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Systematic regularities of molecular SCF energies

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New formulae for the approximate computation of total molecular energies are developed based on *ab initio* calculations of *n*-alkanes. Their application to various kinds of molecules reveals that good expectation values for total molecular energies can be obtained by considering only the one-electron terms h_i and the nuclear repulsion energy. It is further shown that very good agreement with SCF total energies is obtained by a relationship which connects the total energy with the sum of inner-shell (core) orbital energies. The results turn out to be better than those obtained using Ruedenberg's approximation, which takes both inner-shell and valence-shell orbital energies into account.

Key words: *Ab initio* calculations — Total molecular energies — Energy components — New simple heuristic relationships

There has always been a large interest in the formulation of heuristic and simple rules to be used for the rationalization of molecular properties. Actually there is an increasing interest in simple additive schemes for total molecular energies which can be applied, e.g. in semi-empirical theories. In this context Politzer [1] has argued that within the SCF-treatment the approximation

$$E_{\text{tot}} = (3/7) * (V_{\text{ne}} + 2V_{\text{nn}}) \tag{1}$$

(where V_{ne} denotes the nuclear/electronic attraction and V_{nn} the nuclear repulsion) is approximately fulfilled for molecules at their equilibrium structure. Combining (1) with the rigorous Hartree–Fock identity

$$E_{\text{tot}} = \sum_i \nu_i \varepsilon_i + V_{\text{nn}} - V_{\text{ee}} \tag{2}$$

(where ε_i is the ith orbital energy, ν_i the ith occupation number and V_{ee} the total electronic repulsion energy) and the virial theorem, leads to Ruedenberg's approximation [2]

$$E_{tot} = (3/2) * \sum_i \nu_i \varepsilon_i. \tag{3}$$

The corresponding empirical formula is

$$E_{tot} = 1.55 * \sum_i \nu_i \varepsilon_i \tag{4}$$

and is in general a somewhat closer approximation.

Following the ideas of Politzer and Ruedenberg we investigate whether other, generally valid relationships between E_{tot} and its energy components can be found, which could be used in an additive scheme for the computation of E_{tot}. For this purpose, *ab initio* calculations at the SCF/4-31G level were carried out for 40 molecules of various types using the Gaussian 82 program package [3]. For all molecules, standard geometry was assumed [4]. The total energies and their energy components found for n-alkanes ($n = 1$–10) are presented in Table 1. These results are analysed for linear correlations between E_{tot} and their

Table 1. Total molecular energies and their energy components for n-alkanes ($n = 1$–10), determined using a 4-31G model. All energies are given in atomic units

n	E_{tot}	V_{nn}	E_{el}	$-V/T$	T	V
1	−40.1395	13.4354	−53.57494	1.9996	−40.1556	−80.2952
2	−79.1148	42.2334	−121.34821	1.9991	−79.1861	−158.3009
3	−118.0921	82.6934	−200.78546	1.9989	−118.2222	−236.3143
4	−157.0689	131.0088	−288.07773	1.9988	−157.2576	−314.3265
5	−196.0456	185.6137	−381.65936	1.9988	−196.2812	−392.3268
6	−235.0224	245.2445	−480.26686	1.9987	−235.3283	−470.3506
7	−273.9991	309.1696	−583.16873	1.9987	−274.3557	−548.3548
8	−312.9758	376.7704	−689.74622	1.9986	−313.4146	−626.3904
9	−351.9525	447.6294	−799.58194	1.9986	−352.4459	−704.3984
10	−390.9292	521.3814	−912.31061	1.9986	−391.4773	−782.4065

n	V_{el}	V_{ee}	V_{ne}	$2\sum_i \varepsilon_i$	$2\sum_k \varepsilon_{1s,k}$	$2\sum_p \varepsilon_{val,p}$
1	−93.7306	26.0548	−119.7854	−27.52010	−22.3735	−5.1466
2	−200.5343	67.5218	−268.0561	−53.82646	−44.7676	−9.0589
3	−319.0076	120.6524	−439.6600	−80.13304	−67.1548	−12.9783
4	−445.3354	181.6501	−626.9854	−106.42768	−89.5381	−16.8896
5	−577.9405	248.9417	−826.8822	−132.71768	−111.9198	−20.7979
6	−715.5951	321.2627	−1036.8579	−159.00414	−134.3005	−24.7036
7	−857.5245	397.8806	−1255.4051	−185.28808	−156.6804	−28.6076
8	−1003.1608	478.1760	−1481.3368	−211.57024	−179.0599	−32.5103
9	−1152.0279	561.7308	−1713.7587	−237.85112	−201.4390	−36.4121
10	−1303.7879	648.1794	−1951.9673	−264.13118	−223.8179	−40.3133

components, which are then tested on the entire list of molecules (see Tables 1 and 2).

The examination of Table 1 leads to the following observations:

1. The total energy E_{tot} is a linear function of n. Since the virial theorem is obeyed rather closely ($-V/T \sim 2.0$), the same is true for V and T. A linear regression calculation for $E_{tot}(n)$ yields

$$E_{tot}(n) = (-1.1621 \pm 0.0004) - (38.9767 \pm 0.0131)n \qquad (5)$$

with a standard error $s = 0.0003$. Note that this strict linearity is not an artefact resulting from the use of standard geometry. Test calculations have shown that an equally good regression is obtained when the geometry of the molecules is optimized.

2. Although E_{tot} is a linear function of n, its components, V_{nn} and E_{el} (where E_{el} is the total electronic energy), show a more complex dependence on n, as can be seen in Fig. 1.

3. Forming the sum $V_{ne} + 2V_{nn}$ as well as the difference $V_{ee} - V_{nn}$ for each n leads to the linear functions depicted in in Fig. 2. Also included in Fig. 2 is the ratio $-(V_{ne} + 2V_{nn})/(V_{ee} - V_{nn})$ (filled triangles) for each n, which was discussed by Politzer [1] and was widely tested by Snyder and Basch [5]. It exhibits approximately constant values for each n, the mean being 7.21 with a standard deviation of 0.06. This value lies somewhat outside the range of the reference value (6.7 ± 0.44) given by Snyder and Basch.

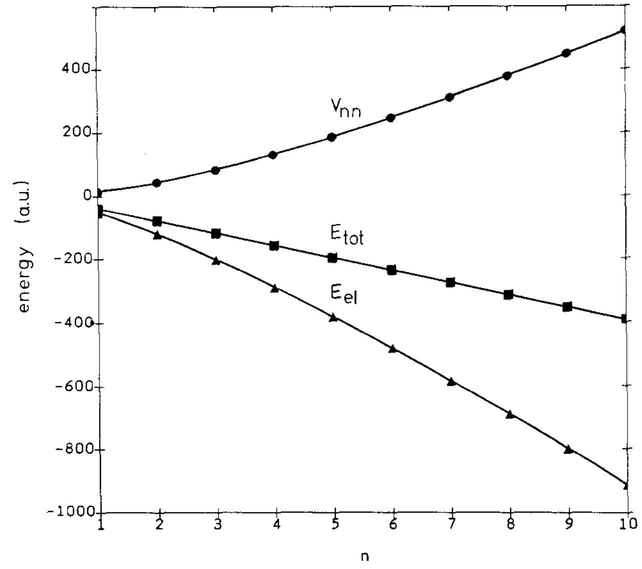

Fig. 1. The total energy E_{tot} and its energy components V_{nn} and E_{el} showing their dependence on n

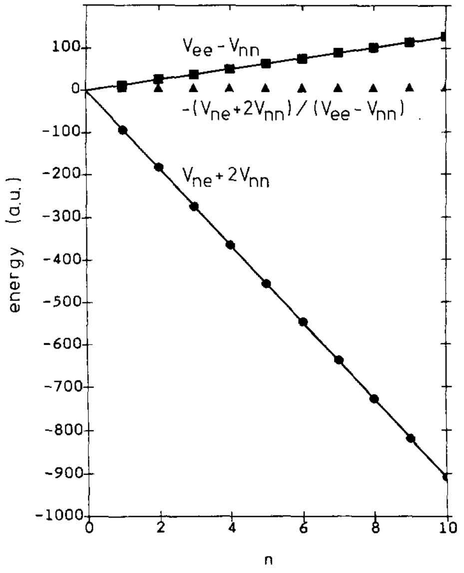

Fig. 2. The sum $V_{\mathrm{ne}}+2V_{\mathrm{nn}}$ and the difference $V_{\mathrm{ee}}-V_{\mathrm{nn}}$ as well as their ratio $-(V_{\mathrm{ne}}+2V_{\mathrm{nn}})/(V_{\mathrm{ee}}-V_{\mathrm{nn}})$ showing their dependence on n

4. From the linear dependence on n of both E_{tot} and the difference $V_{\mathrm{ee}}-V_{\mathrm{nn}}$ as well as from Eq. (2), it follows that $\sum \varepsilon_i$ is linear in n. $\sum \varepsilon_i$ can be written in terms of two sums according to

$$\sum_i \varepsilon_i = \underbrace{\sum_i h_i}_{H} + \underbrace{\sum_{i,k} (2J_{ik} - K_{ik})}_{V_{\mathrm{ee}}} \tag{6}$$

with

$$H = (1/2) * (V_{\mathrm{ne}} + T),$$

where J_{ik}, K_{ik} are the matrix elements for the Coulomb- and exchange-interaction, respectively. Since $(V_{\mathrm{ee}}-V_{\mathrm{nn}})$ turns out to be linear in n, the same must be true for $(H+V_{\mathrm{nn}})$. Combining Ruedenberg's formula with Eq. (2) implies that

$$f_{\mathrm{ee/nn}} = E_{\mathrm{tot}}/(V_{\mathrm{ee}} - V_{\mathrm{nn}}) \tag{7}$$

and therefore

$$f_{H/\mathrm{nn}} = E_{\mathrm{tot}}/(H + V_{\mathrm{nn}}) \tag{8}$$

have to be independent of n.

5. The energies ε_{1s}, describing the inner-shell (C_{1s})-electrons, are all of the same size and are well separated from the orbital energies associated with the valence electrons. Thus $\sum_i \varepsilon_i$ can be partitioned into a sum of nk inner-shell orbital energies $\varepsilon_{1s,k}$ and a sum of np valence-shell orbital energies $\varepsilon_{\mathrm{val},p}$. The ratios between E_{tot} and their energy components $\sum_i \varepsilon_i(f_R)$, $\sum_k \varepsilon_{1s,k}(f_{1s})$ and $H+V_{\mathrm{nn}}$ $(f_{H/\mathrm{nn}})$ are collected in Table 2 for the whole list of molecules investigated.

Table 2. The ratios $f_R = E_{\mathrm{tot}}/2\sum \varepsilon_i, f_{1s} = E_{\mathrm{tot}}/2\sum \varepsilon_{1s,k}$, and $f_{H/\mathrm{nn}}$ for various kinds of molecules. Total energies E_{tot} in atomic units obtained using the ratio $f_{H/\mathrm{nn}}$ and the SCF-method. The values in parentheses are deviations in E_{tot} in percent

Molecules	f_R	f_{1s}	$f_{H/\mathrm{nn}}$	E_{tot} ($f_{H/\mathrm{nn}}$)	(Δ%)	E_{tot} (SCF)
1. Methane	1.459	1.794	1.522	−39.4538	(−1.71)	−40.1395
2. Ethane	1.470	1.767	1.516	−78.0711	(−1.32)	−79.1148
3. Propane	1.474	1.759	1.514	−116.6881	(−1.19)	−118.0921
4. Butane	1.476	1.754	1.512	−155.0689	(−1.06)	−157.0689
5. Isobutane	1.476	1.754	1.513	−155.3058	(−1.12)	−157.0706
6. Pentane	1.477	1.752	1.512	−193.9710	(−1.06)	−196.0456
7. Isopentane	1.477	1.752	1.512	−193.9682	(−1.06)	−196.0427
8. Neopentane	1.477	1.752	1.512	−193.9751	(−1.06)	−196.0497
9. Hexane	1.478	1.750	1.511	−232.6893	(−0.99)	−235.0224
10. Isohexane	1.478	1.750	1.511	−232.6862	(−0.99)	−235.0193
11. 1,1-dimethylbutane	1.478	1.750	1.512	−232.5298	(−1.06)	−235.0168
12. 2,3-dimethylbutane	1.478	1.750	1.511	−232.6829	(−0.99)	−235.0160
13. Heptane	1.479	1.749	1.511	−271.2791	(−1.06)	−273.9991
14. Octane	1.479	1.748	1.511	−309.8688	(−1.06)	−312.9758
15. Nonane	1.480	1.747	1.510	−348.6894	(−0.93)	−351.9525
16. Decane	1.480	1.747	1.510	−387.3047	(−0.93)	−390.9292
17. Cyclopropane	1.478	1.737	1.512	−115.6097	(−1.06)	−116.8462
18. Ethylene	1.480	1.738	1.510	−77.9806	(−0.93)	−77.9205
19. Acetylene	1.492	1.709	1.504	−76.3031	(−0.53)	−76.7111
20. Pyrazine	1.486	1.697	1.507	−260.3607	(−0.73)	−262.2751
21. Diazirine	1.507	1.725	1.496	−147.2962	(0.00)	−147.2962
22. Tetrazine	1.509	1.723	1.495	−294.2936	(0.07)	−294.0969
23. CH_3CN	1.505	1.723	1.498	−131.4816	(−0.13)	−131.6574
24. Propenal	1.527	1.753	1.487	−190.2177	(−0.13)	−190.4720
25. Ketene	1.533	1.753	1.484	−152.4113	(0.61)	−151.4944
26. Acetamide	1.535	1.771	1.480	−209.8627	(1.08)	−207.6182
27. Isocyanamide	1.545	1.759	1.479	−169.4182	(1.15)	−167.4930
28. Methanol	1.557	1.808	1.473	−116.6634	(1.56)	−114.8698
29. CO_2	1.563	1.719	1.470	−190.6413	(1.77)	−187.3280
30. NO_2	1.554	1.780	1.475	−206.5968	(1.42)	−203.6967
31. N_2O	1.545	1.757	1.478	−185.5982	(1.22)	−183.3651
32. N_2O_4	1.580	1.778	1.463	−416.5429	(2.26)	−407.3545
33. H_2O	1.606	1.850	1.452	−78.2076	(3.03)	−75.9074
34. NH_3	1.532	1.809	1.486	−56.4802	(0.67)	−56.1027
35. N_2H_2	1.534	1.758	1.484	−110.6984	(0.81)	−109.8104
36. N_2H_4	1.533	1.787	1.484	−111.7176	(0.81)	−110.8215
37. HCN	1.520	1.725	1.490	−93.1042	(0.40)	−92.7308
38. NF_3	1.635	1.855	1.441	−339.2745	(−2.31)	−351.9746
39. B_2H_6	1.405	1.729	1.552	−54.4458	(3.82)	−52.4441
40. BF_3	1.651	1.860	1.434	−336.7404	(4.32)	−322.7846
Mean values	1.511	1.759	1.496			
Standard deviations	0.049	0.036	0.023			

Examination of Table 2 leads to the following conclusions:

1. The ratios $f_{H/\mathrm{nn}}$ exhibit the smallest standard deviation. Thus a good approximation for E_{tot} is given by

$$E_{\mathrm{tot}} = 1.496 * (H + V_{\mathrm{nn}}). \tag{9}$$

The corresponding ratios $f_{\mathrm{ee/nn}}$ are not so well behaved and are therefore not included in Table 2.

2. The ratios f_{1s} exhibit a smaller standard deviation than f_R. This reveals that instead of connecting the total energy to the sum of inner-shell and valence-shell orbital energies, better agreement with SCF total energies is obtained by taking only the inner-shell orbital energies into account. Thus one can write

$$E_{\mathrm{tot}} = 1.759 * \sum_k \varepsilon_{1s,k}. \tag{10}$$

Note that f_{1s} exhibits the same values for the branched hydrocarbons in this list (5, 7, 8, 10–12) as for the unbranched ones. This guarantees that the estimates for E_{tot} based on f_{1s} lead to the correct order of relative stability for these compounds. Unfortunately, no consistent value could be found for the ratio of E_{tot} to the sum of valence-shell energies.

3. The agreement between the total energies computed using Eq. (8) and the SCF-results (see Table 2) is most satisfactory.

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