics is to be studied, the inner-shell energy variations can not be disregarded. The energy of the inner-shells does depend on the chemical environment as revealed by the XPS spectroscopy [17]. Interestingly, the changes in inner-shell energy account for more than 10% of the changes in total electronic energy for a large number of chemical reactions involving hydrocarbons [18], the contribution of closed shell electrons being in many cases as high as 20–30%. In fact, as Jolly has shown in his thermochemical approach [19], the ESCA chemical shifts can be expressed in terms of the heats of formation of reactants and products of appropriate chemical reactions. Hence inclusion of inner-shell orbital energies in our analysis is necessary. We shall employ for this purpose the method of Hartman and Zerner [20] which is based on the earlier work of Zerner [21]. Briefly, the valence orbitals are Schimdt-orthogonalized to the inner-shell AOs which in turn remain unchanged. The eigenvalue of the 1s orbital denoted by α is approximately given by:

$$
\begin{aligned}
\varepsilon_\alpha \cong F_{\alpha\alpha} &\cong (\zeta_\alpha^2/2) - Z_\mathrm{A}\,\zeta_\alpha + 0.625\,\zeta_\alpha \\
&\quad - \sum_{\mathrm{B} \neq \mathrm{A}}{}' \,(n_{\mathrm{Bv}}/R_{\mathrm{AB}} + \sum_{i,j} P'_{ij}\, g_{ij} \langle i |\, 1/r_\mathrm{A} \,| j \rangle \\
&\quad - (1/2) \sum_{i}^{\mathrm{A}} P'_{ii} \langle \alpha' i' | \alpha' i' \rangle \,. \qquad (2)
\end{aligned}
$$

Here, Z_A is the atomic number, n_{Bv} is the number of valence electrons placed on the atom B and ζ_α is the the effective charge of the inner-shell orbital α ($\zeta_\alpha = (Z_\mathrm{a} - S_\alpha)$). The valence and closed shell orbitals are denoted by Roman and Greek letters, respectively. Primed entities refer to the orthogonalized basis set. The weighting factors g_{ij} are equal to unity if φ_i and φ_j are centered on different atoms. It is equal to $g_{ii} = \langle \alpha\alpha | i' i' \rangle / \langle \alpha\alpha | i\, i \rangle \cong \langle \alpha\alpha | i' i' \rangle / \langle i |\, 1/r \,| i \rangle = n_i \langle \alpha\alpha | i' i' \rangle / \zeta_i$, where n_i is the principal quantum number and the intergrals are calculated for free atoms. These g_{ii} values are also very close to unity. The last two terms in (2) describe Coulomb and exchange interactions. The corresponding matrix elements were computed exactly in the Clementi-Raimondi basis set. Other details of this approximate treatment can be found in original papers [20, 21]. The SCC-MO orbital eigenvalues were correlated with the Snyder-Basch energy expectation results according to the formula

$$
E_\mathrm{t} = k_1 \left(\sum_{i=1}^{\mathrm{occ}} \varepsilon_i \right) + k_2 \qquad (3)
$$

and the least-squares fitting gave the following adjustable parameters: $k_1 = 1.552$ and $k_2 = -2.071$ au.

3. Results and Discussion

The SCC-MO and ab initio DZ estimates of total energies obtained by using (3) and (1), respectively, for a selection of characteristic molecules are compared with Snyder-Basch expectation values in Table 1. The SCC-MO results exhibit substantial deviations, the largest error being that of 7% in H_2O. The ab initio DZ values obtained by Ruedenberg's relation (1) are not significantly better indicating that the source of errors is the relation (1) itself rather than orbital energies. This contention is substantiated by the more complete examination of DZ results performed independently by Castro [22] involving all Snyder-Basch molecules which shows that the average energies are reproduced with an averaged error of 3.3%. Hence the performance of the simple Ruedenberg's formula is clearly unsatisfactory. Present and earlier results [8, 22] cast some doubts on its ability to provide reliable semiquantitative information about molecular energetics. Due to the errors inherent in the very form of the Ruedenberg's relation, it is not expected that other semiempirical methods would do better than SCC-MO. This impression is further enhanced by the comparison of the $\sum \varepsilon_i$ results (either SCC-MO or ab initio DZ ones) with the energy estimates obtained by the simple multiple regression analysis

Table 1. Comparison of the total energies estimated by the sums of orbital energies for a selection of characteristic molecules with the ab initio DZ energy expectation values (in au).

Molecule	E_t (DZ)	Sum of orbital energies		Multiple regression		Deviations	
		SCC-MO	ab initio DZ	A	B	Δ(SCC)	Δ(DZ)
H_2O	− 76.00	− 70.56	− 73.49	− 75.99	− 76.00	5.44 (7%)	2.51 (3%)
NH_3	− 56.17	− 54.92	− 56.81	− 56.15	− 56.17	2.25 (2%)	−0.64 (1%)
HCN	− 92.83	− 94.03	− 94.89	− 92.82	− 92.85	−1.20 (1%)	−2.06 (2%)
H_2CO	−113.82	−111.99	−113.38	−113.83	−113.85	1.83 (1%)	0.44 (0)
HCOOH	−188.69	−185.56	−186.47	−188.65	−188.68	3.13 (1%)	2.22 (1%)
CH_4	− 40.18	− 41.85	− 42.71	− 40.19	− 40.19	−1.66 (4%)	−2.53 (6%)
CO_2	−187.54	−184.49	−186.12	–	–	3.05 (1%)	1.41 (1%)
C_2H_2	− 76.79	− 79.52	− 78.79	− 76.86	− 76.81	−2.73 (3%)	−2.0 (3%)
C_3O_2	−263.16	−266.52	−265.73	−263.16	−263.15	−3.36 (1%)	−2.57 (1%)
N_2	−108.87	−108.56	−110.39	–	–	0.31 (0)	−1.52 (1%)
NNO	−183.58	−183.22	−184.27	–	–	0.36 (0)	−0.69 (0)
CH_3OH	−115.01	−117.25	−114.59	−115.00	−115.02	−2.24 (2%)	0.42 (0)
C_2H_4	− 78.01	− 82.22	− 81.92	− 78.03	− 78.00	−4.21 (5%)	−3.91 (5%)
N_2H_4	−111.13	−111.08	−112.26	−111.12	−111.14	0.05 (0)	−1.14 (1%)

[23]. The energy for each molecule was expressed in the simple linear form

$$E_t = h E_H + c E_C + n E_N + o E_O + f E_F \,, \tag{4}$$

where $h, c, \ldots, f$ are the numbers of the atoms in the molecule and $E_H, E_C, \ldots, E_F$ are their atomic energies obtained by fitting Snyder-Basch results. The notion of atomic energies introduced by McCreery and Hall [23] corresponds to the concept of atom in a molecule which in turn is intuitively appealling. Slightly more refined model was used by McCreery and Hall which involved heteronuclear bond energy components

$$\begin{aligned} E_t = {} & h E_H + c E_C + n E_N + o E_O \\ & + f E_F + \chi E_{CH} + \ldots + \varphi E_{HF} \,, \end{aligned} \tag{5}$$

where χ is the number of C–H bonds and E_{CH} is their energy contribution. Multiple bonds are counted in terms of the single bonds, e.g., C≡C is "heavy" as three CC bonds. The homonuclear bond energies were incorporated in atomic energies as in (4). The results of the empirical formulae (4) and (5) are given in Table 1 under headings A and B, respectively. Both models work surprisingly well in view of their utmost simplicity. The second model B is only slightly better than the atomic approach A. The success of these extremely simple models shows that Ruedenberg's formulae (1) and (3) are too crude indeed for chemical purposes. One obtains much better results by using (4) and (5) without any calculation. Ruedenberg's relation, however, does reproduce the major part of the total energy and could be used for qualitative arguments but caution has to be excercised in interpreting the results. Of course, some more work is needed before the final conclusion is drawn. It would be interesting to explore the more general form of the "sum over orbital energies" model introduced by Schaad et al. [10].

Finally, it should be mentioned that the total molecular energy could be expressed as a sum of electrostatic potentials at the nuclei [24, 25]. It is noteworthy that the energy is again given as a sum of atom-like quantities being thus related to (4). This approach seems to be more promissing since the results obtained so far for molecules [25, 26] and atoms [27] are in better accordance with more rigorous ab initio energy expectation values.

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