

Atomic Additivity of the Correlation Energy in Molecules by the DFT-B3LYP Scheme[§]Danijela Barić[†] and Zvonimir B. Maksić^{*,†,‡}

Quantum Organic Chemistry Group, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia, and
 Division of Physical Chemistry, Faculty of Science and Mathematics, The University of Zagreb,
 Marulićev trg 19, 10000 Zagreb, Croatia

Received: August 19, 2003; In Final Form: October 20, 2003

The problem of the electron correlation in the DFT-B3LYP method is considered. It is suggested that the effective correlation energy can be retrieved by a difference $E(\text{corr})_t^{\text{B3LYP}} = E(\text{B3LYP}) - E(\text{HF})$. Subsequently, it is shown that $E(\text{corr})_t^{\text{B3LYP}}$ exhibits remarkable atomic additivity, similar to that found earlier for ab initio MP2, MP3, MP4, and G3 methods. Performance of the additivity formula in reproducing the B3LYP correlation energies of Lewis' systems described by a single dominant resonance structure is astonishing as evidenced by $\text{AAD} = 1.3$ kcal/mol and $R^2 = 0.99999$. The effective correlation energies span a very large range of values extending from 199 to 1963 for the cc-pVDZ basis sets and from 204 to 1980 (in kcal/mol) if the G3Large basis set is employed. The calculations can be performed on the back of an envelope by elementary arithmetic operations. Importantly, it is shown that there is a close relation between $E(\text{corr})_t^{\text{B3LYP}}$ and the correlation energy $E(\text{corr})_t^{\text{G3}}$ calculated by the G3 computational scheme. Moreover, it turns out that their difference can be resolved into atomic contributions too. By utilization of this simple correction term, it is possible to scale down $E(\text{corr})_t^{\text{B3LYP}}$ values to the quite accurate G3 correlation energies. The underlying picture behind the additivity property is that of the neutral atoms in their canonical hybridization states placed at the equilibrium positions, which strongly indicates that the composite Fermi–Coulomb holes are localized on atoms or that they behave as if they were localized in the atomic domains. In other words, the FC holes significantly contribute to the total molecular energy only if the reference electron is placed in the domains of the inner-core, valence-bond, and lone-pair electrons. They are highly insensitive to the fine details of the electron distributions caused by chemical bonding. Support for these conjectures is offered by the Luken–Baerends model description of the total correlation holes in molecules.

1. Introduction

It is common knowledge that an accurate description of molecular properties and chemical bonding requires an explicit account of the electron correlation effects. A great deal of the tremendous success of computational chemistry in the last two decades is due to a successful treatment of the latter in small- and medium-sized molecules. Developed strategies for tackling the electron-correlation problem based on the MO formalism¹ have been implemented in a number of computer codes^{2–4} now widely in use by the chemical community. Another line of thought, focused on the 3D electron-density distribution,^{5,6} has led to a development of a family of the density functional theory (DFT) methods, which were designed to mimic the exact electronic structure of molecules and solids. Much of the progress in both fields is reflected in two series of books by Lipkowitz and Boyd⁷ and by Politzer et al.⁸ As a result of this development, a large number of papers appeared in the literature reporting the correlation energies in a wide variety of molecules. In contrast, relatively small efforts are devoted to their interpretation and understanding. A pioneering work in this sense was published first by Sinanoglu,⁹ who partitioned the total correlation energy $E(\text{corr})_t$ defined by Löwdin¹⁰ into nondy-

namical $E(\text{ND})$ and dynamical $E(\text{D})$ parts

$$E(\text{corr})_t = E(\text{exact})_{\text{NR}} - E(\text{HF})_{\text{L}} = E(\text{ND}) + E(\text{D}) \quad (1)$$

Here NR stands for the energy obtained by the nonrelativistic Hamiltonian, whereas L denotes the basis set limit for the Hartree–Fock single-determinant energy. The nondynamical electron correlation energy arises from a strong coupling between the HF wave function and those of the low-lying excited configurations. It is also sometimes termed as a static or quasidegeneracy correlation. The nondynamical correlation is long range in nature because it is a consequence of the global features of a system, not to mention its symmetry. The dynamical correlation has short-range character because it mirrors a tendency of electrons to keep apart as much as possible at each moment in their collective motion. Although this division is conceptually simple, it is more qualitative than quantitative since in practice it is not easy to make a clear-cut distinction between these two distinctly different types of correlation. Some other names appeared in the meantime, like, e.g., left–right, in–out, angular, etc. correlation, which cannot be apportioned to the nondynamical or dynamical electron correlations in a unique way. The former classification, however, seems to be more appropriate.

The quantitative description of various types of the correlation energy in molecules is a formidable task since it is a many-body problem par excellence. On the other hand, the edifice of chemistry is built on the electron-pair (inner-shell electrons,

* Corresponding author. Fax: +385-1-4561-118. E-mail: zmaksić@spider.irb.hr.

[†] Ruđer Bošković Institute.

[‡] University of Zagreb.

[§] Dedicated to professors I. Hubač, P. Čarsky, and M. Urban on the occasion of their sixtieth birthday.

bonding electrons, lone pairs) building blocks. Consequently, it would be useful to have a simple interpretation of the electron correlation in terms of coupled electron pairs although collective motion of three, four, or more electrons clustered in small regions might be important in some cases. The first attempt in this sense was made by Cremer as early as 1982,¹¹ who showed that it was possible to partition the MP2 correlation energy of small molecules into contributions related to the inner-core electrons and valence-coupled electron pairs belonging to local bonds or unshared lone pairs. These contributions proved useful in estimation of unknown MP2 energies in large molecules and their enthalpies of formation. Unfortunately, this work was not extended later by employing larger basis sets and the basis set extrapolation procedures.

Recently, we have shown that the π -electron correlation energy in planar hydrocarbons and heteroatomic systems follows a simple atomic additivity rule, which holds also for the extrapolated complete basis set values.¹² It appeared that the additivity formulas performed very well for both nondynamical and dynamical $E(\text{ND})^\pi$ and $E(\text{D})^\pi$ correlation energies. They were conveniently calculated by the CASSCF^{13,14} and CASPT2^{15,16} methods. Furthermore, the dynamical $E(\text{D})^{(\pi)+\sigma}$ correlation energy, which includes all valence electrons in the PT2 procedure, was persistently additive too. It goes without saying that the total correlation energies $E(\text{corr})_t = E(\text{ND})^\pi + E(\text{D})^\pi$ (or $E(\text{D})^{(\pi)+\sigma}$) follow, mutatis mutandis, the same additivity rule in planar π systems. A useful byproduct of these calculations was a finding that the nondynamical correlation energy $E(\text{ND})^\pi$ was extremely insensitive to the basis set quality presumably due to a cancellation of errors. The latter is a consequence of the fact that the nondynamical correlation energy $E(\text{ND})^\pi$ is defined as the difference $E(\text{ND})^\pi = E(\text{CASSCF})^\pi - E(\text{HF})$, where a large number of MOs used in the CASSCF wave function were taken over from the same HF wave function. Another interesting finding was also a result that a sum of the nondynamical and dynamical correlation energies $E(\text{ND})^\pi + E(\text{D})^{(\pi)+\sigma}$, calculated by the CASSCF ^{π} and CASPT2 ^{$(\pi)+\sigma$} methods, reproduces quite closely the correlation energy of planar molecules obtained by the single-reference MP2 approximation. It turned out that double excitations involved in the MP2 perturbational calculations covered the nondynamical correlation energy of the π electrons thus mimicking the multiconfigurational character of the wave functions in planar systems.¹² If this is so, then it should hold also for the MP3 and MP4 approximations, too, because they introduce only corrections into MP2 wave functions and energies. Concomitantly, this conclusion should be also valid for the G3 scheme. Thus, the next step was an extension of the additivity formula of the electron correlation energy from 2D to 3D organic molecules employing MP2, MP3, MP4, and G3 methods.¹⁷ It turned out that the additivity survived the increase in the level of sophistication of the employed theoretical frames and a transition from 2D to 3D systems. To substantiate this claim, we would like to point out that the additive formula has excellent performance in reproducing G3 correlation energies for 91 neutral closed shell organic molecules in their ground states as evidenced by $\text{AAD} = 1.2$ kcal/mol, $R^2 = 0.99998$, and $\text{MAD} = 7.2$ kcal/mol, where AAD and MAD stand for the average absolute deviation and maximum absolute deviation, respectively. The underlying physical picture leading to the additivity rules is astonishingly simple; atoms are assumed to be neutral and placed at their equilibrium positions. The influence of the chemical environment is represented by the polarization of the local atomic electron density and described by the canonical

sp^3 , sp^2 , and sp^1 hybridization schemes for carbon, nitrogen, and oxygen atoms. The hydrogen and fluorine atoms are considered spherical. The calculations require knowledge of the average correlation energy in molecules for each atom in the corresponding hybridization state obtained by fitting the calculated G3 correlation energies. The rest just involves stoichiometric formula and a pocket calculator. A similar and potentially more flexible model is developed by Bytautas and Ruedenberg,¹⁸ who used localized full-orbital reaction space (FORS) molecular orbitals. Their striking feature is that FORS MOs exhibit quasiautomatic character, possessing the shape of deformed minimal basis-set AOs. The latter can be utilized to form hybridized AOs (HAOs), which in turn are directed toward the nearest neighbor atoms or describe a lone pair.¹⁹ Concomitantly, each HAO is supposed to host exactly one or two electrons depending on whether they participate in a local bond formation or form a lone pair, respectively. The average correlation energies are determined for each combination of one-center or nearest-neighbor two-center HAOs by fitting quite accurate coupled cluster with single, double, and perturbative triple excitations (CCSD(T)) correlation energies^{20,21} for molecules composed of H, B, C, N, O, and F atoms. It was shown that eight fitting parameters reproduced CCSD(T) correlation energies obtained for complete basis-set functions with MAD values of only 1.5 kcal/mol.¹⁸ It is noteworthy that Bytautas and Ruedenberg¹⁸ used the model of neutral atoms in molecules in estimating the correlation energies, too, although their scheme is based on the coupled electron pairs. The fact that the correlation energies at the G3 and CCSD(T) levels can be calculated with reasonable accuracy with no effort at all and without any specific knowledge about the spatial or electronic structure of molecules, requiring only stoichiometric formula and canonical hybridization states of constituent atoms, provides some food for thought. All these results deserve attention and call for additional investigations, which will eventually shed more light on the nature of the correlation energies in molecules including their additivity.

It is the aim of the present work to examine a possible additivity of the exchange–correlation energy (ECE) built in the B3LYP DFT method, which in turn seems to be the most popular and widely used density functional approach nowadays. In particular, we would like to explore a relation between B3LYP ECEs and the molecular correlation energies produced by the G3 computational protocol. Finally, we would like to try to offer some tentative qualitative arguments, which might provide clues for understanding the additive feature of the molecular correlation energies.

2. Theoretical Preliminaries

Elements of the density functional theory are well covered by several books.^{22–24} The most successful computational scheme is provided by the hybrid B3LYP method involving the following ECE expression

$$E_{\text{XC}}^{\text{B3LYP}} = (1 - a)E_{\text{X}}^{\text{LSD}} + aE_{\text{XC}} + bE_{\text{X}}^{\text{B88}} + cE_{\text{C}}^{\text{LYP}} + (1 - c)E_{\text{C}}^{\text{LSD}} \quad (2)$$

Here, both $E_{\text{X}}^{\text{LSD}}$ and $E_{\text{X}}^{\text{B88}}$ stand for the exchange term calculated in the local spin density (LSD) and Becke's²⁵ generalized gradient approximations (GGA), respectively. Similarly, $E_{\text{C}}^{\text{LSD}}$ and $E_{\text{C}}^{\text{LYP}}$ correspond to local spin density and Lee–Yang–Parr²⁶ correlation functionals, respectively. E_{XC} represents the HF exchange energy. The employed Becke's B88X functional

is determined to reproduce the HF exchange energies for the noble gas atoms. On the other hand, the E_C^{LYP} correlation functional is tailored to reproduce the correlation energy in the He atom based on an earlier Colle–Salvetti functional.²⁷ The three empirical parameters were chosen in such a way that the atomization, ionization, and protonation energies of molecules involved in the G2 database²⁸ were optimally reproduced. They are $a = 0.20$, $b = 0.72$, and $c = 0.81$.²³ It should be mentioned that the empirical parameters serve the purpose to balance the contributions of various terms in eq 2 and to enable cancellation of their errors as close as possible.

It is of interest to examine the correlation energies obtained by various DFT schemes. In principle, the exact correlation energy is given by the appropriate correlation functional which will provide $E(\text{corr})_{\text{exact}}^{\text{DFT}}$ by employing the exact electron-density distribution ρ_{exact} . Neither this functional nor the exact density distribution are known for any realistic molecular system. Nevertheless, it is useful to start discussion with exact energies obtained for a given system by the exact density ρ_{exact} within the DFT theory, tacitly assuming that they are known, and by the exact wave function Ψ_{exact} obtained by solving Roothaan–Hall equation employing, e.g., full CI method with an infinite basis set. Both total energies $E(\rho_{\text{exact}})^{\text{DFT}}$ and $E(\Psi_{\text{exact}})^{\text{ab initio}}$ are equal leading to a trivial identity (eq 3), where the HF energy calculated at the basis set limit L is subtracted from the left and right

$$E(\rho_{\text{exact}})^{\text{DFT}} - E(\text{HF})_L = E(\Psi_{\text{exact}})^{\text{ab initio}} - E(\text{HF})_L \quad (3)$$

Consequently, it follows that both DFT and ab initio exact correlation energies $E(\text{corr})_{\text{exact}}^{\text{DFT}}$ and $E(\text{corr})_{\text{exact}}^{\text{ab initio}}$ determined by the left and right sides of eq 3, respectively, are equal by definition in the limiting case. However, FCI calculations for L basis set are not feasible as a rule for molecules of chemical interest, whereas the functional of the density leading to ρ_{exact} and $E(\rho_{\text{exact}})^{\text{DFT}}$ is unknown, although it does exist.⁵ Consequently, the correlation energies obtained by various DFT and ab initio methods are necessarily different. A more detailed discussion of these differences will be given later (vide infra). An interesting question arises, however, in whether their differences could tell us something about the approximate DFT exchange and correlation functionals now in use in an ever-increasing number of practical calculations, provided the correlation energies obtained by appropriate ab initio methods are well understood. If the correlation energies are calculated by the B3LYP and G3 computational procedures, one can write

$$E(\text{corr})_t^{\text{G3}} = E(\text{corr})_t^{\text{B3LYP}} + \Delta \quad (4)$$

where Δ is an unspecified term for the time being. Strictly speaking, $E(\text{corr})_t^{\text{B3LYP}} = E(\text{B3LYP}) - E(\text{HF})$ is not pure correlation energy. The reason behind is, inter alia, a well-known fact that both local density approximation (LDA) and GGA exchange functionals involve the self-interaction error (SIE). A number of researchers noticed, paradoxically as it is, that SIE unintentionally simulates the nondynamical part of the correlation energy but unfortunately in a nonspecified and uncontrolled manner.^{29–31} Particularly instructive and pictorial studies of SIE have been performed by Cremer et al.^{32–34} by examining the electron-density distributions in some small characteristic molecules obtained by various DFT and ab initio schemes. It was found that SIE mimics the nondynamical pair correlation effects indeed, which are larger in the Slater than in the Becke exchange functional,³³ whereas the hybrid functionals

suffer much less from SIE. Accordingly, hybrid functionals are better suited for introduction of nondynamical correlation via the wave function connections. The bottom line is that SIE is an integral part of all DFT methods. Somewhat unexpectedly, it was also shown that DFT X functionals cover some dynamical electron correlation effects, which are reminiscent of two- and three-electron correlation effects similar to those inherent in the MP2 and MP4 approximations as far as the electron density distribution is concerned.^{35,36} Hence, it appears that X functionals yield both some nondynamical and dynamical correlation energies in addition to the exchange interaction. It is, however, difficult to delineate percentage of SIE, which corresponds to a true correlation energy. To put it in another way, it is not known how much of SIE still remains as a nonphysical consequence of approximate XC functionals and affects the resulting total molecular energies. All that should be kept in mind when the $E(\text{corr})_t^{\text{B3LYP}}$ energy is discussed. Concomitantly, we shall call $E(\text{corr})_t^{\text{B3LYP}}$ the correlation energy only conditionally as a technical term for the sake of simplicity, although in addition to the dynamical correlation energy, it involves an uncontrolled amount of the exchange and nondynamical correlation and possibly admixture of some unphysical contributions. A justification that $E(\text{corr})_t^{\text{B3LYP}}$ is essentially the correlation energy indeed will be given a posteriori by comparison with the G3 correlation energies. Analogous to a previous study,¹⁷ we shall try to determine $E(\text{corr})_t^{\text{B3LYP}}$ as a multilinear function of the number of H, C, N, O, and F atoms in a large variety of organic molecules, which represents the most elementary form of the additivity rules

$$E(\text{corr})_t^{\text{B3LYP}} = \sum_A \sum_{m=1}^3 K_A(\text{sp}^m) n_A(\text{sp}^m) \quad (5)$$

Here, the sum over different A is extended over atoms in a molecule, $n_A(\text{sp}^m)$ is the number of atoms A in the sp^m hybridization state, and $K_A(\text{sp}^m)$ are average correlation energies of these atoms in organic molecules. The adjustable coefficients $K_A(\text{sp}^m)$ are estimated by fitting multilinear relations to the calculated B3LYP correlation energies (by eq 3) in the least-squares sense. Since we would like to compare $E(\text{corr})_t^{\text{B3LYP}}$ with the correlation energy $E(\text{corr})_t^{\text{G3}}$ obtained by the G3 procedure, a corresponding additive formula

$$E(\text{corr})_t^{\text{G3}} = \sum_A \sum_{m=1}^3 L_A(\text{sp}^m) n_A(\text{sp}^m) \quad (6)$$

is parametrized on the same calibration set of molecules. Obviously, in eq 3, the HF energy obtained by the infinite basis-set limit should be utilized. This is not necessarily the case in formula 4 where we study the differences between G3 and B3LYP correlation energies. Whereas the G3 computational protocol is fixed, in B3LYP we have the freedom of choosing any basis set at our will, which would serve our purposes reasonably well. We selected two bases for comparative reasons. The first is Dunning's cc-pVDZ basis set³⁷ for B3LYP/cc-pVDZ/HF/cc-pVDZ and HF/cc-pVDZ calculations because it is the simplest correlation-consistent basis set. The second is G3Large since it is used for calculations of the $E(\text{corr})_t^{\text{G3}}$ energy, which is obtained by a difference

$$E(\text{corr})_t^{\text{G3}} = E(\text{G3}) - E(\text{HF}/\text{G3Large}/\text{MP2}(\text{fu})/6-31\text{G}^*) \quad (7)$$

The HF energies in eq 7 are obtained at the MP2(fu)/6-31G*-

TABLE 1: Average Atomic Energies in 101 Organic Molecules $K_A(\text{sp}^m)$ and $L_A(\text{sp}^m)$ Obtained by B3LYP/cc-pVDZ//HF/cc-pVDZ, B3LYP/G3Large//MP2(fu)/6-31G*, and G3 Theoretical Schemes^a

atom A	$E(\text{corr})_{\text{B3LYP}}^{\text{mol}(1)}$	$E(\text{corr})_{\text{B3LYP}}^{\text{mol}(2)}$	$E(\text{corr})_{\text{G3}}^{\text{mol}}$	$E(\text{corr})_{\text{B3LYP}}^{\text{fa}(1)}$	$E(\text{corr})_{\text{B3LYP}}^{\text{fa}(2)}$	$E(\text{corr})_{\text{G3}}^{\text{fa}}$	δ_1	δ_2	δ_3
hydrogen	11.79	12.97	11.61	0	0	0	11.79	12.97	11.61
carbon									
C(sp ³)	150.34	150.18	133.68	103.8	105.0	86.3	46.5	45.2	47.7
C(sp ²)	149.47	149.80	132.25	103.8	105.0	86.3	45.7	44.8	46.0
C(sp)	148.27	150.14	131.88	103.8	105.0	86.3	44.5	45.1	45.6
nitrogen									
N(sp ³)	189.04	191.34	167.16	124.3	126.7	103.8	64.7	64.6	63.4
N(sp ²)	187.53	190.58	165.34	124.3	126.7	103.8	63.2	63.9	61.5
N(sp)	182.94	188.63	166.54	124.3	126.7	103.8	58.6	61.9	62.7
oxygen									
O(sp ³)	223.72	227.63	192.28	139.1	176.9	173.4	50.3	50.7	53.2
O(sp ²)	222.16	226.32	189.20	173.4	176.9	139.1	48.8	49.4	50.1
fluorine	251.50	254.85	207.05	220.5	226.0	177.2	31.0	28.9	29.9
AAD	1.3	1.2	1.3						
MAD	6.4	9.9	7.2						
R ²	0.99999	0.99998	0.99998						

^a These values were obtained via eqs 5 and 6, respectively. They are compared with the corresponding energies of free atoms in their ground states (in kcal/mol). Superscripts “1” and “2” denote cc-pVDZ and G3Large basis set, respectively. Superscripts “mol” and “fa” refer to molecular and free atom quantities, respectively. Differences are $\delta_1 = E(\text{corr})_{\text{B3LYP}}^{\text{mol}(1)} - E(\text{corr})_{\text{B3LYP}}^{\text{fa}(1)}$, $\delta_2 = E(\text{corr})_{\text{B3LYP}}^{\text{mol}(2)} - E(\text{corr})_{\text{B3LYP}}^{\text{fa}(2)}$, and $\delta_3 = E(\text{corr})_{\text{G3}}^{\text{mol}} - E(\text{corr})_{\text{G3}}^{\text{fa}}$. $E_A(\text{corr})_{\text{B3LYP}}^{\text{mol}(1)} = K_A(\text{sp}^m)^{(1)}$, $E_A(\text{corr})_{\text{B3LYP}}^{\text{mol}(2)} = K_A(\text{sp}^m)^{(2)}$, and $E_A(\text{corr})_{\text{G3}}^{\text{mol}} = L_A(\text{sp}^m)$, where K_A and L_A are parameters appearing in formula 8.

optimized geometries by using the largest basis set (G3Large) involved in the G3 protocol.³⁸ Thus the differences between the correlation energies computed by B3LYP/G3Large and G3 schemes could be ascribed solely to different theoretical frameworks employed. Further, the zero-point vibrational energies are excluded in formula 7 since they have little to do with the correlation energy. In other words, we shall assume that they are determined at the same theoretical level for both G3 and HF methods, thus canceling out exactly.

We would like to underline once again the utmost simplicity of the additive formulas 5 and 6. They contain 10 adjustable parameters, which will be determined on a set of 101 organic molecules. It should be noticed that the intramolecular charge transfer is neglected and atoms are considered to be neutral in their idealized hybridization states. It would appear that the $E(\text{corr})_{\text{t}}^{\text{B3LYP}}$ and $E(\text{corr})_{\text{t}}^{\text{G3}}$ could be obtained with a reasonable accuracy via the additive relations 5 and 6 by using stoichiometric formulas and canonical hybridization states of the constituent atoms only, in addition to pencil and paper needed for elementary arithmetic operations.

All B3LYP and G3 calculations are carried out by using the Gaussian 98 program.²

3. Results and Discussion

We shall consider correlation energy as a positive quantity for simplicity. The results of the least-squares fitting procedure performed on more than 100 closed-shell neutral organic molecules are summarized in Table 1, where the average correlation energies per atom in a particular hybridization state, obtained by the B3LYP and G3 methods, are compared to each other and to the corresponding free-atom correlation energies. Let us mention first that $L_A(\text{sp}^m)_{\text{G3}}^{\text{mol}}$ values, where A = H, C, N, O, and F atoms and $m = 1, 2, 3$, are slightly different than earlier average atomic correlation energies in molecules¹⁷ since the present calibration set of molecules is larger. The most striking result is that the increase in atomic energy upon formation of chemical bonds δ is appreciable and described almost equally well by B3LYP and G3 methods. The corresponding values δ_i ($i = 1, 2, 3$) compare very well, implying that they do not strongly depend on the theoretical method or on the quality of the basis set. Here, $\delta_1 = E(\text{corr})_{\text{B3LYP}}^{\text{mol}(1)} -$

$E(\text{corr})_{\text{B3LYP}}^{\text{fa}(1)}$, $\delta_2 = E(\text{corr})_{\text{B3LYP}}^{\text{mol}(2)} - E(\text{corr})_{\text{B3LYP}}^{\text{fa}(2)}$, and $\delta_3 = E(\text{corr})_{\text{G3}}^{\text{mol}} - E(\text{corr})_{\text{G3}}^{\text{fa}}$, where the superscripts “mol” and “fa” correspond to molecular and free atom quantities, respectively. It follows also that the electron correlation significantly contributes to the stability of molecules and atomization energies. The ratios between the atomic correlation energies for sp³ atoms in molecules and those in free atoms for the B3LYP (G3) method(s) are 1.45 (1.55), 1.52 (1.61), 1.29 (1.38), and 1.15 (1.17) for C(sp³), N(sp³), O(sp³), and F, respectively. It follows that the largest increase in the (dynamical) correlation energy upon chemical bond formation is exhibited by the nitrogen atom to be followed by oxygen and carbon. Fluorine changes its correlation energy in molecules the least. A plausible explanation is that fluorine is highly correlated already in its free atom ground state in view of the number of its valence electrons and its retention of electronic structure. Variation in $L_A(\text{sp}^m)_{\text{G3}}^{\text{mol}}$ caused by stepwise change in m is very small, but it is significant since it greatly improves performance of the additive model. It appears that importance of the atomic correlation energy in molecules decreases as the s character of local HAOs increases, with one notable exception; $L_{\text{N}}(\text{sp}^1)_{\text{G3}}^{\text{mol}}$ is larger than $L_{\text{N}}(\text{sp}^2)_{\text{G3}}^{\text{mol}}$. We would not like to push the hybridization model too far, but one is tempted to conclude that the electrons are more correlated in the perfect tetrahedral arrangement of four covalent bonds, since they avoid each other in space in an optimal way, than in deformed tetrahedra where local two-electron bonds come closer to each other. Illustrative examples of the latter are given by the double and triple bonds in, e.g., H₂C=CH₂ and HC≡CH, which are both described by sp⁵ hybrids in the bent-bond picture. Their mutual angle in multiple bonds is smaller than 109.5° (being 101.5°), implying that the correlated motion of electrons in strongly deformed tetrahedra is less efficiently realized. Going back to the σ - π picture of multiply bonded atoms, one should recall that π systems have low-lying virtual orbitals meaning that the nondynamical correlation might play a significant role, which is not explicitly taken into account in the G3 procedure. It is possible that a multireference G3 method might change the trend of the correlation energies as a function of the hybridization s characters, but this remains to be seen. In any case, we believe that hybridization might be very important, if the composite

exchange–Coulomb holes are strongly localized in Lewis molecules (see later). The B3LYP average atomic energies in molecules $K_A(sp^m)_{B3LYP}^{mol}$ are considerably larger than those in molecules $L_A(sp^m)_{G3}^{mol}$ as expected. Hence, it is appropriate to consider at this place the difference between the correlation energies obtained by the DFT and wave function ab initio methods for finite basis sets in more detail. The DFT correlation energy involves: (a) the energy resulting from the correlation functional, which is dynamical in nature in the standard DFT methods such as, e.g., B3LYP; (b) the SIE of the correlation functional, which mimics a contraction of the density to regions of the molecular 3D space where the electron density is amplified and leads to a decrease in the exchange repulsion effect; (c) the difference in intraelectronic (self-) exchange between the HF and DFT exchange, which in turn defines the exchange SIE. The latter mimics both the nondynamical and dynamical correlation effects; (d) the difference between interelectronic HF and DFT exchange, which leads to underestimation of the long-range exchange of two electrons of the same spin; and (e) the correlation energy of the kinetic energy. This explains why the DFT correlation energy defined by eq 3 must be larger for approximate functionals and finite basis sets than the G3 correlation energy. Finally, it should be noted that $K_A(sp^m)_{B3LYP}^{mol}$ average atomic correlation energies in molecules are slightly increased in H and C atoms upon enlargement of the basis set from cc-pVDZ to G3Large. A more significant increase in the average correlation energy upon introduction of a much more flexible basis set is observed in oxygen and fluorine atoms. Nitrogen assumes a more uniform change of the correlation energy upon the change in hybridization if the G3Large set in the B3LYP method is employed.

The total correlation energy in a wide variety of organic molecules obtained by B3LYP and G3 calculations is presented in Table 2. Performance of the additivity formulas 5 and 6 is excellent for both methods as evidenced by a very low AAD = 1.3 kcal/mol and a very high R^2 value, which is practically equal to 1.0 (Table 1). It is noteworthy that computations by B3LYP/cc-pVDZ and B3LYP/G3Large have practically the same performance. The maximum average deviation is found in H_2O_2 by both G3 and B3LYP methods. This molecule exhibits the highest electron density congestion due to four diffuse lone pairs confined in a relatively small space. The correlation energy in this kind of system is particularly difficult to describe. It was shown by Cremer and He³⁹ that molecules can be divided in two broad classes. Molecules belonging to the first class possess well-separated bonded and unshared coupled electron pairs in addition to inner-shell highly localized electrons. In these molecules, D excitations are the dominating contribution to the correlation energy and MP n series converges smoothly and monotonically. In contrast, molecules possessing strongly congested electron densities within a small molecular space, like H_2O_2 , exhibit clustering of three, four, or more electrons. Then the T excitations become very important, and the MP n series assumes erratic behavior. The realistic correlation energies can be obtained at the MP6 level of calculations. It follows that the deviation from additivity in H_2O_2 is something which is not completely unexpected.

It is remarkable that in all three additivity formulas, the free constant is missing, implying that there is not a spurious additive term. It follows that the correlation energies are strictly additive over atoms. Moreover, they do not depend on the details of the electronic structure around atoms apart from their idealized hybridization state (i.e., the corresponding coordination number) or on the intramolecular charge transfer. It is astounding that

all $K_A(sp^m)$ or $L_A(sp^m)$ correlation energies for a particular A and m have the same value irrespective of their nearest neighbors. How can we interpret these peculiar findings? The first and the most important reason is that the dynamical correlation has $(1/r^6)$ dependence. The situation is, however, more subtle than that. An important hint is given by the work of Luken on the properties of the exchange (Fermi) holes some 20 years ago.^{40–44} Luken has shown that Fermi holes in molecules are completely different from those in a free electron gas. For instance, they never have a spherical shape unless the probe electron is placed near a nucleus other than a proton.⁴⁴ In molecules, which are well described by a single resonance structure, the Fermi hole in the HF density distributions closely resemble the localized two-center molecular orbital (LMO), if the probe electron is placed in the domain of this LMO. Similarly, the probe electron situated in the electron-density basin of a lone pair produces a Fermi hole resembling the hybrid AO describing this unshared electron pair. In fact, Luken used the concept of the Fermi hole to produce LMOs in some small molecules. From LMOs to their constituent HAOs placed on bonded atoms is just one little step. Furthermore, Luken has shown that the Fermi hole can be described by the absolute square of the Fermi orbital,^{40–42} which in turn is expressed as a linear combination of the occupied HF orbitals divided by the square root of the total density at the position of the probe electron (\bar{r}_2). Each HF orbital in this linear combination is multiplied by its value at (\bar{r}_2). It follows that the Fermi holes in molecules are either strongly localized on atoms, if created by the inner-shell electrons, or they behave as if they were localized on atoms in the valence regions. Taking into account a general behavior of the electron density distribution calculated by the MP2 model, that a portion of the electron density is shifted to the atoms particularly via the left–right electron pair correlation,⁴⁵ one concludes that the Fermi hole calculated by the correlated wave functions amplifies its local atomic components too. Admittedly, MP2 approximation exaggerates this effect, which is most appropriately described by the coupled cluster (SD) approach.⁴⁵ Nevertheless, it seems reasonable to assume that the composite Fermi–Coulomb holes are essentially localized on atoms. Recent results of Baerends et al.^{46–48} support this intuitive conjecture. By building on Luken's concept of Fermi orbital, Baerends was able to model the Coulomb hole and the composite exchange–correlation hole^{46,47} along similar lines. It appeared that the composite hole exhibited strong atomic localization in simple diatomics. This is consistent with earlier results of Bytautas and Ruedenberg¹⁸ on the additivity of the CCSD(T) correlation energies by utilizing (atomic-localized) FORS orbitals as well as with some earlier findings^{12,17} and present results.

The next important conceptual question is given by relation between the $E(\text{corr})_t^{B3LYP}$ and $E(\text{corr})_t^{G3}$ energies. Their perusal across Table 2 reveals that $E(\text{corr})_t^{B3LYP}$ values are not only always larger than $E(\text{corr})_t^{G3}$ but that the difference increases linearly with the number of atoms in a molecule. One is therefore tempted to express the differences Δ (eq 4) as

$$E(\text{corr})_t^{G3} - E(\text{corr})_t^{B3LYP(1)} \cong \sum_A \sum_{m=1}^3 (L_A(sp^m) - K_A(sp^m)^{(1)}) n_A(sp^m) \quad (8)$$

where superscript (1) denotes the B3LYP/cc-pVDZ//HF/cc-pVDZ results. Formula 8 reproduces fairly well the differences between G3 and B3LYP/cc-pVDZ correlation energies as easily

TABLE 2: Correlation Energies of 117 Molecules Obtained by B3LYP/cc-pVDZ//HF/cc-pVDZ, B3LYP/G3Large//MP2(fu)/6-31G*, and G3 Methods Compared to Their Additivity Values Obtained by Additivity Formulas 5 and 6 and Coefficients Presented in Table 1 (in kcal/mol)

molecule	$E(\text{corr})_{\text{B3LYP}}^{(1)}$	$E(\text{corr})_{\text{B3LYP}}^{\text{add}(1)}$	$E(\text{corr})_{\text{B3LYP}}^{(2)}$	$E(\text{corr})_{\text{B3LYP}}^{\text{add}(2)}$	$E(\text{corr})_{\text{G3}}$	$E(\text{corr})_{\text{G3}}^{\text{add}}$
methane	199.2	197.5	203.9	202.1	180.7	180.1
ethane	372.7	371.4	379.4	378.2	337.0	337.0
propane	546.5	545.3	555.3	554.3	494.8	493.9
butane	720.4	719.2	731.2	730.4	652.5	650.8
isobutane	720.4	719.2	731.5	730.4	654.0	650.8
pentane	894.1	893.1	907.0	906.6	810.4	807.7
neopentane*	894.6	893.1	907.5	906.6	814.6	807.7
fluoromethane	436.6	437.2	444.7	444.0	374.7	375.6
difluoromethane	675.3	676.9	685.6	685.8	569.8	571.0
trifluoromethane	914.0	916.6	926.0	927.7	765.1	766.4
tetrafluoromethane	1151.9	1156.3	1165.2	1169.6	960.0	961.9
1,2-difluoroethane	849.0	850.8	861.2	862.0	726.0	727.9
1,1,2-trifluoroethane	1088.3	1090.5	1102.3	1103.8	921.8	923.3
1,1,2,2-tetrafluoroethane	1327.5	1330.2	343.2	1345.7	1117.4	1118.8
fluoropropane	785.5	785.0	796.6	796.2	689.9	689.4
methanol	421.6	421.2	430.5	429.7	371.6	372.4
dihydroxymethane	645.0	644.9	657.6	657.3	564.0	564.7
trihydroxymethane	867.7	868.7	883.7	885.0	756.2	757.0
tetrahydroxymethane	1089.5	1092.4	1108.8	1112.6	948.4	949.2
ethanol	595.7	595.1	606.6	605.8	529.3	529.3
1,2-dihydroxyethane	817.9	818.8	832.6	833.5	720.5	721.6
1,1,2-trihydroxyethane	1041.7	1042.6	1059.6	1061.1	913.9	913.9
2-propanol	770.2	769.0	782.6	782.0	687.9	686.2
fluorohydroxymethane	659.6	660.9	671.8	671.6	566.7	567.8
1-hydroxy-2-fluoroethane	833.4	834.8	846.8	847.7	723.1	724.7
aminomethane	398.7	398.3	407.0	406.4	357.7	358.9
diaminomethane	598.7	599.1	610.5	610.7	536.1	537.7
triaminomethane	799.4	800.0	814.2	815.0	715.9	716.4
tetraaminomethane	999.4	1000.8	1017.1	1019.3	896.2	895.2
dimethylamine	573.6	572.2	583.0	582.5	514.8	515.8
trimethylamine	748.8	746.1	759.4	758.6	674.0	672.7
aminoethane	572.7	572.2	582.9	582.5	515.3	515.8
1,2-diaminoethane	772.5	773.1	786.1	786.8	693.7	694.6
aminopropane	747.1	746.1	759.1	758.6	674.6	672.7
1-amino-2-fluoropropane	985.3	985.9	999.9	1000.5	869.6	868.1
1-amino-2,3-difluoropropane	1224.1	1225.6	1240.9	1242.4	1063.4	1063.6
HNO ₂ *	666.4	645.2	679.8	657.5	578.3	558.4
nitromethane*	839.4	819.1	853.8	833.6	732.9	715.3
methylnitrite*	833.3	819.1	848.8	833.6	730.1	715.3
HCN	341.7	343.0	349.1	351.7	307.3	310.0
NCCN	663.9	662.4	679.3	677.5	596.9	596.8
acetonitrile	515.2	516.9	525.2	527.9	462.5	466.9
CF ₃ CN	1234.6	1236.0	1250.9	1253.5	1052.5	1053.2
CH ₂ CHCN	663.4	665.5	674.9	677.3	594.3	597.8
dimethyl ether	597.3	595.1	606.1	605.8	527.6	529.3
methylethyl ether	771.1	769.0	782.0	782.0	685.1	686.2
formaldehyde	394.1	395.2	401.7	402.1	344.7	344.7
F ₂ C=O	873.8	874.6	886.1	885.8	736.4	735.5
glyoxal	766.0	766.8	777.8	778.2	667.2	666.1
acetaldehyde	569.4	569.1	578.3	578.2	501.1	501.6
acetylfluoride	809.0	808.8	820.9	820.1	697.7	697.0
acetone	743.4	743.0	754.3	754.3	658.4	658.5
formic acid	619.7	618.9	630.2	629.7	536.8	536.9
acetic acid	792.8	792.8	805.6	805.8	693.2	693.9
methyl formate	794.3	792.8	805.9	805.8	693.1	693.9
acetamide	770.4	770.0	782.5	782.5	678.5	680.3
cyclopropane	520.8	521.7	528.3	528.4	469.3	470.7
fluorocyclopropane	760.7	761.4	770.5	770.3	664.5	666.1
1,2-difluorocyclopropane	1000.7	1001.2	1012.5	1012.1	860.0	861.6
1,2,3-trifluorocyclopropane	1241.0	1240.9	1254.6	1254.0	1055.5	1057.0
1,1,2,3-tetrafluorocyclopropane	1481.5	1480.6	1496.3	1495.9	1251.9	1252.5
pentafluorocyclopropane	1722.1	1720.3	1738.3	1737.8	1448.6	1447.9
hexafluorocyclopropane	1962.9	1960.0	1980.5	1979.7	1645.6	1643.3
methylencyclopropane	670.4	670.3	678.8	677.8	600.9	601.5
cyclobutane	695.6	695.7	704.0	704.5	628.4	627.6
bicyclobutane	671.1	672.1	679.1	678.6	604.6	604.4
cyclopentane	868.6	869.6	879.1	880.6	786.7	784.5
spiropentane	844.4	846.0	854.7	854.7	760.4	761.3
tetrahydrane	649.0	648.5	655.5	652.6	581.2	581.2
[1.1.1]propellane*	821.6	822.4	829.9	828.7	745.0	738.1
aziridine	547.9	548.7	556.5	556.6	490.8	492.6

TABLE 2 (Continued)

molecule	$E(\text{corr})_{\text{B3LYP}}^{(1)}$	$E(\text{corr})_{\text{B3LYP}}^{\text{add}(1)}$	$E(\text{corr})_{\text{B3LYP}}^{(2)}$	$E(\text{corr})_{\text{B3LYP}}^{\text{add}(2)}$	$E(\text{corr})_{\text{G3}}$	$E(\text{corr})_{\text{G3}}^{\text{add}}$
oxirane	572.7	571.6	580.9	579.9	504.9	506.1
ethylene	345.5	346.1	351.0	351.5	310.2	310.9
propylene	519.9	520.0	527.9	527.6	469.8	467.8
allene	496.2	494.4	502.8	501.6	442.0	442.8
isobutene	694.2	693.9	704.1	703.7	626.1	624.7
<i>trans</i> -butadiene	668.2	668.6	676.9	677.0	598.6	598.7
fluoroethene	586.7	585.8	594.4	593.4	506.2	506.4
tetrafluoroethene	1310.1	1304.9	1323.5	1319.0	1095.3	1092.7
CH ₂ =NH	371.8	372.4	378.7	379.3	331.7	332.4
CH ₂ =CH-CH=NH	694.1	694.9	702.4	704.8	617.6	620.1
CH ₂ =N-CH ₃	547.5	546.3	555.7	555.4	489.0	489.3
ketene	545.4	543.5	553.7	552.2	476.1	476.5
cyclopropene	496.2	496.4	502.6	501.7	444.6	444.6
cyclobutadiene*	645.8	648.5	652.5	651.1	581.4	575.4
benzene	966.1	967.6	975.5	976.6	862.4	863.2
pyrrole*	848.6	847.8	857.6	854.6	756.1	752.4
furan*	872.5	872.2	881.2	878.7	770.3	767.7
acetylene	317.8	320.1	323.2	326.2	286.0	287.0
propyne	492.0	494.0	499.8	502.4	442.1	443.9
2-butyne	666.1	667.9	676.4	678.5	598.6	600.8
water	246.4	247.3	255.4	253.6	217.5	215.5
hydrogen peroxide	477.4	471.0	491.1	481.2	415.0	407.8
hydrogen fluoride	260.5	263.3	270.3	267.8	222.1	218.7
carbon dioxide	591.4	592.6	601.8	602.8	510.6	510.3
ammonia	224.6	224.4	231.5	230.3	202.2	202.0
NH ₂ F	467.1	464.1	477.9	472.1	400.5	397.4
NHF ₂ *	712.7	703.8	724.6	714.0	602.0	592.8
NF ₃ *	960.6	943.5	977.5	955.9	805.8	788.3
HN=NH	398.7	398.6	408.5	407.1	355.7	353.9
hydrazine	426.6	425.2	437.4	434.6	381.1	380.7
N ₂ O*	610.8	592.6	615.1	605.5	527.4	521.1
1,3-butadiene	615.5	616.7	625.5	626.5	551.0	550.7
1-methyl-1,3-butadiene	789.7	790.6	802.2	802.6	707.4	707.6
1,4-dimethyl-1,3-butadiene	963.7	964.5	979.0	978.8	863.9	864.5
cianoacetylene	639.2	639.5	651.8	652.0	573.4	573.8
1-methyl-2-cyanoacetylene	813.4	813.5	828.6	828.1	729.4	730.7
1-fluoro-1,3-butadiene	858.2	856.4	869.9	868.4	747.8	746.2
1,4-difluoro-1,3-butadiene	1100.8	1096.1	1114.3	1110.3	944.5	941.6
vinylacetylene	640.5	642.6	649.7	651.8	573.9	574.7
tetracyanoethylene	1624.7	1623.8	1656.3	1654.7	1461.4	1458.2
isoprene	842.6	842.5	853.4	853.2	757.9	755.6
styrene	1288.8	1290.1				
fluorobenzene	1207.5	1207.3				
1,2-difluorobenzene	1449.3	1447.0				
1,3-difluorobenzene	1448.7	1447.0				
1,4-difluorobenzene	1449.1	1447.0				

checked by using data given in Tables 1 and 2. However, the difference Δ should be diminished in principle by introducing optimal difference per atom $D_A(\text{sp}^m)^{(1)}$ determined by fitting the left-hand side of eq 8 in the least-squares sense. Then one can express $E(\text{corr})_t^{\text{G3}}$ as

$$E(\text{corr})_t^{\text{G3}} \cong E(\text{corr})_t^{\text{B3LYP}(1)} - \sum_A \sum_{m=1}^3 D_A(\text{sp}^m)^{(1)} n_A(\text{sp}^m) \quad (9)$$

where D_A is defined as a positive quantity. It turns out that the optimal $D_A(\text{sp}^m)^{(1)}$ contributions are given by $D_A(\text{sp}^m)^{(1)} = K_A(\text{sp}^m)^{(1)} - L_A(\text{sp}^m)$, where $K_A(\text{sp}^m)^{(1)}$ and $L_A(\text{sp}^m)$ are constants given in Table 1. The statistical characteristics are excellent; AAD = 1.2 kcal/mol, MAD = 6.2 kcal/mol, and $R^2 = 0.9995$. One concludes that formula 9 represents a very simple means for scaling down the B3LYP⁽¹⁾ correlation energies to the G3 ones. This is seemingly a very surprising result, which testifies against the widespread opinion that DFT and ab initio correlation energies cannot be compared because they are completely different. In fact, the G3 correlation energy can be obtained from the B3LYP/cc-pVDZ//HF/cc-pVDZ correlation energy by using a correction term (eq 9), which is a sum of

atomic D_A contributions. Performance of the formula 9 is remarkable indeed in view of the low level of the B3LYP⁽¹⁾ calculations. Similar results are obtained by B3LYP⁽²⁾ calculations employing the G3Large basis set by using $K_A(\text{sp}^m)^{(2)}$ parameters presented in Table 1. It follows straightforwardly as an important corollary that the DFT correlation energy determined as a difference $E(\text{corr})_t^{\text{B3LYP}} = E(\text{B3LYP}) - E(\text{HF})$ has a well-defined meaning even in the cases of approximate semiempirical XC functionals, e.g., like that employed in the B3LYP DFT method, and by using very modest basis set. These results are less surprising if it is taken into account that both DFT and MPn methods involve a certain degree of nondynamical correlation^{32-34,45} and that the correlation energies are persistently additive for Lewis molecules. On the practical side of the problem, the present results indicate that good G3 estimates of the correlation energy in Lewis molecules can be obtained by using B3LYP/cc-pVDZ calculations and approximate formula 9. It goes without saying that approximate, but pretty good, estimates of the total G3 molecular energies are obtained by calculating $E(\text{HF}/\text{G3Large}/\text{MP2}(\text{fu})/6-31\text{G}^*)$ values and by adding up the $L_A(\text{sp}^m)_{\text{G3}}^{\text{mol}}$ constants given in Table 1, implying that only the HF/G3Large//MP2(fu)/6-31G*

computations are necessary in well-behaved Lewis systems. This extends the application of the G3 method to large molecules.

The usefulness of the additivity rules governing the correlation energies is manifold. Let us consider isodesmic⁴⁹ and homodesmotic⁵⁰ reactions first. The former preserve the number and types of atoms and chemical bonds, whereas in the latter the canonical hybridization states of atoms of reactants are retained in the products as well. It should be recalled in this respect that Snyder and Basch^{51,52} were the first to use formal chemical reactions in order to exclude the correlation error as much as possible from the reaction energies. In particular, they have shown that changes in the correlation energy were small for some selected reactions involving saturated closed shell reactants and products. A characteristic isodesmic reaction like, e.g., the valence isomerization is exemplified here by the transformation of the so-called acetylenic compound tetrahedrane into two acetylenes. Let us consider a change in the correlation energy

$$(\text{tetrahedrane})_{\text{corr}} = 2(\text{acetylene})_{\text{corr}} + E(\text{corr})_{10} \quad (10)$$

where the name of a molecule and its subscript denote the correlation energy of a molecule in question. The correlation energy $E(\text{corr})_{10}$ obtained by this isodesmic reaction is 9.2 (6.8) and 13.4 (8.3) in kcal/mol by the G3 and B3LYP⁽¹⁾/cc-pVDZ calculations, respectively, where the additivity values are given within parentheses. The latter are in fair agreement with ab initio and DFT calculations despite the extremely high strain energy of tetrahedrane. In what follows, the first number will always refer to the G3 and the second to B3LYP⁽¹⁾ result, whereas the corresponding additivity values will be given within parentheses. An additional illustrative isodesmic reaction is provided by the ring opening of cyclopropane

$$2(\text{cyclopropane})_{\text{corr}} = 3(\text{ethylene})_{\text{corr}} + E(\text{corr})_{11} \quad (11)$$

The change in the correlation energy $E(\text{corr})_{11}$ is 8.0 (8.7) and 5.1 (5.1) kcal/mol. In both isodesmic reactions 10 and 11, the changes in the correlation energies are significant due to a change in hybridization in reactants and products, implying that the influence of the electron correlation cannot be neglected. To put eq 11 into a perspective, we calculated the reaction energy at the G3 level. It is -13.9 kcal/mol, which compares well with -12.1 kcal/mol obtained by using the experimental ΔH_f values.⁵³ In contrast to isodesmic reactions, the effect of the correlation in homodesmotic reactions can be abandoned in the first approximation. For example

$$(\text{cyclopentane})_{\text{corr}} + 5(\text{ethane})_{\text{corr}} = 5(\text{propane})_{\text{corr}} + E(\text{corr})_{12} \quad (12)$$

It turns out that the correlation energy $E(\text{corr})_{12}$ is -1.8 (0.0) and -0.4 (0.1) kcal/mol thus being small. Obviously, homodesmotic reactions can be successfully treated at the HF level by employing an adequate basis set. It is interesting to note in passing that the electron correlation provides a very small if not negligible contribution to the aromaticity of benzene. The corresponding homodesmotic reaction reads

$$(\text{benzene})_{\text{corr}} + 3(\text{ethylene})_{\text{corr}} = 3(1,3\text{-butadiene})_{\text{corr}} + E(\text{corr})_{13} \quad (13)$$

It appears that $E(\text{corr})_{13}$ is -2.8 (-0.2) and -2.0 (0.1) kcal/mol meaning that the correlation energy is practically insignificant in stabilizing benzene, particularly if the error bars of the G3 and B3LYP methods are taken into account. This is in

TABLE 3: Correlation Energies of 18 α -Amino Acids Obtained by the B3LYP/cc-pVDZ//HF/cc-pVDZ Method Compared to Their Additivity Predictions (in kcal/mol) and Estimates of Total Energies on the G3 Level Obtained by Adding $L_A(\text{sp}^m)$ Additive Constants to the HF Energies on HF/G3Large//MP2(fu)/6-31G* (in au)

amino acid	$E(\text{corr})_{\text{B3LYP}}$	$E(\text{corr})_{\text{B3LYP}}^{\text{add}}$	Δ^a	$E(\text{G3})$
glycine	993.1	993.7	-0.6	-284.32973
alanine	1167.2	1167.6	-0.4	-323.62791
valine	1515.5	1515.5	0.0	-402.21833
leucine	1689.4	1689.4	0.0	-441.51542
isoleucine	1690.2	1689.4	0.8	-441.51158
proline	1489.4	1491.9	-2.5	-401.00552
phenylalanine	2109.3	2111.6	-2.3	-554.57391
tryptophan	2611.9	2609.8	2.1	-686.08415
serine	1391.7	1391.3	0.4	-398.81583
threonine	1566.0	1565.2	0.8	-438.11996
tyrosine	2335.4	2335.3	0.1	-629.76714
asparagine	1738.8	1738.6	0.2	-492.26507
glutamine	1916.7	1914.0	2.7	-531.55784
aspartic acid	1761.3	1763.0	-1.7	-512.12873
glutamic acid	1939.0	1936.9	2.1	-551.42154
lysine	1889.7	1890.2	-0.5	-496.57703
arginine	2266.4	2265.9	0.5	-606.31375
histidine	2019.5	2014.7	4.8	-548.55341

$$^a \Delta = E(\text{corr})_{\text{B3LYP}} - E(\text{corr})_{\text{B3LYP}}^{\text{add}}$$

accordance with our earlier observation that nondynamical and dynamical correlation effect practically cancel out in aromatic compounds.¹² In view of the importance of the concept of aromaticity, we give here the G3 reaction energy for 13, which indicates the increase in the stability of benzene of -21.3 kcal/mol in good accordance with experiment deduced from the measured heats of formation (-21.6 ± 1.5 kcal/mol).⁵⁰ Similar results are obtained by using B3LYP/G3Large correlation energies. To conclude this section, one can say that the additivity of the correlation energy explains why homodesmotic chemical reactions do not depend on correlation, whereas isodesmic reaction are dependent on it.

The additivity formulas 5 and 6 are useful in predicting correlation energy in molecules, which are not included in the parametrization set. To illustrate this point, we list in Table 2 the correlation energies of styrene, fluorobenzene, 1,2-, 1,3-, and 1,4-difluorobenzene obtained by the B3LYP⁽¹⁾ method. The additivity values are in good agreement with the calculated correlation energies. Next, we turn attention to very important α -amino acids. The B3LYP correlation energies for 18 α -amino acids (cysteine and methionine are not included because they contain sulfur) are presented in Table 3. It turns out that the additivity works reasonably well, a notable exception being histidine. Delocalization within the five-membered ring and strong intramolecular bonding might be the reasons for this discrepancy. This finding is of some importance since it indicates that the additivity scheme for the correlation energy in small peptides and proteins is possible. An important molecule in this respect is acetamide, which possesses a peptide bond and conforms to the additivity rule very well (Table 2).

As an example of the utility of the additivity formula for $E(\text{corr})_{\text{G3}}^{\text{mol}}$ correlation energies, we list the estimated total G3 molecular energies for 18 α -amino acids in Table 3 obtained by adding $L_A(\text{sp}^m)$ additive constants to the HF energies $E(\text{HF}/\text{G3Large}/\text{MP2}(\text{fu})/6-31\text{G}^*)$, which in turn requires a very modest computational effort.

Finally, it should be always kept in mind that each model has its limits, which should be carefully examined and firmly established. Some molecules denoted with an asterisk in Table 2 exhibit considerable nonadditivities and were consequently

excluded from the parametrization. They usually possess a large nondynamical component of the correlation energy, which is not properly covered in B3LYP and G3 schemes. Typical examples are given by HNO_2 and N_2O , where a strong zwitterionic resonance takes place. This was discussed earlier¹⁷ and will not be repeated here. We note in passing only that HNO_2 and N_2O are electron-congested systems, where three-electron excitations play certainly an important role,³⁹ implying that these molecules deserve a special treatment, which goes beyond B3LYP and G3 methods. Deviation from additivity in neopentane at the G3 level is probably a consequence of the fact that this is the only compound in our set which contains a quaternary carbon atom linked to four carbons. It has to be pointed out, however, that the additivity can serve as a very useful tool for the correlation energy diagnostics by pinpointing systems, where nonadditivity occurs. These molecular systems should be subsequently meticulously scrutinized, which would shed more light on the special electron correlation effects leading to their better understanding. The additivity rule provides a useful reference standard, which satisfactorily describes “well-behaved” molecules. Deviations from the standard measure special correlation features.

4. Concluding Remarks

The main results obtained by the present study can be summarized as follows:

(1) The effective correlation energy $E(\text{corr})_t^{\text{B3LYP}}$ can be defined as a difference between the B3LYP total energy $E(\text{B3LYP})$ and the corresponding HF energy $E(\text{HF})$.

(2) The $E(\text{corr})_t^{\text{B3LYP}}$ exhibits the atomic additivity property similar to that found earlier for the ab initio MP2, MP3, and MP4 theoretical models as well as for the G3 computational scheme. High performance of the additivity formulas in Lewis' molecules described by a dominant single resonance structure is astounding. The calculations require knowledge of the stoichiometric formula and the canonical hybridization states in molecules, the back of an envelope, and a pencil for elementary arithmetic operations. The atomic additivity model can be refined by switching to the bond additive scheme, which is more flexible.

(3) There is a close relation between the correlation energies $E(\text{corr})_t^{\text{B3LYP}}$ and $E(\text{corr})_t^{\text{G3}}$. Their difference can be broken down into atomic contributions, which are easily retrieved from the known average atomic correlation energies in molecules.

(4) The underlying physical picture leading to the additivity of the molecular correlation energies is extremely simple. It consists of neutral atoms placed at their equilibrium positions. The influence of the chemical environment is reflected in the local polarization of the atomic cloud described by the canonical hybridization states. The nature of the neighbor(s) surrounding the particular atom and the intramolecular charge transfer are less important. This would suggest that the composite exchange–correlation holes are localized on atoms or that they behave as if they were localized. The total Fermi–Coulomb holes are highly insensitive to the finer details of the chemical bonding. It is highly desirable that the Luken–Baerends^{41–43,46,47} model description of the composite correlation holes is applied to larger molecules. It would be interesting to learn about the difference in composite correlation holes calculated in Lewis molecules and compare them with systems exhibiting highly congested electron densities involving many-electron clustering like that appearing in H_2O_2 , HNO_2 , and N_2O , which beyond doubt involve strong triple excitation (T) type of the dynamical energy as well as an appreciable portion of the nondynamical correlation

energy due to a strong zwitterionic resonance. Distribution of composite holes should explain the additivity of the correlation energy in molecules and deviations from this additivity. This is of importance for interpreting the correlation energy in general and that inherent in the DFT density methods in particular.

(5) The additivity rules can serve for diagnostic purposes by providing standards for well-behaved systems. They can pinpoint interesting nonadditive effects, which could lead to better understanding of the versatile correlation effects.

(6) As a final comment, we would like to point out that it is both surprising and gratifying that a lot of useful information about molecules can be derived from simple facts that they are composed of atoms, that atoms are held by chemical bonds, and that chemical bonding has directional character leading to well-organized structures. The knowledge of the molecular geometries is particularly helpful in understanding behavior of molecules. A number of molecular properties can be calculated on the back of an envelope by using the concept of neutral atoms and their equilibrium coordinates. Very good illustrative examples are given by diamagnetic shielding of the nuclei^{54,55} and the diamagnetic part of the temperature-independent magnetic susceptibility of molecules (Langevin term).^{56,57} They can be reduced to very simple expressions involving nuclear charges and interatomic distances because of an extremely high insensitivity of $1/r$ and r^2 operators on the electron density distributions. There is a class of molecular properties, which are completely independent of the molecular geometry, being transferable as atomic entities in a wide variety of molecules. They encompass, for instance, characteristic average atomic force constants, which summed over all atoms in a molecule give a sum of the squared frequencies of the $3N - 6$ (or $3N - 5$) normal vibrations.^{58,59} The same holds for the total molecular vibrational energies.^{60–62} It is astonishing that the molecular correlation energy in Lewis molecules, which is very difficult to describe theoretically and to compute quantitatively, belongs to this class of molecular features.

Acknowledgment. We would like to thank an anonymous reviewer for a number of very useful comments. We thank the John von Neumann Institut für Computing des Forschungszentrums, Jülich, for computing time. This work was supported partially by the Ministry of Science and Technology of Croatia (Project No. 0098058).

References and Notes

- (1) Yarkony, D. R. *Modern Electronic Structure Theory*; World Scientific: Singapore, 1995: Parts 1 and 2.
- (2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (3) GAMMES 1997, Schmidt, M. W.; Baldrige, K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M. A.; Montgomery, J. A. *J. Comput. Chem.* **1997**, *14*, 1347.
- (4) MOLPRO, Lindh, R.; Ryu, U.; Liu B. *J. Chem. Phys.* **1991**, *95*, 5889. Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053. Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 259. Werner, H.-J. *Mol. Phys.* **1996**, *89*, 645.
- (5) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.
- (6) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, A1133.

- (7) *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 1990.
- (8) *Theoretical and Computational Chemistry*; Politzer, P., Maksić Z. B., Eds.; Elsevier: Amsterdam, 1994.
- (9) Sinanoglu, O. *Adv. Chem. Phys.* **1964**, *3*, 358.
- (10) Löwdin, P. O. *Adv. Chem. Phys.* **1959**, *2*, 207.
- (11) Cremer, D. *J. Comput. Chem.* **1982**, *3*, 154; *J. Comput. Chem.* **1982**, *3*, 165.
- (12) Maksić, Z. B.; Barić, D.; Petanjek, I. *J. Phys. Chem. A* **2000**, *104*, 10873. Smith, D. M.; Barić, D.; Maksić, Z. B. *J. Chem. Phys.* **2001**, *115*, 3474.
- (13) Ruedenberg, K.; Cheung, L. M.; Elbert, S. T. *Int. J. Quantum Chem.* **1979**, *16*, 1069.
- (14) Roos, B. O. *Int. J. Quantum Chem. Symp.* **1980**, *18*, 175.
- (15) Andersson, K.; Malmquist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483.
- (16) Andersson, K.; Malmquist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.
- (17) Barić, D.; Maksić, Z. B. *J. Phys. Chem. A* **2002**, *106*, 1612. Barić D.; Maksić, Z. B.; Yáñez, M. *Mol. Phys.* **2003**, *101*, 1377.
- (18) Bytautas, L.; Ruedenberg, K. *Mol. Phys.* **2002**, *100*, 757.
- (19) Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. *Chem. Phys.* **1982**, *71*, 41; *Chem. Phys.* **1982**, *71*, 51; *Chem. Phys.* **1982**, *71*, 65.
- (20) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1998**, *108*, 154.
- (21) Rościszewski, K. *Int. J. Quantum Chem.* **1996**, *58*, 471.
- (22) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- (23) Koch, W.; Holthausen, M. C. A *Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim-New York, 2000.
- (24) *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J. W., Eds.; Springer-Verlag: Heidelberg–New York–Berlin, 1990.
- (25) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.
- (26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *337*, 785.
- (27) Colle, R.; Salvetti, O. *Theor. Chim. Acta* **1975**, *37*, 329.
- (28) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063. Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 42.
- (29) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040.
- (30) Gritsenko, O. V.; Schipper, P. R. T.; Baerends, E. J. *J. Chem. Phys.* **1997**, *107*, 5007.
- (31) Gritsenko, O. V.; Ensing, B.; Schipper, P. R. T.; Baerends, E. J. *J. Phys. Chem. A* **2000**, *104*, 8558.
- (32) Polo, V.; Kraka, E.; Cremer, D. *Mol. Phys.* **2002**, *100*, 1771.
- (33) Polo, V.; Kraka, E.; Cremer, D. *Theor. Chem. Acc.* **2002**, *107*, 291.
- (34) Polo, V.; Gräfenstein, J.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **2002**, *352*, 469.
- (35) He, Y.; Gräfenstein, J.; Kraka, E.; Cremer, D. *Mol. Phys.* **2000**, *98*, 1639.
- (36) Cremer, D. *Mol. Phys.* **2001**, *99*, 1899 and references therein.
- (37) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (38) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
- (39) Cremer, D.; He, Y. *J. Phys. Chem.* **1996**, *100*, 6173. He, Y.; Cremer, D. *Theor. Chem. Acc.* **2000**, *105*, 110. He, Y.; Cremer, D. *Mol. Phys.* **2000**, *98*, 1415.
- (40) Luken, W. L.; Beratan, D. N. *Theor. Chim. Acta* **1982**, *61*, 265.
- (41) Luken, W. L. *Int. J. Quantum Chem.* **1982**, *22*, 889.
- (42) Luken, W. L.; Culberson, J. C. *Int. J. Quantum Chem. Symp.* **1982**, *16*, 265; *Theor. Chim. Acta* **1984**, *66*, 279.
- (43) Gauss, J.; Cremer, D. *Croat. Chem. Acta* **1984**, *57*, 1289.
- (44) Luken, W. L. In *Theoretical Models of Chemical Bonding, The Concept of the Chemical Bond*; Maksić, Z. B., Ed.; Springer-Verlag: Berlin–Heidelberg–New York, 1990; Vol. 2, pp 287–320.
- (45) Gauss, J.; Cremer, D. *Adv. Quantum Chem.* **1992**, *23*, 205. Cremer, D. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III., Schreiner, P. R., Eds.; Wiley: Chichester, U.K., 1998; Vol 3., pp 1706–1735.
- (46) Baerends, E. J. *Phys. Rev. Lett.* **2001**, *87*, 133004–1.
- (47) Buijse, M. A.; Baerends, E. J. *Mol. Phys.* **2002**, *100*, 401.
- (48) Buijse, M. A.; Baerends, E. J. In *Electronic Density Functional Theory of Molecules, Clusters and Solids*; Ellis, D. E., Ed.; Kluwer Academic Publishers: Dordrecht, 1995; pp 1–46.
- (49) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.
- (50) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317; *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222; *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036.
- (51) Snyder, L. C.; Basch, H. *J. Am. Chem. Soc.* **1969**, *91*, 2189.
- (52) Snyder, L. C. *J. Chem. Phys.* **1967**, *46*, 3602.
- (53) *NIST Chemistry WebBook*, Linstrom, P. J., Mallard, W. G. Eds., NIST Standard Reference Database Number 69, National Institute of Standards and Technology: Gaithersburg, MD, 2003 (<http://webbook.nist.gov>).
- (54) Ramsey, N. F. *Am. Sci.* **1961**, *49*, 509.
- (55) Maksić, Z. B.; Supek, S. *Theor. Chim. Acta* **1988**, *74*, 275.
- (56) Maksić, Z. B.; Bloor, J. E. *Chem. Phys. Lett.* **1972**, *13*, 571.
- (57) Maksić, Z. B. *THEOCHEM* **1988**, *170*, 39.
- (58) King, W. T.; Zelano, A. J. *J. Chem. Phys.* **1967**, *47*, 3197. Gaughan, R. R.; King, W. T. *J. Chem. Phys.* **1972**, *57*, 4530.
- (59) King, W. T. *J. Chem. Phys.* **1972**, *57*, 4535.
- (60) Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1985**, *113*, 291.
- (61) Ibrahim, M. R.; Fataftah, Z. A. *Chem. Phys. Lett.* **1986**, *125*, 149.
- (62) Barić, D.; Maksić, Z. B.; Vianello, R. In press.