

Performance of Multiplicity-Based Energy Correctors for Molecules Containing Second-Row Elements

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Received: December 12, 2005; In Final Form: February 2, 2006

We introduce a posteriori multiplicity-based corrections to ab initio energies in order to reproduce experimental atomization energies. This simple approach, as compared to the alternative ones to improve density functionals and standard correlated methods, requires less computational resources than higher levels of theory. We extend our approach to include molecules containing second-row elements. Molecules are taken from the Gaussian sets for which experimental values are known with errors of less than 1 kcal/mol. We postulate that inexpensive multiplicity-based corrections can account for effects that are not accounted because of the low level of theory of the method or because of the small basis used for the calculations.

1. Introduction

In a previous work,¹ it was shown that the application of simple correction factors to the total electronic energies dramatically improved the estimation of atomization energies. For instance, for the largest first-row molecules from the G3 basis, which were not used for the fitting of the correctors, the HF/3-21G and LSDA/3-21G yielded 11.4 and 17.6 kcal/mol errors, respectively, down from their original errors of 249 and 132 kcal/mol, respectively. The improvement was actually down to 12.9 and 9.2 kcal/mol, respectively, when using the molecules used for the fitting. Undoubtedly, these are extraordinary improvements when we take into consideration that the errors for higher levels of theory without any corrections were (in kcal/mol) as follows: 15.4 for the MP4/6-311G(d,p), 8.3 for the MP4/6-311G(2df,p), 16.7 for the QC1/6-311G(d,p), 12.5 for the CCSD/cc-pVTZ, and 9.4 kcal/mol for the PW91PW91/6-31G(d,p). However, other levels of theory yielded precise energetics without corrections such as 1.5 for the G1, 2.7 for the B3PW91/cc-pVTZ, 3.6 for the CCSD(T)/cc-pVQZ, and 4.1 kcal/mol for the B3PW91/6-31G(d,p).

The Gn test sets are composed of molecules with energies experimentally precise within less than 1 kcal/mol of error (chemical accuracy), and they have been used extensively to validate the accuracy of several other methods.^{2–9} Other test sets have been published in the literature; however, they are less restrictive in the requirement of chemical accuracy, e.g., (i) the HCTH407 test set of Boese and Handy,^{10–12} which was used for the development of a new GGA functional; (ii) the test set published by Cioslowski,¹³ which contains 600 experimental enthalpies of formation; and (iii) the test set of Lynch,¹⁴ used to calibrate the contribution of the Hartree–Fock (HF) exchange operator in a gradient-corrected density functional theory (DFT) exchange functional. Thus, the development of new density theory functionals has tremendously benefited from precise experimental sets. These sets have allowed us to introduce corrections to first principles functionals much in the same way that empirical corrections are introduced to highly correlated standard ab initio methods such as done in the G1–

G3 procedures. The used of experimental sets triggered the pioneering work of Becke creating fully nonlocal functionals such as the B3PW91 by introducing an additional component to the exchange part of the functional calculated a la HF and then fitting coefficients to mix it with the exchange and correlation components of the energy functional. Although, after almost two decades since the introduction of the first nonlocal functionals, the accuracy of new functionals has not improved radically, and the accuracy for practical methods is much better than any other standard ab initio methods.

2. Methodology

We test our procedure with molecules containing elements of the second row (Na–Cl) using the following density functionals: (1) the local spin density approximation (LSDA), which was theoretically constructed to account for the spin densities of electrons and is a synonym of the S-VWN in the Gaussian 2003 program.¹⁵ It is composed of the Slater ($X\alpha$) exchange functional and the Vosko, Wilk, and Nusair correlation functional.¹⁶ (2) The nonlocal functional PW91^{17–20} corrected the LSDA functional by including a generalized gradient approximation (GGA). (3) We also tested a fully nonlocal functional, the B3PW91 functional, that included an exchange contribution calculated a la HF (commonly but perhaps imprecisely called “hybrid” and “exact exchange”) in addition to the local and nonlocal contributions to the exchange and correlation. The B3PW91 functional is defined

$$E_{\text{XC}} = A \times E_{\text{X}}^{\text{Slater}} + (1 - A) \times E_{\text{X}}^{\text{HF}} + B \times \Delta E_{\text{X}}^{\text{B88}} + E_{\text{C}}^{\text{VWN}} + C \times \Delta E_{\text{C}}^{\text{PW91}} \quad (1)$$

with the parameters A , B , and C fitted to minimize the atomization energies with respect to the G1 test set. The B88 exchange functional²¹ $E_{\text{X}}^{\text{B88}} = E_{\text{X}}^{\text{Slater}} + \Delta E_{\text{X}}^{\text{B88}}$ includes the local ($E_{\text{X}}^{\text{Slater}}$) and nonlocal ($\Delta E_{\text{X}}^{\text{B88}}$) correction contributions. The correlation functional PW91 includes the local and nonlocal contributions, $E_{\text{C}}^{\text{PW91}} = E_{\text{C}}^{\text{VWN}} + \Delta E_{\text{C}}^{\text{PW91}}$.^{17,20,22,23} Notice that small corrections to pure ab initio methods as well as to functionals are commonly accepted and still these functionals

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TABLE 1: Experimental Values of Atomization Energies ($\sum D_0^{\text{experimental}}$) for Second-Row Molecules^a

molecule	$\sum D_0^{\text{experimental}}$ (kcal/mol)	molecule	$\sum D_0^{\text{experimental}}$ (kcal/mol)
SiH	68.7	SH ₂	173.2
SiH ₂ (¹ A ₁)	144.4	PO	141.8
SiH ₂ (³ B ₁)	123.4	CIO	63.3
SiH ₃	214.0	Si ₂ H ₆	500.1
SiH ₄	302.8	CH ₃ SH	445.1
PH ₂	144.7	CH ₃ Cl	371.0
PH ₃	227.4	SO ₂	254.0
SH	81.7		

^a From ref 41.

can be considered ab initio. For instance, the G1, G2, and G3 methods also contain a small component of empirical information; nevertheless, they are considered ab initio. A related circumstance can be found in other approximations such as CCSDT, MP5SDTQ, CISD, etc. whereby their expansion series have been truncated with the goal to obtain practical results or when the exact functional expansions are truncated in order to have a workable version such as the PW91 functionals. Strictly speaking, only a full-CI with infinite or no basis set (since the basis sets are also empirically determined) would fit a strict definition of ab initio. In practice, several other wave-based and DFT methods are considered ab initio.

The use of fitting parameters is commonly used to create new functionals; however, an alternative approach to simply correct the calculated energies, without attempting to redesign or modify the functionals, is less common but very important to quickly calculate large systems. In the former case, the parameters actually modify the energy functionals from either theoretical or experimental feedback, whereas in the latter case, the parameters correct the energies found using the original procedures. We follow the latter, noninvasive methodology for our energy corrections. This approach consists of choosing contributions to the total energy thought to be the cause of errors; then, coefficients or weights, which we call correctors, are assigned to them. These correctors are found by minimizing the deviations with respect to precise theoretical or experimental values.

Similar work has already been performed using correctors; for instance, Duan²⁴ used this methodology to correct for the electron correlation energy missing in the HF method. Adding weighted descriptors to the HF energy, the weighting values were found by fitting to the experimental values of heat of formation energy using a linear regression; instead, we choose to fit to the dissociation energy by using a Newton minimization scheme. More sophisticated minimization methods have also been tried; Wang²⁵ has used a neural network-based scheme to find the weighting coefficients. The population of electrons obtained from natural bond orbital theory^{26–30} has also been used as physical descriptors, proving to be especially suited for the estimation of reaction barrier energies.^{31,32}

Our target quantity to fit is the total atomization energy ($\sum D_0$) of a molecule, which is the energy required to dissociate a molecule into its atoms; it is computed from

$$\sum D_0 = \left(\sum_{i=\text{atoms}} E_i \right) - (E_{\text{molecule}} + E_{ZPE}) \quad (2)$$

E_{molecule} and E_i are the total electronic energy of the molecule and atoms, respectively. To compare $\sum D_0$ to experimental values, the zero-point vibrational energy (E_{ZPE}) is accounted.

We choose E , E_{ZPE} , and the electron-spin multiplicity (M) as the target quantities. We correct E and E_{ZPE} with multiplicative

factors (ϵ_E and ϵ_{ZPE}) and an additive but multiplicity-related correction factor, $\Delta E_{\text{multiplicity}}$. The resulting corrected total electronic energy is expressed as

$$E^{\text{corrected}} = \epsilon_E E + 0.985 \times E_{ZPE} + \Delta E_{\text{multiplicity}} \quad (3)$$

for the molecules and as

$$E^{\text{corrected}} = \epsilon_E E + \Delta E_{\text{multiplicity}} \quad (4)$$

for atoms.

Then, an explicit expression for the corrected total atomization energy, $\sum D_0^{\text{corrected}}$, is given by

$$\sum D_0^{\text{corrected}} = \left(\sum_{i=\text{atoms}} [\epsilon_E E + \Delta E_{\text{multiplicity}}]^i \right) - (\epsilon_E E + 0.985 \times E_{ZPE} + \Delta E_{\text{multiplicity}})^{\text{molecule}} \quad (5)$$

The total electronic energy (E) for each molecule of the training set is calculated using different levels of theory, and basis sets are reported in Table 2. The zero-point electronic energy is calculated at the HF/6-31G(d,p) level for all of the non-DFT methods in Table 3; for the density functional methods (B3PW91 and LSDA), it is calculated using their corresponding levels of theory. We wanted to emphasize multiplicity-based corrections and corrections to the total electronic energy; therefore, we fixed the correction to the zero-point electronic energy to a value calculated in our previous work,¹ 0.985, which has also been found elsewhere.³³

The additive correctors, $\Delta E_{\text{multiplicity}}$, ΔE_4 , ΔE_3 , ΔE_2 , and ΔE_1 , and the multiplicative corrector, ϵ_E , are optimized to minimize the mean average deviation (MAD) of the calculated energy with respect to the experimental values

$$\text{MAD} = \left(\sum_{i=1}^N |D_{0,i}^{\text{corrected}} - D_{0,i}^{\text{experimental}}| \right) / N \quad (6)$$

and the results are shown in Table 3. To corroborate the portability of the correctors, we created a validation set composed of 18 molecules, which are not included in the training set. We chose the largest molecules, which contained second-row elements from the G2-2 set,³⁴ and they are shown in Table 5. Then, we calculated their corrected atomization energy using eq 5 and the correctors previously obtained with the training set. These atomization energy errors, with and without applying our corrector factors, are reported in Table 5. The experimental atomization energies for the molecules of the training set (Table 1) were obtained based on the enthalpy of formation,³⁴ as suggested by Curtiss.³³

3. Effect of the Correctors

Table 4 shows the effect of the correctors on the accuracy of atomization energy estimations. The index used for comparison corresponds to the average of the atomization energy errors for all of the molecules belonging to a set. For the training set, the tremendous improvement in the case of the inexpensive LSDA method, from an error of 33.1 down to 3.3 kcal/mol, should be noticed. Moreover, the errors also decrease tremendously for the validation set, from 68.3 to 19.5 kcal/mol when using the small 3-21G basis set and, even better, from 100.7 to 15.4 kcal/mol when using the 6-31G(d,p) basis set. We point out again the strong change, 75% of the LSDA electronic energy, that our correctors suggest and how that change is perfectly

TABLE 2: Total Electronic Energies, E , in Hartrees for 15 Chosen Second-Row Molecules Calculated for Different Methods and Basis Sets^a

molecules	M1 ^b	M2 ^b	M3 ^b	M4 ^b	M5 ^b	M6	M7	M8	M9	M10	M11	M12
H(² S)	-0.50000 ^c	-0.49981 ^c	-0.49981 ^c	-0.49981 ^c	-0.49981 ^c	-0.50218	-0.50398	-0.49086	-0.49394	-0.50027	-0.49743	-0.49891
O(³ P)	-74.98204 ^c	-74.93333 ^c	-74.93724 ^c	-74.96478 ^c	-74.93402 ^c	-75.03133	-75.06125	-74.24571	-74.64334	-75.06061	-74.97378	-75.02652
C(³ P)	-37.78464 ^c	-37.76430 ^c	-37.76520 ^c	-37.77483 ^c	-37.76669 ^c	-37.82569	-37.83683	-37.36339	-37.56616	-37.84628	-37.78287	-37.81567
Na(² S)	-161.84618	-161.84593	-161.84599	-161.84593	-161.84593	-162.23494	-162.25207	-160.63343	-161.63801	-162.27988	-162.14876	-162.24018
Mg(¹ S)	-199.64613	-199.63811	-199.63818	-199.63815	-199.63988	-200.02477	-200.04283	-198.20434	-199.34909	-200.07936	-199.93018	-200.03437
Al(² P)	-241.93167	-241.91534	-241.91556	-241.92323	-241.91723	-242.31346	-242.33456	-240.22597	-241.54868	-242.36823	-242.20792	-242.32501
Si(³ P)	-288.93378	-288.90778	-288.90806	-288.92544	-288.90932	-289.31886	-289.34296	-286.96132	-288.46373	-289.37173	-289.20201	-289.33263
P(⁴ S)	-340.81800	-340.78371	-340.78541	-340.80915	-340.78415	-341.20909	-341.23604	-338.55589	-340.26415	-341.25808	-341.08018	-341.22475
S(³ P)	-397.65493	-397.59889	-397.60028	-397.64001	-397.59976	-398.05150	-398.08453	-395.07752	-397.01793	-398.10500	-397.91037	-398.07017
Cl(² P)	-459.67670	-459.60263	-459.60377	-459.65629	-459.60329	-460.08092	-460.11849	-456.77226	-458.96200	-460.13626	-459.92710	-460.10264
SiH(² Π)	-289.55074	-289.51556	-289.51618	-289.53497	-289.51824	-289.93543	-289.96201	-287.57337	-289.08602	-289.98980	-289.81309	-289.94609
SiH ₂ (¹ A ₁)	-290.17920	-290.13616	-290.13685	-290.15707	-290.13918	-290.56031	-290.58815	-288.19521	-289.71866	-290.61527	-290.43216	-290.56751
SiH ₂ (³ B ₁)	-290.14181	-290.10850	-290.10890	-290.12672	-290.11053	-290.53586	-290.56272	-288.16963	-289.68828	-290.58379	-290.40758	-290.54273
SiH ₃ (² A ₁)	-290.79362	-290.75283	-290.75327	-290.77257	-290.75483	-291.18499	-291.21315	-288.81639	-290.34282	-291.23578	-291.05004	-291.18760
SiH ₄ (¹ A ₁)	-291.44871	-291.40132	-291.40156	-291.42197	-291.40326	-291.83558	-291.86430	-289.46575	-290.99907	-291.88802	-291.69358	-291.83359
PH ₂ (² B ₁)	-342.06030	-342.00841	-342.00958	-342.03856	-342.01037	-342.45667	-342.48929	-339.79370	-341.52905	-342.50769	-342.31870	-342.46783
PH ₃ (¹ A ₁)	-342.69991	-342.64129	-342.64209	-342.67275	-342.64309	-343.09452	-343.12826	-340.43151	-342.17742	-343.14507	-342.95168	-343.10300
SH(³ Π)	-398.29138	-398.22656	-398.22774	-398.27032	-398.22786	-398.69046	-398.72684	-395.71179	-397.67074	-398.74328	-398.54603	-398.70796
SH ₂ (¹ A ₁)	-398.94250	-398.87085	-398.87201	-398.91564	-398.87199	-399.34052	-399.37935	-396.35950	-398.33437	-399.39163	-399.19245	-399.35638
PO(² Π)	-416.02406	-415.90870	-415.91893	-415.98891	-415.90273	-416.44664	-416.51560	-413.03884	-415.18556	-416.53057	-416.28321	-416.48192
CIO(² Π)	-534.75744	-534.60075	-534.61019	-534.70607	-534.60565	-535.20870	-535.28318	-531.14466	-533.76279	-535.29223	-535.01964	-535.24830
Si ₂ H ₆ (¹ A _{1g})	-581.71606	-581.62362	-581.62443	-581.66894	-581.62695	-582.48879	-582.54389	-577.77021	-580.82597	-582.58928	-582.22066	-582.49628
CH ₃ SH(¹ A ₁)	-438.18963	-438.07705	-438.07899	-438.14328	-438.07849	-438.64083	-438.68929	-435.24265	-437.42640	-438.70566	-438.44874	-438.64967
CH ₃ Cl(¹ A ₁)	-499.58838	-499.46324	-499.46575	-499.54188	-499.46424	-500.04498	-500.09539	-496.31466	-498.73343	-500.11255	-499.84453	-500.05916
SO ₂ (¹ A ₁)	-548.01908	-547.80776	-547.82199	-547.96432	-547.79306	-548.47874	-548.59331	-543.95336	-546.81380	-548.58746	-548.27162	-548.53754

^a M1 = G1, M2 = MP4/6-311G(d,p), M3 = MP4/6-311+G(d,p), M4 = MP4/6-311G(2df,p), M5 = QCI/6-311G(d,p), M6 = B3PW91/6-31G(d,p), M7 = B3PW91/cc-pVTZ, M8 = LSDA/3-21G, M9 = LSDA/6-31G(d,p), M10 = B3LYP/6-31G(d,p), M11 = PBEPBE/6-31G(d,p), and M12 = PW91PW91/6-31G(d,p). ^b Calculated using data from ref 41. ^c Calculated using data from ref 42.

TABLE 3: Values of the Additive (ΔE_4 , ΔE_3 , ΔE_2 , and ΔE_1) and the Multiplicative (ϵ_E) Correctors that Minimize the Average Error of the Atomization Energies for the Set of 15 Second-Row Molecules Shown in Table 2

method/basis set	kcal/mol				ϵ_E
	ΔE_4	ΔE_3	ΔE_2	ΔE_1	
G1	-0.3	-0.1	-2.8	-1.4	1.026
MP4/6-311G(d,p)	6.7	1.1	-5.1	-5.6	1.087
MP4/6-311+G(d,p)	6.5	2.6	-3.5	-5.1	1.064
MP4/6-311G(2df,p)	6.3	4.1	1.8	2.3	1.003
QCI/6-311G(d,p)	8.9	3.1	-5.6	-4.4	1.088
B3PW91/6-31G(d,p)	10.7	9.1	1.2	0.7	0.962
B3PW91/cc-pVTZ	6.6	8.3	2.1	-1.5	0.954
LSDA/3-21G	21.8	21.3	10.9	2.3	0.747
LSDA/6-31G(d,p)	9.8	10.2	12.2	10.6	0.761
B3LYP/6-31G(d,p)	3.6	4.6	-2.2	-2.6	1.001
PBEPBE/6-31G(d,p)	16.3	13.0	9.8	2.6	0.854
PW91PW91/6-31G(d,p)	12.5	12.4	8.9	5.3	0.869

TABLE 4: Average Error of the Atomization Energies (kcal/mol), as Compared to the Experimental Values Reported in Table 1, after (A) and before (B) Using the Correctors Reported in Table 3^a

method/basis set	errors B	errors A
G1	2.1 ^b	1.3
MP4/6-311G(d,p)	16.0 ^b	3.6
MP4/6-311+G(d,p)	15.4 ^b	3.3
MP4/6-311G(2df,p)	9.2 ^b	1.4
QCI/6-311G(d,p)	16.7 ^b	4.4
B3PW91/6-31G(d,p)	5.0	2.6
B3PW91/cc-pVTZ	3.6	1.8
LSDA/3-21G	17.4	4.6
LSDA/6-31G(d,p)	33.1	3.3
B3LYP/6-31G(d,p)	4.2	2.7
PBEPBE/6-31G(d,p)	4.0	2.8
PW91PW91/6-31G(d,p)	3.7	2.2

^a The chosen set of molecules is shown in Table 2. All values are in kcal/mol. ^b Calculated using data from ref 41.

compensated by the application of the $\Delta E_{\text{multiplicity}}$ additive correctors to end up in acceptable values of corrected energies.

Perhaps the most interesting result aside from the effect of the correctors is the extraordinary precision of the DFT methods when compared to the highly correlated standard ab initio ones. Before the corrections, the very expensive G1 method, which includes several contributions from methods scaling as $O(N^7)$, yields an average error of 2.1 kcal/mol, and this is followed by the much less expensive B3PW91/cc-pVTZ with an error of only 3.6 kcal/mol, which is much better than the pure ab initio MP4 and QCI methods. After the corrections, all methods chosen for this work seem to work perfectly well. Among them, the MP4/6-311G(2df,p) and B3PW91/cc-pVTZ deserve special attention because their errors of 1.4 and 1.8 kcal/mol, respectively, are already within the chemical accuracy range.

The fact that we can accomplish such an improvement using simple correctors obtained by fitting to a modest 15 element set gives us again an insight on the advantage of using multiplicity-related physical descriptors for energy corrections or, furthermore, in the design of new density functionals. Polarization functions allow for an asymmetric distribution of the electron density and consequently yield higher density gradients. Then, any local functional that neglects the density gradient (and higher derivatives) performs worse if polarization functions are used as it is observed in the noncorrected calculations: The local LSDA performs better when combined with the smaller 3-21G basis set rather than when using the larger and qualitatively better 6-31G(d,p). The LSDA/3-21G yields an error of 68.3 kcal/mol; however, the LSDA/6-31G(d,p) yields an error of 100.7 kcal/mol.

Conversely, the corrected LSDA/6-31G(d,p) yields an average error smaller than the corrected LSDA/3-21G, 15.39 and 19.48 kcal/mol, respectively. This prompts us to state that the corrective power of a multiplicity-based approach is strengthened when dealing with a more asymmetric electron density, thus improving the fully nonlocal corrections. Therefore, a multiplicity-based correction to a local functional does not perform well when dealing with symmetric electron densities where the local features are predominant. This is shown in Table 5; the only four cases when the corrected LSDA estimations are worse than the noncorrected calculations correspond to AlCl_3 , SiF_4 , SiCl_4 , and PF_3 , which are highly symmetric nonpolar molecules except for PF_3 (0.9 D) but all with polar bonds (electronegativity differences of 1.5, 2.2, 1.2, and 1.9, respectively). However, when dealing with a nonpolar molecule with polar bonds, C_2Cl_4 , the correctors provide an improved estimation. Upon the introduction of polarization functions, the corrected LSDA method lowered the energy error for all molecules contained in the validation set. We point out some drastic improvements for individual cases such as CH_3SCH_3 , from 117.6 to 0.01 kcal/mol, and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$, from 153.7 to 0.03 kcal/mol, for $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$, when using the 6-31G(d,p) basis set.

We propose the concept that correction based on multiplicity is more suitable than based on density gradient for the estimation of atomization energies. Therefore, upon the use of the same small basis set such as 3-21G, the corrected LSDA should yield better accuracy than any of the other methods. In other words, we propose that correction based on multiplicity should better account for the nonlocal effects. Conversely, more elaborated functionals such as the PW91PW91 should yield a much lower atomization energy error than the LSDA, since the former already accounted for nonlocal effects. Comparing the LSDA with the PW91PW91 (PW91) before (B) and after (A) the corrections, we get the errors following this trend: $\text{PW91/6-31G}^{**}_A < \text{LSDA/6-31G}^{**}_A < \text{PW91/6-31G}^{**}_B \ll \text{LSDA/3-21G} < \text{LSDA/6-31G}^{**}_B$ or $11.2 < 15.4 < 18.0 \ll 68.3 \ll 100.7$ kcal/mol, respectively.

Also notice that the LSDA correctors (Table 3) using the 6-31G(d,p) basis set are practically constant: ~ 10 kcal/mol except for the doublet corrector that goes to 12 kcal/mol. None of the other methods shows such a constancy of the multiplicity correctors. This is in good agreement with important work showing that a linear correction of the local energies was needed to compensate for the size of the molecules.^{4,5,35,36}

Although results in Table 4 show room for improvement, a slight increase of the error, ~ 2 kcal/mol, for the B3PW91³⁷ indicates that this functional already accounts for most of the errors that we try to correct. Becke used a basis set-free numerical procedure³⁸ to fit the B3PW91 functional, getting a MAD of 2.4 kcal/mol for all of the 56 atomization energies of the G2 set,³⁷ whereas the B3PW91/6-31+G(3df,2p) yielded a MAD of 2.59 kcal/mol³⁹ for the 55 atomization energies of the G2 set (excluding H_2). The MAD between the basis set-free B3PW91 and the B3PW91/6-31+G(3df,2p) for the 55 molecules of the G2 set was 0.93 kcal/mol.⁷ A comparison of these results with the average results from the previous¹ and present work is shown Table 6.

Notice the systematic improvement of energies as the basis set is improved from the smallest 6-31(d,p) to the free basis case, i.e., 4.4, 3.0, 2.6, and 2.4 kcal/mol as the basis set improves. The corrected cases go beyond any further improvement that can be obtained increasing the basis set. We attribute much of the success of the B3PW91 functional to its fully

TABLE 5: Validation Table^a

molecule	B3PW91/ cc-pVTZ		B3PW91/ 6-31G(d,p)		LSDA/ 3-21G		LSDA/ 6-31G(d,p)		B3LYP/ 6-31G(d,p)		PBEPBE/ 6-31G(d,p)		PW91PW91/ 6-31G(d,p)	
	B	A	B	A	B	A	B	A	B	A	B	A	B	A
AlCl ₃	8.3	12.0	13.5	20.6	9.0	29.2	34.4	8.8	20.0	25.8	6.9	13.9	5.2	14.3
SiF ₄	27.2	33.9	28.6	36.1	24.7	63.6	86.1	23.0	24.4	25.2	4.6	37.7	0.3	31.9
SiCl ₄	13.7	12.4	24.7	25.1	7.5	39.6	51.9	3.7	34.5	35.6	11.1	15.7	9.5	15.7
CINO	2.4	12.1	1.0	12.1	48.2	39.6	79.5	36.3	0.7	8.2	32.4	36.4	32.0	31.4
PF ₃	14.5	15.9	21.8	21.2	20.6	24.3	76.0	6.7	17.8	17.6	3.1	7.1	6.2	8.3
ClF ₃	1.7	2.5	9.9	10.1	44.3	43.0	94.4	80.1	10.9	16.9	28.9	43.1	30.7	40.6
C ₂ Cl ₄	0.5	4.8	4.6	0.2	75.9	22.9	124.9	42.1	20.1	16.4	28.7	19.2	28.8	19.2
CH ₂ Cl ₂	1.6	0.0	1.5	2.1	48.3	5.6	68.5	12.4	6.4	7.3	11.2	5.5	12.1	5.0
CHCl ₃	3.3	0.5	5.6	5.1	48.2	12.2	77.6	25.6	14.0	15.0	13.2	11.0	13.8	9.9
CH ₃ SiH ₃	6.4	3.6	3.2	1.9	59.9	7.3	73.3	10.5	1.1	1.1	1.1	9.6	1.8	7.1
CH ₃ SCH ₂	1.5	8.2	3.9	11.7	84.7	11.5	108.0	2.4	2.7	6.2	20.1	2.4	21.0	4.8
(CH ₃) ₂ SO	10.3	1.0	13.9	2.6	82.6	5.2	141.5	7.4	17.9	8.3	13.0	4.5	15.5	0.1
CH ₃ CH ₂ SH	3.0	1.6	1.1	6.0	97.8	6.7	116.9	0.9	1.7	3.1	14.5	3.8	16.6	0.1
CH ₃ SCH ₃	2.1	2.5	2.3	7.3	98.4	7.4	117.6	0.0	0.6	4.3	15.9	2.3	18.1	1.4
CH ₃ CH ₂ Cl	1.2	1.6	3.6	2.2	94.9	2.6	106.7	0.4	0.1	0.2	16.6	3.7	18.4	0.9
CH ₃ COCl	0.6	5.2	2.2	8.3	104.1	14.8	129.2	7.9	3.0	5.9	29.7	4.2	30.9	7.6
CH ₃ CH ₂ CH ₂ Cl	1.6	2.7	5.8	4.8	139.8	5.2	153.7	0.0	0.5	1.4	24.5	6.9	27.1	1.4
C ₄ H ₄ S	2.5	10.3	2.4	15.5	140.4	1.0	173.4	8.5	11.0	7.5	35.3	7.9	36.2	1.4
Average	5.7	7.3	8.3	10.7	68.3	19.5	100.7	15.4	10.4	11.4	17.3	13.1	18.0	11.2

^a Atomization energy errors (in kcal/mol) after (A) and before (w/o) using the energy correctors (ΔE_4 , ΔE_3 , ΔE_2 , ΔE_1 , and ϵ_E) shown in Table 3. The 18 molecules containing first- and second-row elements were chosen from the G2-2 set of molecules,³⁴ given preference to the larger ones. All of the molecular systems are closed shell ($M = 1$).

TABLE 6: Comparisons of Results Obtained with Different Basis Sets and Those Using the Correctors Obtained in This and Previous Work for the B3PW91 Functional^a

basis used with the B3PW91 functional	MAD (kcal/mol)	basis used with the B3PW91 functional	MAD (kcal/mol)
free ³⁷	2.4	6-31G(d,p)	4.4
6-31+G(3df,2p) ³⁹	2.6	cc-pVTZ (corrected)	1.4
cc-pVTZ	3.0	6-31G(d,p) (corrected)	2.3

^a Previous work¹ contributed with 32 atomization energies and the present work with 15 for the MAD. The two cases corrected by the multiplicity correctors are also shown.

nonlocal character of the exchange a la HF, the use of the nonlocal corrections ΔE_X^{B88} and ΔE_C^{PW91} , and indirectly to the spin-density gradients, $\nabla\rho_\alpha(\vec{r})$ and $\nabla\rho_\beta(\vec{r})$. The fact that we are able to modify the B3PW91 energies, eqs 3 and 4, scaling it by the $\epsilon_E \sim 0.96$ factor, and then compensate them with multiplicity-related additive correctors ($\Delta E_{\text{multiplicity}}$) to get energies within ~ 2 kcal/mol of the B3PW91 errors gives us confidence about the physical validity of the correctors.

The atomization energy errors can be ordered as B3PW91/6-31G**_B < PW91/6-31G**_A < LSDA/6-31G**_A < PW91/6-31G**_B < LSDA/3-21G < LSDA/6-31G**_B or 8.3 < 11.2 < 15.4 < 18.0 < 68.3 < 100.7 kcal/mol, respectively.

For verification purposes, we calculate, using the same basis set, the energy errors using another fully nonlocal hybrid functional such as the B3LYP^{21,40} and another nonlocal functional such as the PBEPBE. These calculations yielded errors similar to the ones obtained using the fully nonlocal hybrid B3PW91 and the nonlocal PBEPBE,¹⁸ respectively. This verification reassures the following tendency for the energy errors: fully nonlocal \leq multiplicity-corrected < nonlocal \ll local.

4. Conclusions

As also found with the first-row atoms, the DFT methods show an extraordinary precision when compared to the standard ab initio methods. The corrector improvements suggest that most of the ab initio methods, standard and DFT, do not equally treat the spin of the molecules and atoms. Interestingly, the LSDA

with a moderate basis set is the only one that equally treats the different multiplicities.

By including explicitly the electron-spin multiplicity as a physical descriptor, we add flexibility to better account for the complete nonlocal role of the spin in the calculation of molecular energies. The inclusion of spin or multiplicity correctors allows us to get better precision that cannot be obtained with present functionals no matter what basis sets are used.

Acknowledgment. We highly appreciate the support of ARO (DURINT and DURIP grants), DOE, and DARPA/ONR.

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