J. Phys. Chem. A 2002, 106, 1612−1618

Additivity of the Correlation Energy in Some 3D Organic Molecules

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Received: October 1, 2001; In Final Form: December 14, 2001

We found, by using the theoretical MP2 model, that correlation energy of the valence electrons in a large number of 3D organic molecules follows a very simple additivity rule resembling that established earlier in planar π-systems. Namely, it turns out that the total correlation energy is a multilinear function of the number of atoms of each element entering a molecule. Extrapolating the calculated correlation energies to the complete basis set (CBS) values, it occurs that the additivity holds for $E(\text{CBS})_{\text{corr}}$ too. We believe that computational methods more rigorous than MP2 will confirm the additivity in the future and show that it is a genuine molecular property. The additivity formula for the valence electrons correlation energies could serve as a diagnostic tool to identify cases where significant nonadditivity takes place. In such situations the electronic structure apparently exhibits some subtleties, which are not present in other, more or less related molecules, thus deserving a meticulous scrutiny. The additivity of the Hartree−Fock energies was examined too. Deviations from the additivity in the selected set of gauge molecules (substituted alkanes) is much higher than for the correlation energy. Highly strained molecules exhibit dramatic nonadditivities, which are identified as the angular strain energies. It is found that HF energies extrapolated to the complete basis yield the angular strain destabilizations much closer to the experimental estimates. Introduction of the offset value enables almost quantitative prediction of the angular strain effect in the series cyclopropane, cyclobutane, cyclopentane, and tetrahedrane.

Introduction

It has been realized for a long time that a quantitative description of a large body of the molecular properties requires explicit account of the electron correlation effects. The latter was unfortunately the largest bottleneck in the computational quantum chemistry since its beginnings in 1960s. To some extent this bottleneck still exists, because very accurate calculations are not feasible in large molecules for the time being. It is gratifying, however, that several promising methodologies have been developed so far, enabling reasonable estimates of the correlation energies in small and medium size molecules. They encompass configuration interaction (CI), multireference configuration interaction (MRCI), MR perturbation theory methods, and the coupled-cluster (CC) procedures.[1] Some other computational schemes include G2,[2] G3,[3] W1 (W2),[4] and CBS[5] recipes.

A generally accepted definition of the correlation energy is that of Löwdin:[6]

$$E(\text{corr}) = E(\text{exact})_{\text{NR}} - E(\text{HF})_{\text{L}} \qquad (1)$$

meaning that it is given as the difference between the exact nonrelativistic energy $E(\text{exact})_{\text{NR}}$ and the best possible Hartree−Fock (HF) energy. The latter is obtained by using the complete basis set yielding $E(\text{HF})_{\text{L}}$, where L denotes the basis set limit.

Notwithstanding development and remarkable success of the electron correlation methods in recent years, as well as their implementation in a number of efficient computer codes, relatively little attention has been devoted to the interpretation of calculated correlation energies, perhaps because that was not an easy task. A pioneering work on the conceptual side of the problem was performed by Sinanoglu,[7] who resolved the total correlation energy into two distinctly different contributions:

$$E(\text{corr})_{\text{t}} = E(\text{ND}) + E(\text{D}) \qquad (2)$$

where $E(\text{ND})$ and $E(\text{D})$ denote the nondynamical and dynamical part, respectively. Another contribution in this direction was given by the work of Cremer et al.,[8,9] who analyzed various contributions to the estimates of the correlation energies in Møller−Plesset(n) perturbational method and the density functional theory (DFT) calculations. Lately, we have been able to show that the correlation energy of π-electrons in planar (2D) organic molecules exhibits a simple additivity rule[10−12] by employing CASSCF[13,14] and CASPT2 formalisms.[15] It turned out that both the nondynamical and dynamical parts of the total π-electron correlation energy are multilinear functions of the numbers of atoms of each element entering a molecule. It is interesting to mention in this connection that the higher level correction $\Delta E(\text{HLC})$ in G2 scheme also relies to some extent on additivity since

$$\Delta E(\text{HLC}) = c_1 n_\alpha + c_2 n_\beta \qquad (3)$$

where c_1 and c_2 are empirically adjustable parameters and n_α and n_β are the number of α and β electrons, respectively.[2] Interestingly, we found that deviation of the nondynamical correlation energy from the additivity rule provides a descriptive index of anti/aromaticity.[10,11] In this work we explore the

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10.1021/jp013659f CCC: $22.00

additivity of the valence electrons correlation energy in some organic 3D molecules employing perturbational MP theory[16] at the second order approximation. Particular attention will be given to the extrapolation of the correlation energies to the complete basis (CBS) set limit. If the additivity rule performs reasonably well in 3D molecules too, it would provide a strong indication that the elusive electron correlation exhibits additivity as its general and genuine property at least in organic molecules. Nonadditivity would then imply some special effects, which should be examined separately and very carefully. To put it in another way, the additivity rule could serve as a diagnostic tool for identification of some electronic structure subtleties and/or peculiarities. Finally, the additivity of the Hartree−Fock energy is considered too. It will appear that their deviations from the additivity reflect some gross features such as, e.g., molecular angular strain. It should be pointed out that the additivity hypothesis was used by Cremer[17] as early as 1982. He employed it first within the context of improving the basis set errors in the Hartree−Fock and MP2 models. Thus the influence of the polarization functions was estimated in small molecules yielding the energy increments for characteristic bonds, which were subsequently transferred to larger molecules in order to obtain approximate estimates of the HF limits and MP2 energies. In the next paper Cremer[18,19] showed that it was possible to partition MP2 correlation energy in small molecules into contributions related to inner-core electrons, lone electron pairs, and coupled bond electrons. These contributions proved useful in estimating the unknown MP2 energies in large molecules and their enthalpies of formation. Cremer's calculations were hampered, however, by the fact that the very large basis sets were not practical at that time and that the extrapolating procedures to the complete basis set energies were not known.

Methodology

In our previous work[10,11] on the correlation energy of π-electron in 2D systems we used the following expressions for the correlation energies:

$$E(\mathrm{ND})^{\pi} = E(\mathrm{HF}) - E(\mathrm{CASSCF}^{\pi}) \tag{4}$$

$$E(\mathrm{D})^{\pi} = E(\mathrm{CASSCF}^{\pi}) - E(\mathrm{CASPT2}^{\pi}) \tag{5}$$

where, in general,

$$E(\mathrm{CASPT2}) = E(HF) - E(\mathrm{ND}) - E(\mathrm{D}) \tag{6}$$

and the correlation energies were defined as positive numbers for the sake of convenience, despite the fact that they are intrinsically negative quantities according to eq 1. Using the CASSCF$^{\pi}$ wave function as the zeroth approximation in the perturbational calculations, two types of the CASPT2 energies are possible.[12] The first, referred to as CASPT2$^{\pi}$, involves only the dynamical correlation of the π-electrons alone. The second, denoted as CASPT2$^{(\pi)+\sigma}$, includes all valence electrons, thus allowing for a more active participation of the σ-electrons in the dynamical correlation. It turned out that for a set of the gauge molecules C_2H_4, H_2CO, H_2CNH, N_2H_2, HNO, and CH_2F^+, the sum of $E(\mathrm{ND})^{\pi} + E(\mathrm{D})^{(\pi)+\sigma}$ gave total correlation energies very close to the standard single reference MP2 approximation. The total correlation energy of the latter was given by a standard formula:

$$E(\mathrm{MP2}) = E(\mathrm{HF}) + E(\mathrm{corr})_{\mathrm{MP2}} \tag{7}$$

This finding gave an impetus for the application of the single reference MP2 formalism in studying the additivity of the total valence correlation energy in 3D molecules presented here. The MP2 correlation energy $E(\mathrm{corr})_{\mathrm{MP2}}$ will be abbreviated heretofore as E(corr).

The choice of the basis set in studying electron correlation is of utmost importance, particularly in the context of truncation errors involved in incomplete sets. It is advantageous to use Dunning's correlation consistent polarized valence multiple ζ (cc-pVmZ) basis sets,[20] because they are well balanced and, as a consequence, improvements in the total energy become controlled and predictable as m increases along the series of cc-pVmZ basis set calculations. Here m = D, T, Q, 5, and 6 signifies double-, triple-, quadruple-, quintuple-, and sextuple-ζ, respectively. Dunning's basis sets enable use of various extrapolation schemes, which offer approximate estimates of the complete basis set (CBS) limits. There are several formulas developed for that purpose. Exponential expressions,[21] which require at least three different m values, perform well for the extrapolation of the HF energy,[22] but they are less successful with respect to the correlation energies.[23] The simplest and yet very useful extrapolation formula was advocated by Helgaker et al.[22,24] based on the inverse power law in m:

$$E_m = E_{\mathrm{CBS}} + P/m^{\epsilon} \tag{8}$$

where E_{CBS} is the energy at the complete basis set limit to be determined and m assumes values 2, 3, 4, etc., as specified above for Dunning's basis functions. The adjustable parameter is denoted by P. A fixed exponent[22,24] ($\epsilon = 3$) yields very good estimates of E_{CBS} but requires high m values (4, 5, or 6), which is impractical in larger molecules of chemical interest. To circumvent this obstacle, Truhlar et al.[25,26] developed a modified procedure, which performs very well by utilizing only cc-pVDZ and cc-pVTZ functions. Truhlar's approach proved useful in obtaining $E(\mathrm{ND})^{\pi}$, $E(\mathrm{D})^{\pi}$, and $E(\mathrm{D})^{(\pi)+\sigma}$ correlation energies in planar polyenes.[12] For that reason it was employed in this work too.

There is a point of considerable interest related to the additivity of the correlation energy at the complete basis set. If the additivity holds separately for two different Dunning's basis sets characterized by m_1 and m_2, then it is easy to show that E_{CBS} is given in an additive way too. Two consecutive calculations employing sets m_1 and m_2 yield

$$E_{\mathrm{CBS}} = \frac{(m_1)^{\epsilon}}{(m_1)^{\epsilon} - (m_2)^{\epsilon}} E_{m_1} - \frac{(m_2)^{\epsilon}}{(m_1)^{\epsilon} - (m_2)^{\epsilon}} E_{m_2} \tag{9}$$

provided the extrapolation formula (8) is adopted. Energies calculated by basis sets m_1 and m_2 are denoted by E_{m_1} and E_{m_2}, respectively. Now, since it is assumed that the additivity holds for both basis sets, the total correlation energies can be concisely written as

$$E_{m_1} = \sum_{i}^{\mathrm{atoms}} c_i^{m_1} n_i \qquad \text{and} \qquad E_{m_2} = \sum_{i}^{\mathrm{atoms}} c_i^{m_2} n_i \tag{10}$$

where summations are extended over all atoms in a molecule, n_i denotes the number of atoms of the element i, while $c_i^{m_1}$ are adjustable coefficients deduced from the ab initio calculations of the correlation energies. Substitution of (10) in (9) yields

$$E_{\mathrm{CBS}} = \sum_{i}^{\mathrm{atoms}} c_i^{\mathrm{CBS}} n_i \tag{11}$$

where

$$c_i^{\mathrm{CBS}} = w_{m_1} c_i^{m_1} - w_{m_2} c_i^{m_2} \tag{12}$$

Here, the weighting factors are $w_{m_1} = (m_1)^{\epsilon}/[(m_1)^{\epsilon} - (m_2)^{\epsilon}]$ and $w_{m_2} = (m_2)^{\epsilon}/[(m_1)^{\epsilon} - (m_2)^{\epsilon}]$. In other words, if conditions (10) are fulfilled, then the correlation energy is additive at the complete basis set limit too.

All calculations are carried out by using the MP2(fc)/cc-pV*m*Z//HF/cc-pVDZ model, where m = D and T, by employing the GAUSSIAN 94 program.[27]

Results and Discussion

A set of alkanes starting from methane up to pentane and neopentane is examined together with their fluoro, hydroxy, and amino derivatives. This family of molecules is extended by mono- and polycyclic molecules such as cyclopropane, cyclobutane, cyclopentane, bicyclo(1.1.0)butane, [1.1.1]propellane, and tetrahedrane. Molecules used in obtaining a posteriori additivity formulas are denoted by an asterisk (Table 1). The MP2 correlation energies obtained by cc-pVDZ and cc-pVTZ basis sets are presented in Table 1. They lead to the atomic additivity formulas:

$$E_{\mathrm{A}}(\mathrm{corr})^{\mathrm{DZ}} = 79.24n_{\mathrm{C}} + 99.21n_{\mathrm{N}} + 111.76n_{\mathrm{O}} + 114.74n_{\mathrm{F}} + 5.17n_{\mathrm{H}} \tag{13}$$

and

$$E_{\mathrm{A}}(\mathrm{corr})^{\mathrm{TZ}} = 94.86n_{\mathrm{C}} + 123.73n_{\mathrm{N}} + 144.77n_{\mathrm{O}} + 155.84n_{\mathrm{F}} + 7.11n_{\mathrm{H}} \tag{14}$$

TABLE 1: Valence Electrons Correlation Energy of Alkanes, Obtained by the MP2(fc)/cc-pV*m*Z//HF/cc-pVDZ (m = 2, 3) Model and by the Additivity Rule Based on the Atomic Scheme by Formulas 13 and 14, in kcal/mol[a]

	basis set cc-pVDZ			basis set cc-pVTZ		
molecule	E_{corr}	$E_{\mathrm{corr}}^{\mathrm{add}}$	Δ_{add}	E_{corr}	$E_{\mathrm{corr}}^{\mathrm{add}}$	Δ_{add}
methane*	101.2	99.9	1.3	124.4	123.3	1.1
ethane*	189.6	189.5	0.1	232.2	232.4	−0.2
propane*	279.3	279.1	0.2	341.4	341.5	−0.1
butane*	369.1	368.7	0.4	450.7	450.6	0.1
isobutane	370.5	368.7	1.8	452.1	450.6	1.5
pentane*	458.9	458.2	0.7	560.1	559.7	0.4
neopentane	463.3	458.2	5.1	564.6	559.7	4.9
cyclopropane	265.5	268.7	−3.2	324.8	327.3	−2.5
cyclobutane	356.6	358.3	−1.7	434.2	436.3	−2.1
cyclopentane	447.6	447.9	−0.3	544.6	545.4	−0.8
tetrahedrane	330.7	337.6	−6.9	403.2	407.9	−4.7
bicyclobutane	344.6	348.0	−3.4	419.3	422.1	−2.8
[1.1.1]propellane	431.1	427.2	3.9	521.4	517.0	4.4
fluoromethane*	209.2	209.5	−0.3	272.1	272.1	0.0
difluoromethane*	319.6	319.1	0.5	421.4	420.8	0.6
trifluoromethane*	431.2	428.6	2.6	571.0	569.5	1.5
tetrafluoromethane	542.7	538.2	4.5	719.6	718.3	1.3
fluoroethane*	298.0	299.1	−1.1	380.5	381.1	−0.6
difluoroethane*	406.1	408.6	−2.5	528.3	529.9	−1.6
trifluoroethane*	517.1	518.2	−1.1	678.0	678.6	−0.6
tetrafluoroethane*	628.2	627.8	0.4	827.4	827.4	0.0
fluoropropane*	388.0	388.7	−0.7	490.1	490.2	−0.1
fluorocyclopropane	374.7	378.3	−3.6	472.9	476.0	−3.1
difluorocyclopropane	484.1	487.9	−3.8	621.5	624.8	−3.3
trifluorocyclopropane	593.8	597.5	−3.7	770.0	773.5	−3.5
tetrafluorocyclopropane	705.3	707.0	−1.7	919.7	922.2	−2.5
pentafluorocyclopropane	817.1	816.6	0.5	1069.5	1071.0	−1.5
hexafluorocyclopropane	929.2	926.2	3.0	1219.5	1219.7	−0.2
methanol*	211.5	211.7	−0.2	267.9	268.1	−0.1
dihydroxymethane*	323.7	323.4	0.3	413.1	412.8	0.3
trihydroxymethane*	436.2	435.2	1.0	558.2	557.6	0.6
tetrahydroxymethane	548.7	547.0	1.7	702.9	702.3	0.6
ethanol*	300.7	301.3	−0.6	376.7	377.2	−0.5
dihydroxyethane*	411.3	413.0	−1.7	520.6	521.9	−1.3
trihydroxyethane	524.4	524.8	−0.4	666.7	666.7	0.0
propanol*	391.5	390.8	0.7	487.0	486.2	0.8
aminomethane*	203.9	204.3	−0.4	253.6	254.1	−0.5
diaminomethane*	307.8	308.7	−0.9	384.1	384.9	−0.8
triaminomethane*	413.4	413.1	−0.4	516.3	515.8	0.5
tetraaminomethane	519.6	517.4	2.2	648.8	646.6	2.2
aminoethane*	293.5	293.9	−0.4	362.7	363.2	−0.5
diaminoethane	397.2	398.3	−1.1	493.1	494.0	−0.9
aminopropane*	384.7	383.5	1.2	473.4	472.3	1.1
fluorohydroxymethane	321.3	321.3	0.0	417.1	416.8	0.3
1-hydroxy-2-fluoroethane	408.6	410.8	−2.2	524.4	525.9	−1.5
1-hydroxy-1-fluoroethane	410.6	410.8	−0.2	526.0	525.9	0.1
1-amino-2-fluoropropane	492.0	493.0	−1.0	620.6	621.0	−0.4
1-amino-2,3-difluoropropane	600.4	602.6	−2.2	768.8	769.7	−0.9

[a] Molecules used in the parametrization are denoted by an asterisk.

where n_{X} (X = C, N, O, F, H) denotes the number of atoms in a molecule and the subscript A signifies atomic additivity scheme. It is noteworthy that coefficients $c_i^{m_1}$ and $c_i^{m_2}$ increase along the first row of the system of elements, i.e., with number of valence electrons placed on the respective nuclei, as intuitively expected. Coefficients for the TZ basis set are larger by 19.6% (C), 24.7% (N), 29.5% (O), 35.8% (F), and 37.5% (H). Apparently, the role of more flexible basis set(s) in describing the electron correlation increases with the atomic number, hydrogen being a notable exception. The quality of both regression analyses is very good, as reflected in the low average absolute errors and the high coefficient R^2, which are $\Delta_{\mathrm{abs}}(\mathrm{DZ}) = 0.8$ kcal/mol, $R^2(\mathrm{DZ}) = 0.99996$, and $\Delta_{\mathrm{abs}}(\mathrm{TZ}) = 0.6$ kcal/mol, $R^2(\mathrm{TZ}) = 0.99999$ for the gauge molecules. The corresponding average absolute errors for a set of all molecules presented in Table 1 read: $\Delta_{\mathrm{abs}}(\mathrm{DZ}) = \Delta_{\mathrm{abs}}(\mathrm{TZ}) = 1.2$ kcal/mol. Perusal of data displayed in Table 1 reveals that the largest deviations from the additivity are found in neopentane, and molecules possessing small carbocycles such as cyclopropane, tetrahedrane, etc. Since the latter compounds possess bent bonds and exhibit very high angular strain, it is plausible to assume that a large portion of discrepancy could be an inherent inadequacy of the DZ and TZ basis sets to describe highly distorted density distributions. This conjecture is corroborated by a decrease in the deviation Δ_{add}, which in turn becomes slightly but significantly smaller for the more flexible TZ basis set. It is conceivable that more intricate basis sets will decrease these nonadditivity values even more than the TZ set. In fact, the extrapolation to the complete basis set limit gives more satisfactory additivity values indeed (vide infra), improving performance to a quite acceptable level. It is therefore safe to conclude that discrepancies found for strained molecules are at least partly consequences of imperfections involved in the DZ and TZ basis sets and that they cannot be completely ascribed to the intrinsic limitations of the additivity rule. Deviation found in neopentane is not easy to rationalize, but it is possible that the quarternary C atom requires a separate parametrization. We note in passing that this molecule has the highest nonbonded repulsion *per* C atom. It is interesting to notice that multiply subtituted fluoromethanes and fluoroethanes do not exhibit any abnormal deviations of the correlation energy from the additivity, despite the strong negative hyperconjugation in these systems (see later). Similarly, polysubstituted hydroxy- and aminomethanes and -ethanes exhibit a regular behavior. The same holds for derivatives involving several different substituents (Table 1). It follows that the valence electrons correlation energy in 3D organic molecules complies with a simple atomic additivity rule given by eqs 13 and 14.

TABLE 2: Parameters Entering the Truhlar Extrapolation Scheme

molecule	γ(HF)	$\gamma(E_{corr})$	α(HF)	$\beta(E_{corr})$
methane, T_d	4.14	2.94	3.77	2.53
ethane, D_{3d}	4.26	2.85	3.65	2.46
propane, C_{2v}	4.32	2.84	3.58	2.43
cyclopropane, D_{3h}	4.46	2.75	3.58	2.38
methanol, C_s	4.03	2.61	3.35	2.27
aminomethane, C_s	3.97	2.73	3.34	2.37
fluoromethane, C_{3v}	3.95	2.50	3.35	2.20
difluoromethane, C_{2v}	4.01	2.43	3.37	2.14
trifluoromethane, C_{3v}	4.03	2.39	3.38	2.11
average values	4.13	2.67	3.49	2.32

It is of some interest to examine whether an analogous additivity scheme based on bonds is operative as well. Results not given here show that this is the case too. The corresponding formulas for the same set of gauge molecules read:

$$E_B(\mathrm{corr})^{DZ} = 39.62n_{C-C} + 129.36n_{C-N} + 136.70n_{C-O} + 134.55n_{C-F} + 24.98n_{C-H} \quad (15)$$

$$E_B(\mathrm{corr})^{TZ} = 47.43n_{C-C} + 161.64n_{C-N} + 175.58n_{C-O} + 179.57n_{C-F} + 30.83n_{C-H} \quad (16)$$

where subscript B signifies the bond additivity scheme. Performance of (15) and (16) is virtually equal to that of their counterparts (13) and (14), with the average absolute errors being 0.8 and 0.6 kcal/mol, respectively, and the correlation coefficients 0.99996 and 0.99999, respectively. Consequently, we shall not discuss them any more. Instead, we shall focus now on the problem of the basis set incompleteness and try to remedy its inherent truncation error by applying Truhlar's extrapolation procedure. It is not necessary to describe it in detail here because it is well documented elsewhere.[12,25,26] Truhlar's extrapolation parameters for a selection of the gauge molecules consisting of methane, ethane, propane, cyclopropane, methanol, aminomethane, fluoromethane, difluoromethane, and trifluoromethane are given in Table 2. The α(HF) and $\beta(E_{corr})$ are Truhlar's parameters for the exponent ϵ in formula (8). The average α(HF) and $\beta(E_{corr})$ parameters, 3.49 and 2.32, respectively, will be utilized in estimating CBS values for molecules studied here. The complete basis set values CBS(DT) for the HF and correlation energies obtained by employing DZ and TZ Dunning's basis functions are displayed in Table 3. The respective additivity formulas are of the form

$$E(\mathrm{HF})^{add}_{CBS} = -37.89481n_C - 54.47811n_N - 74.90033n_O - 99.48581n_F - 0.57881n_H \quad (17)$$

and

$$E(\mathrm{corr})^{add}_{CBS} = 104.85n_C + 139.38n_N + 165.88n_O + 182.18n_F + 8.37n_H \quad (18)$$

The CBS Hartree−Fock results will be compared to those obtained by the cc-pVDZ total electronic energy values (not shown here). Both $E(\mathrm{HF})_{CBS}$ and $E(\mathrm{HF})_{DZ}$ energies exhibit relatively high average absolute errors for the gauge set of molecules (about 3 kcal/mol), which is probably a consequence of the fact that the HF energies are very large numbers in contrast to the electron correlation energies. More specifically, $\Delta_{abs}(\mathrm{HF})_{DZ}$ is 3.2 kcal/mol, implying that it is higher by 0.2 kcal/mol than $\Delta_{abs}(\mathrm{HF})_{CBS}$. Percentagewise, this is only 64 parts per million (ppm) for ethane, whereas these deviations are 43 and 32 ppm for propane and butane, respectively, not to mention heavier molecules. Hence, from the conceptual point of view these values are quite acceptable. In fact, some nonadditivities of the E(HF) energies are very interesting and important, because they indicate the presence of new features. For example, they are highly pronounced in molecules involving small three- and four-membered rings. The actual E(HF) values are substantially higher than those offered by the additivity, thus indicating considerable angular strain in these compounds. Let us consider a series cyclopropane, cyclobutane, cyclopentane, bicyclo(1.1.0)-butane, tetrahedrane, and [1.1.1]propellane. The corresponding deviations from the additivity obtained by $E(\mathrm{HF})_{DZ}$ ($E(\mathrm{HF})_{CBS}$) are 31.0 (29.9), 30.3 (28.8), 11.4 (10.2), 75.7 (71.2), 151.4 (143.5), and 115.7 (110.1) kcal/mol, respectively. These results compare quite well with values derived by the concept of topological atom and HF/6-31G** model and by the experimental strain energies.[28] It should be mentioned that both topological energy analysis and the experimentally estimated angular strain destabilizations are obtained by using the strain-free molecular fragment scheme. Results of Wiberg et al.[28] are given in the same order as above and they read 28.7 (27.5), 26.8 (26.5), 7.1 (6.2), 68.6 (63.9), 140.8 (140.0), and 104.2 (98.0) kcal/mol, where experimental data are given within parentheses. Similar results can be obtained by employing the homodesmotic chemical reactions.[29,30] Although all these approaches have perhaps common roots, they are different in their realization. It is remarkable that the additivity concept introduced here is the most elementary one and yet it gives quite reasonable results. One should also point out that the CBS strain energies are closer to the experimental values than DZ results, illustrating in the best way improvements provided by Truhlar's extrapolation scheme. It is noteworthy that the CBS additive formula overshoots the strain energies by approximately 2.5 kcal/mol in monocyclic compounds and in tetrahedrane. Subtracting this amount from CBS deviations, one obtains almost perfect agreement with experiment. Larger deviations from experiment are found in bicyclo(1.1.0)butane and [1.1.1]propellane. The former molecule has twisted chemical CC bonds, which were identified exactly in this system for the first time,[31] whereas the latter has a highly unusual central CC bond formed by the overlapping of rear lobes of hybrid AOs belonging to the apical carbons.

Interesting nonadditivities are found also in the series $CH_{4-n}F_n$ ($n = 1-4$), where the so-called negative $n_F - \sigma^*_{CF}$ hyperconjugation takes place.[32] In a simple Pauling's no-bond double-bond resonance picture, the number of the resonance spin couplings increases in an extended ratio 1:3:6 in CH_2F_2, CHF_3, and CF_4, respectively. Deviations for the CBS Hartree−Fock energies for $CH_{4-n}F_n$ ($n = 1-4$) series are +3.9, +0.7, −9.3, and −17.6 kcal/mol, respectively. Taking a difference between $\Delta_{add}(\mathrm{HF})_{CBS}$ values for CH_2F_2 and CH_3F, one obtains −3.2 kcal/mol as an amount that can be ascribed to the negative hyperconjugation. Multiplying it by 3 and 6, one gets −9.6 and −19.2 kcal/mol, which is close to results above. It follows that the negative hyperconjugation roughly follows the number of resonance structures, as expected. Similar influence of the negative hyperconjugation is observed in polyaminomethanes and polyhydroxymethanes, but the final picture is not so simple, presumably because of the intramolecular hydrogen bond(s).

It also appears that the strain energy in fluorinated cyclopropanes increases with the number of F atoms, which is in accordance with results obtained by homodesmotic reactions.[33] The most impressive result is perhaps finding that the nonadditivities are quite low for the correlation energies and that the

TABLE 3: Extrapolated HF (au), the Differences between $E(\mathrm{HF})_{\mathrm{CBS}}$ and $E(\mathrm{HF})_{\mathrm{CBS}}^{\mathrm{add}}$ (kcal/mol), and Correlation Energies (kcal/mol) to the Complete Basis Set Values by Truhlar's Scheme, Using Average α and β Parameters for Substituted Alkanes[a]

molecule	$E(\mathrm{HF})_{\mathrm{CBS}}$	$\Delta^{\mathrm{add}}_{\mathrm{HF_{CBS}}}$	$E(\mathrm{corr})_{\mathrm{CBS}}$	$E(\mathrm{corr})^{\mathrm{add}}_{\mathrm{CBS}}$	$\Delta^{\mathrm{add}}_{\mathrm{corr}}$
methane*	−40.21794	−5.0	139.3	138.3	1.0
ethane*	−79.26764	−3.2	259.5	259.9	−0.4
propane*	−118.31488	−2.5	381.2	381.5	−0.3
butane*	−157.36999	−1.7	503.0	503.1	−0.1
isobutane	−157.37048	−2.0	504.5	503.1	1.4
pentane*	−196.42099	−0.8	624.9	624.6	0.3
neopentane	−196.42133	−1.0	629.5	624.6	4.9
cyclopropane	−117.10965	29.9	362.7	364.7	−2.0
cyclobutane	−156.16387	28.8	483.9	486.4	−2.5
cyclopentane	−195.24593	10.2	606.8	608.0	−1.2
tetrahedrane	−153.66574	143.5	449.6	452.9	−3.3
bicyclobutane	−154.93863	71.2	467.2	469.6	−2.4
[1.1.1]propellane	−192.77149	110.1	579.2	574.5	4.7
fluoromethane*	−139.11075	3.9	312.4	312.1	0.3
difluoromethane*	−238.02289	0.7	486.7	485.9	0.8
trifluoromethane*	−336.94586	−9.3	660.5	659.7	−0.8
tetrafluoromethane	−435.86611	−17.6	832.8	833.6	−0.4
fluoroethane*	−178.16907	0.2	433.3	433.7	−0.4
difluoroethane*	−277.06548	6.9	606.5	607.5	−1.0
trifluoroethane*	−375.97908	2.8	780.9	781.3	−0.4
tetrafluoroethane*	−474.88933	0.8	955.0	955.1	−0.1
fluoropropane*	−217.22658	−2.9	555.5	555.3	0.2
fluorocyclopropane	−216.01011	34.0	535.7	538.6	−2.9
difluorocyclopropane	−314.90562	41.2	709.5	712.4	−2.9
trifluorocyclopropane	−413.79390	53.0	882.9	886.2	−3.3
tetrafluorocyclopropane	−512.69576	56.2	1057.0	1060.0	−3.0
pentafluorocyclopropane	−611.59292	62.4	1231.2	1233.8	−2.6
hexafluorocyclopropane	−710.48969	68.8	1405.4	1407.6	−2.2
methanol*	−115.10289	4.7	304.0	304.2	0.2
dihydroxymethane*	−190.01070	0.0	470.3	470.1	0.2
trihydroxymethane*	−264.89489	−7.6	636.4	635.9	0.5
tetrahydroxymethane	−339.84117	−18.7	801.6	801.8	−0.2
ethanol*	−154.15958	2.0	425.4	425.8	−0.4
dihydroxyethane*	−229.05024	8.1	590.6	591.7	−1.1
trihydroxyethane	−303.95897	2.8	757.7	757.5	0.2
propanol*	−193.21516	0.0	548.2	547.4	0.8
aminomethane*	−95.26360	2.1	285.4	286.1	−0.7
diaminomethane*	−150.32065	2.0	433.0	433.8	−0.8
triaminomethane*	−205.38471	−2.5	582.2	581.6	0.6
tetraaminomethane	−260.44365	−3.7	731.5	729.3	2.2
aminoethane*	−134.31785	1.0	407.1	407.6	−0.5
diaminoethane	−189.36769	5.5	554.5	555.4	−0.9
aminopropane*	−173.37132	0.3	530.2	529.2	1.0
fluorohydroxymethane	−214.01793	−0.3	478.4	478.0	0.4
1-hydroxy-2-fluoroethane	−253.05852	7.1	598.4	599.6	−1.2
1-hydroxy-1-fluoroethane	−253.07924	−6.0	599.9	599.6	0.3
1-amino-2-fluoropropane	−272.27596	1.8	702.9	703.1	−0.2
1-amino-2,3-difluoropropane	−371.17373	7.6	876.7	876.9	−0.2

[a] The corresponding estimates offered by the additivity rule based on atomic scheme are given for comparison. Molecules used in the parametrization are denoted by an asterisk.

absolute average error for $E(\mathrm{corr})^{\mathrm{add}}_{\mathrm{CBS}}$ drops to 0.5 kcal/mol, whereas $R^2 = 0.99999$. Although the total MP2 electronic energy does include the Hartree−Fock energy, the latter disappears in correlation energy by the very definition. Another reason for low additivity "errors" is given by the fact that correlation energy is a relatively small perturbation correction of $E(\mathrm{HF})$. Improved extrapolated energies $E(\mathrm{corr})_{\mathrm{CBS}}$ exhibit smaller nonadditivity effects in cyclopropane, cyclobutane, and tetrahedrane to 2.0, 2.5, and 3.3 kcal/mol (in absolute values), respectively, thus supporting earlier conjecture that DZ and TZ basis sets do not provide quite adequate description of highly strained bonds. Similar deviations are found in fluorinated cyclopropanes, exhibiting improvement by CBS extrapolation too.

The increase of c_i^{CBS} coefficients relative to the corresponding c_i^{TZ} ones is of some interest. They are in % as follows: 10.5% (C), 12.6% (N), 14.6% (O), 16.9% (F), and 17.7% (H). Since these numbers are more uniform than those obtained in going from the DT to TZ basis set (vide supra), one is tempted to conclude that the complete basis set limit offers a more balanced description of the correlation energy effect.

In summary, it is fair to say that the working hypothesis about the additivity of the valence electrons correlation energy in organic 3D molecules is vindicated. Having stated this, it should be pointed out that there is room for improvement of the additivity formulas. First, one could employ a more flexible parametrization, which would be able to distinguish fine differences in the chemical enviroment of various atoms. For instance, different weighting parameters (c_i coefficients) could be introduced for primary, secondary, tertiary, and quaternary C atoms or alternatively for the corresponding C−X bonds. The second way in improving performance of the additivity formulas would be to use more flexible basis sets such as, e.g., Dunning's aug-cc-pV*m*Z elementary functions. Finally, one could apply more refined extrapolation formulas.[34] A combination of all these factors would be perhaps the best approach in making the additivity formula more quantitative. This is not attempted in this work, since the focus was on the conceptual side of the problem. It should be also mentioned that we did not consider the correlation energies of inner-core electrons, but it is hard to believe that they do not conform to the additivity rule in view of their high localization. We feel that the additivity formulas given here together with those developed for 2D systems[10−12] provide a step toward understanding of various additivity schemes in estimating enthalpies of molecular formation.[35]

Concluding Remarks

Although the calculations of the elusive correlation energies in molecules is a formidably intricate problem, the resulting energies exhibit surprisingly simple additivity properties. There is, however, a lurking caveat emptor, as is usually the case. It is given by the modest theoretical models employed in studying the additivity rules. Both CASPT2 and MP2 models yield an appreciable amount of the total correlation energy, but not its entire value. We note in passing that MP2 correlation energies can retrieve as much as 80%−95% of the MP6 energies depending on molecular systems in question, as shown by He and Cremer,[8] but this is still not the MP limit. Further, there is some scepticism regarding convergency of the MP perturbation series[36] and about its performance.[37,38] Nevertheless, we feel confident that the additivity is a robust property, which will be confirmed by the more rigorous and accurate electronic structure methods in the future, to mention only CCSD(T) approach. If this would prove true, then it would have some important conceptual and practical consequences. From the cognitive side, it would be useful to know that a bulk of the molecular properties resulting from the very complicated many-body motions could be reduced to a number of subunits, be it constituent atoms or the chemical bonds, i.e., their corresponding electrons. It is of no less importance that the additivity “rule of thumb” could be used as a diagnostic tool. Namely, if severe deviations from the additivity are detected, then they strongly indicate the presence of some subtleties, which distinguish the studied system from the rest of the molecules. These fine nuances deserve then meticulous scrutiny.

The important question arises regarding the range of validity of the additivity rule presented here. Obviously, it cannot be applied to diatomic molecules and other 1D molecules. The reason is that diatomic molecules are very special and as R. G. Parr pointed out once, they have two ends that in turn are very close to each other.[39] Clearly, molecules such as N_2, O_2, F_2, HCN, HNC, etc. deserve a separate study. In fact, these molecules were included by He and Cremer[8] in a category of systems exhibiting a certain crowding of the electron pairs. In such cases three- and four-electron correlation effects as well as their couplings with two-electron effects become important. The MP2 method does not involve the higher order correlation effects but simulates them by exaggerating the role of double excitations.[8] Another way to say it would be that the role of the two-electron effect is diminished in the higher order MPn approximations, because these elecrons take part in many-electron excitations. To illustrate the inadequacy of formula (13), we have calculated $E_A(\text{corr})^{DZ}$ as a difference E(HF/cc-pVDZ) − E(MP2(fc)/cc-pVDZ//HF/cc-pVDZ) for some electron rich molecules such as HF, F_2, N_2, HCN, and H_2O. The corresponding results are compared with the additivity values (given within parentheses): 126.1 (119.9), 242.8 (229.5), 188.4 (198.4), 175.3 (183.6), and 126.0 (122.1) kcal/mol, respectively. It is instructive to compare results for HF and F_2. True correlation energies are correspondingly 6.2 and 13.3 kcal/mol higher than the additivity values in accordance with twice as many lone pairs in F_2. Discrepancies found for other molecules show that a successful general additivity scheme should take into account a number and the nature of unshared electron pairs as well as characteristics of local σ-bond pairs and multiplicity of localized π-bond(s). Such an additivity scheme would certainly gain in accuracy in reproducing MP2 correlation energies being more universal at the same time, as suggested by Cremer.[18] It is also obvious that correlation depends on the hybridization state of atoms. We believe that such an approach would be quite successful. A more difficult question is whether higher correlation effects follow an additivity scheme too. There is not an answer at present, but we would like to point out that MP4 correlation energy appears to be additive to a high extent in some molecules examined in this paper.[40]

The additivity might be also useful in designing new exchange-correlation functional in DFT methods, which would be applicable to very large systems. As to the use of the additivity in the molecular orbital schemes for the electron correlation computations, it should be emphasized that the additivity provides a rationale for the success of the local MO approaches[41,42] (and vice versa). It is important to stress that the additivity at the MP2 level is expected to work very well in molecules described by a single resonance structure in the ground state. For example, a deviation from $E_A(\text{corr})^{DZ}$ for ozone O_3 from the additivity is 42 kcal/mol. This is a consequence of the overcrowded lone pairs in this molecule, but also a result of the fact that it can be described by two equivalent resonance structures $O{=}O^+{-}O^-$ and $O^+{-}O^-{=}O$. We noticed that a similar deviation from the additivity occurs in planar systems, if they incorporate a large resonance effect,[11] but in the opposite direction. This is just one more illustration that the additivity rule can serve as a useful test tube for special effects.

True understanding of the additivity is very difficult to offer, however. Very high electron densities near nuclei and their relatively small polarizations caused by chemical bonding,[43] as well as the shapes of Fermi’s holes, which in turn strongly resemble local hybrid orbitals,[44] are very useful clues, but more work is necessary in this direction. Finally, the additivity of the HF energies is not so strictly obeyed, albeit deviations are percentagewise extremely small. It describes gross molecular properties in terms of atoms and identifies some special features such as dramatic angular strain in small ring compounds or rather modest but significant stabilization via the negative hyperconjugation mechanism in alkanes multiply substituted by electronegative atoms or groups, as reflected in deviations from the additivity rule.

Acknowledgment. We thank John von Neumann Institut für Computing des Forschungzentrums Jülich for allocation of the computer time within the project “The Correlation Energy of π-Electrons in Planar Molecules”.

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