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Comparison of Improved Approximate Energy Formulas for Molecules In Terms of Corrected Free Atom Energies.

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Summary: Two new equations to calculate electronic energies of polyatomic molecules are tested for a large representative set. These formulas are sums of atomic terms. Results are compared against values calculated by means of other approximations and SCF calculations and their quality are discussed in a comparative fashion.

Introduction

The Hartree-Fock Self Consistent Field (HF-SCF) theory is the basic framework to study in a theoretical way the atomic and molecular electronic structure and related phenomena such as conformational analysis, spectroscopy, chemical reactivity, atomic and molecular scattering, etc.

The total nonrelativistic electronic energy within the frame of HF-SCF theory is given by:

$$E = \sum_s n_s e_s + V_{nn} - V_{ee} \qquad (1)$$

where n_s is the occupation number corresponding to the s-th orbital, e_s is the orbital energy, V_{nn} is the total nuclear repulsion energy and V_{ee} is the total electronic repulsion energy.

On the last years several relationships between orbital eigenvalues and total energy were proposed (see ref.[1]) of the form:

$$E = K \sum_s n_s e_s \qquad (2)$$

K being a constant:

The value and interest of this kind of simplified relations rest upon the fact that they make up valid attempts to rationalize the well-known: "Sums of orbital energies" formulas of Huckel type where these classes of relationships are applied for several purposes in semiempirical theories of the Huckel type: Walsh's rules, Woodward-Hoffman correlation diagrams, qualitative molecular orbital theory, etc.

Among the first semiempirical equations for calculating molecular energies can be considered that proposed by Politzer [2].

$$E^{mol} = \frac{3}{7} \sum_A Z_A V^{mol}_{0,A} \qquad (3)$$

$V^{mol}_{0,A}$ is the total electrostatic potential at nucleus. A, located at R_A, due to the electrons and other nuclei

$$V^{mol}_{0,A} = \sum_{B \neq A} \frac{Z_B}{[R_B - R_A]} - \int \frac{\rho_{mol}(r)}{[r-R_A]} dr \qquad (4)$$

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$\rho_{mol}(r)$ is the molecular electronic density function and the summation in Eq. (4) is over all the nuclei in the molecule. The noteworthy aspect of Eq. (3) is that it provides the molecular energy as a sum of atomic-like terms.

In recent papers it was examined the effects of replacing the factor 3/7 by a parameter K_A which would be a specific property of each atom A.

Politzer [3] determined the parameter K_A by requiring that

$$E_A^{atom} = K_A Z_A V_{0,A}^{atom} \qquad (5)$$

be satisfied exactly for each free atom A, taking E_A^{atom} and $V_{0,A}^{atom}$ from numerical Hartree-Fock calculations.

These atomic parameters were then used in testing the proposed approximate formula:

$$E^{mol} = \sum_A K_A Z_A V_{0,A}^{mol} \qquad (6)$$

Eq. (6) showed to be superior to eq. (3) giving results that are comparable to those of a SCF or CI level (see ref.[3]).

Anno [4] showed that subtle changes of K_A due to the modification of the nuclear environment must be taken into consideration in order that one can obtain E^{mol} with a satisfactory accuracy. He obtained the modified expression:

$$E^{mol\ mod} = \sum_A K_A^{mol} Z_A V_{0,A} \qquad (7)$$

by using K_A^{mol} determined from the HF data on the A_2 molecule.

Teruya and Anno [5] determined K_A using HF data for a wide variety of atoms and ions, and they concluded that definitely such a parameter is not constant but changes systematically.

An alternative for this class of formula [3] results when it is considered the effect of replacing K_A in Eq. (6) by its value derived from Eq. (5). The result is:

$$E^{mol} = \sum_A E_A^{atom} \, (V_{0,A}^{mol} / V_{0,A}^{atom}) \qquad (8)$$

This gives the molecular energy as the sum of the free atom energies, each multiplied by a factor reflecting the change in the electrostatic potential at the nucleus of the atom when going from the free state to the molecule.

Eq. (8) indicates that molecular energies may eventually be obtained from experimentally measurable properties related to the potentials at nuclei, such as the chemical shifts in electronic spectroscopy.

Castro and Fernandez [6] have reported results of applying Eq. (8)

Table-I: The f_A values for several atoms.

ATOM	f_A(a)	f_A(b)
H	1.13360	1.0480
B	1.00067	1.00837
C	1.00038	1.00602
O	1.00032	1.00344
N	1.00176	1.00083
F	0.99976	0.99829
P	1.00009	1.00043 (c)
S	1.00004	1.00062 (c)
Cl	1.00003	1.00067 (c)

(a) - ref [6]
(b) - ref [8]
(c) - our results, based in HF atomic data of references [10] and [11].

Table-II: Comparison of nonrelativistic total molecular electronic energies.

MOLECULE	T	V_{NN}	$-V_{en}$	V_{ee}	$-E_{HF}$	-E Eq.(8)	-E Eq.(10)
H_2	1.1280	0.7134	+3.6231	0.6550	1.1336	1.1336	1.048
					1.1266		
BH_3	26.3388	7.4031	+75.2491	15.1330	26.3742	26.2459	26.3064
CH_4	40.1724	13.3918	+119.7670	26.0205	40.1823	39.9701	40.0115
NH_3	56.1579	11.9336	+155.6022	31.3393	56.1714	56.1971	56.1601
H_2O	76.0751	9.1950	+199.0612	37.7876	76.0649	75.9669	75.9195
					76.0035		
HF	100.0102	5.1933	+250.5796	45.3612	100.0705	99.9523	99.7634
H_2C_2	76.7035	24.7917	+228.1976	49.9106	76.7919	76.5395	76.8790
HCN	92.6959	23.8928	+264.9227	55.5054	92.8286	92.7664	93.0276
N_2	108.7360	23.6247	+302.5057	61.2755	108.9928	108.9934	109.1761
					108.8695		
CO	112.6526	22.5141	+310.4046	62.5616	112.7860	112.5363	112.7870
BF	124.1673	18.8242	+332.7367	65.6731	124.0719	123.9309	123.9737
B_2H_6	52.7123	31.7461	+183.9906	46.7647	52.7675	52.4918	52.6127
C_2H_4	77.9429	33.2665	+247.6380	58.4232	78.0054	77.6731	77.9270
N_2H_2	100.0095	32.4678	+323.0972	70.6781	109.8917	110.1269	110.2241
H_2CO	113.8158	31.1681	+330.6402	71.8354	113.8917	113.6699	113.8350
					113.8209		
C_2H_6	79.1524	41.9310	+267.5387	67.2572	79.1981	78.8067	78.9750
N_2H_4	111.1354	50.7611	+342.4822	79.4597	111.1262	111.2606	111.2721
H_2O_2	150.8889	36.7588	+431.7720	93.3870	150.7373	150.8003	150.7910
F_2	198.5430	30.2239	+536.6403	109.1802	198.7701	198.7710	198.4787

Table-II (continued)

MOLECULE	T	V_{NN}	$-V_{en}$	V_{ee}	$-V_{HF}$	-E Eq.(8)	-E Eq.(10)
					198.6932		
CH_3OH	115.0920	40.1893	+351.5595	81.2722	115.0059	114.8035	114.8830
CH_3F	139.0360	37.2542	+405.1112	89.8007	139.0203	138.7888	138.7269
CO_2	187.5403	58.3303	+559.2007	125.7924	187.5377	187.3696	187.6585
C_3H_4	115.7466	59.0885	+387.2674	96.6120	115.8203	115.3760	115.8425
CH_2CO	151.6665	58.5490	+472.9271	111.0521	151.6595	151.3728	151.7505
CH_2N_2	147.7536	61.2808	+467.8158	111.0112	147.7702	147.8323	148.1396
NNO	183.6301	60.8339	+553.5657	125.5265	183.5761	183.8267	184.0476
NH_2CN	147.9541	59.7849	+465.8260	110.2434	147.8437	147.8323	148.1396
BH_3CO	139.1403	56.4993	+438.3049	103.5984	139.0670	138.7867	139.0934
CH_3CN	131.7387	58.3397	+424.2900	102.3442	131.8674	131.6030	131.9911
C_3H_4	115.8291	63.7019	+396.5699	101.2734	115.7655	115.3760	115.8425
CH_2N_2	147.8475	63.8988	+473.3660	113.8910	147.7287	147.8323	148.1396
O_3	224.3859	68.5564	+668.4351	151.3023	224.1905	224.5000	224.6145
CF_2	236.7642	64.7557	+693.3869	155.2555	236.6114	236.4739	236.3942
FNO	228.5536	65.6163	+674.0634	151.3414	228.5521	228.7155	228.6989
$CHONH_2$	169.0049	71.3851	+540.5026	131.2441	168.8685	168.7334	168.9471
CHOOH	188.8443	70.2108	+586.3418	138.5979	188.6888	188.5032	188.7065
CHOF	212.7743	67.4377	+639.9450	147.0489	212.6841	212.4886	212.5504
$CHCO^-$	188.3570	62.9977	+578.3219	138.8412	188.1261	187.9364	188.1825
C_3H_6	117.0667	75.5301	+422.9223	113.3158	117.0099	116.5096	116.9805
C_2H_5N	133.1411	75.9954	+462.4017	120.2914	132.9726	132.7366	133.0391
C_2H_4O	153.0288	75.1645	+509.4354	128.4408	152.8012	152.5064	152.7985

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T	V_{NN}	$-V_{en}$	V_{ee}	$-V_{HF}$	-E Eq.(8)	-E Eq.(10)
148.7337	74.7919	+498.4032	128.0346	148.8430	148.9635	149.1876
237.9639	77.1760	+721.8451	168.8365	237.8687	237.6075	237.4422
155.0225	116.4478	+592.7590	166.4998	154.7889	154.2125	154.8060 (a)
154.8787	103.7251	+567.4201	153.9516	154.8648		(b)
190.7019	102.9360	+652.7978	168.4699	190.6899	190.2093	190.7139
323.4440	112.4931	+996.9585	237.8927	323.1287	322.7019	322.4524
311.6648	119.2167	+979.4089	237.0030	311.5244	311.3073	311.2657
307.4883	113.5196	+957.8421	229.3238	307.5104	307.7643	307.6548
263.0413	122.4164	+862.7476	214.1325	263.1575	262.7755	263.4895
336.9308	133.5501	+1070.7300	263.5334	336.7157	336.4262	336.1576
345.6696	170.5246	+1159.3461	297.7520	345.3999	345.4672	345.5703
435.8603	205.4336	+1450.0541	373.2048	435.5554	435.2449	434.8729
408.4423	239.4982	+1441.3808	385.6049	407.8354	408.3267	438.6621
473.6869	245.6340	+1619.0098	426.3558	473.3331	473.2583	472.7884

Table-III: Comparison of nonrelativistic total molecular electronic energies.

MOLECULE	$-E_{HF}$	-E Eq (8)	-E Eq (10)
H_2	1.1336	1.1336	1.048
	1.1266		
BH_3	26.3742	26.2459	26.3064
CH_4	40.1823	39.9701	40.0115
NH_3	56.1714	56.1971	56.1601
H_2O	76.0649	75.9669	75.9195
	76.0035		
HF	100.0705	99.9523	99.7634
H_2C_2	76.7919	76.5395	76.8790
HCN	92.8286	92.7664	93.0276
N_2	108.9928	108.9934	109.1761
	108.8695		
CO	112.7860	112.5363	112.7870
BF	124.0719	123.9309	123.9737
B_2H_6	52.7675	52.4918	52.6127
C_2H_4	78.0054	77.6731	77.9270
N_2H_2	109.9418	110.1269	110.2241
H_2CO	113.8917	113.6699	113.8350
	113.8209		
C_2H_6	79.1981	78.8067	78.9750
N_2H_4	111.1261	111.2606	111.2721
H_2O_2	150.7373	150.8003	150.7910
F_2	198.7701	198.7710	198.4787
	198.6932		
CH_3OH	115.0059	114.8035	114.8830
CH_3F	139.0203	138.7888	138.7269
CO_2	187.5377	187.3696	187.6585
C_3H_4	115.8203	115.3760	115.8425
CH_2CO	151.6595	151.3728	151.7505
CH_2N_2	147.7702	147.8323	148.1396
NNO	183.5761	183.8267	184.0476

for various molecules. They assumed the transferability of the factor $f_A = V_{O,A}^{mol} / V_{O,A}^{atom}$ among various molecules and determined them from the HF data on the A_2 molecule. They concluded that E^{mol} in Eq. (8) agrees with E_{HF}.

Thakkar [7] has recently reported the empirical relationship:

$$E^{mol} \cong 1.048 \sum_A (\sum_i v_i \varepsilon_i)^A - 0.924 \sum_A V_{ee} \qquad (9)$$

where E^{mol} denotes the total electronic energy of a given molecule; $(\sum_i v_i \varepsilon_i)^A$ represents the sum of one-electron eigenvalues and V_{ee} the total electron repulsion energy for the atom A.

Sen [8] has combined Eq. (9) and Eq. (8) to obtain an empirical average estimate of $V_{O,A}^{mol}$ from purely atomic quantities

$$V_{0,A}^{mol} \cong [1.048 + 0.124 (V_{ee}^A / E^A)] V_{0,A} \qquad (10)$$

substituting for $(\sum_i v_i \varepsilon_i)^A$ the Hartree-Fock equivalent $E^A + V_{ee}^A$.

The main purpose of this paper is to extend Sen's calculation on the f_A factors, and also to report results of the application of Eq. (8) and (10) to these molecules included in the Snyder and Basch boiok of SCF wave functions and in ref.[6].

Results and Discussion

In Table I we show the f_A values for several atoms which were obtained from Eq. (8) and Eq. (10). These ratios are used for calculating non-relativistic total molecular electronic energies which are reported in Table II.

The average error of Eq. (8) and Eq. (10) for poly-atomic molecules is about 0.1% and 0.3% respectively.

Values obtained from Politzer's formula are more confident since they are derived from atomic energies while those values obtained by the Sen's relation are derived from an empirical relationship.

The average error of Eq. (3), Eq. (6) and Eq. (7) [2-5] are 1.5%, 0.2% and 0.5%, respectively. It is clear that Eq. (8) and Eq. (10) yield the same errors.

From Table II we can conclude that there is an excellent agreement between the exact (SCF) energies and the calculated ones via Eq. (8). These numerical results represent a strong support for the use of very simple approximate sums to calculate total molecular energies in terms of atomic-like terms, and they are in line with our previous research on this topic [6,12-21].

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