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Accurate Calculation of the Heats of Formation for Large Main Group Compounds with Spin-Component Scaled MP2 Methods

Stefan Grimme*

Theoretische Organische Chemie, Organisch-Chemisches Institut der Universität Münster,
Corrensstraβe 40, D-48149 Münster, Germany

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Three MP2-type electron correlation treatments and standard density functional theory (DFT) approaches are used to predict the heats of formation for a wide variety of different molecules. The SCF and MP2 calculations are performed efficiently using the resolution-of-the-identity (RI) approximation such that large basis set (i.e., polarized valence quadruple-ζ quality) treatments become routinely possible for systems with 50−100 atoms. An atom equivalent scheme that corrects the calculated atomic energies is applied to extract the "real" accuracy of the methods for chemically relevant problems. It is found that the spin-component-scaled MP2 method (SCS-MP2, *J. Chem. Phys,* **2003**, *118*, 9095) performs best and provides chemical accuracy (MAD of 1.18 kcal/mol) for a G2/97 test set of molecules. The computationally more economical SOS-MP2 variant, which retains only the opposite-spin part of the correlation energy, is slightly less accurate (MAD of 1.36 kcal/mol) than SCS-MP2. Both spin-component-scaled MP2 treatments perform significantly better than standard MP2 (MAD of 1.77 kcal/mol) and DFT-B3LYP (MAD of 2.12 kcal/mol). These conclusions are supported by results obtained for a second test set of complex systems containing 70 molecules, including charged, strained, polyhalogenated, hypervalent, and large unsaturated species (e.g. C_{60}). For this set, DFT-B3LYP performs badly (MAD of 8.6 kcal/mol) with many errors >10−20 kcal/mol while the spin-component-scaled MP2 methods are still very accurate (MAD of 2.8 and 3.7 kcal/mol, respectively). DFT-B3LYP shows an obvious tendency to underestimate molecular stability as the system size increases. Out of six density functionals tested, the hybrid functional PBE0 performs best. All in all, the SCS-MP2 method, together with large AO basis sets, clearly outperforms current DFT approaches and seems to be the most accurate quantum chemical model that routinely can predict the thermodynamic properties of large main group compounds.

1. Introduction

There has been considerable interest and progress in the development of reliable quantum chemical methods for prediction of thermochemical data of molecules.[1,2] The extent to which modern high-level calculations can be competitive with experiment in the precise determination of, e.g., heats of formation (ΔH_f^0), strongly depends on the size of the molecular species in question. For three to four atomic systems with up to about 20 electrons, there is little question that ab initio theory can provide very accurate energetic data (errors <1 kJ/mol).[3] For larger systems up to about 10 nonhydrogen atoms, wave function approaches, such as the G*n* ($n = 1-3$)[4−6] family of model chemistries, on the average still reach the so-called chemical accuracy of about 1 kcal/mol. However, these and even more accurate approaches[7,8] are based on coupled-cluster-type treatments [CCSD(T) or QCISD(T)] that have an unfavorable scaling behavior with system size such that the extension to systems of more practical relevance seems difficult.

Prior to the advent of density functional theory (DFT),[9,10] second-order Møller−Plesset perturbation theory (MP2)[11,12] was the simplest and least expensive way of incorporating the energetically important electron correlation effects in ab initio electronic structure calculations. It still has certain advantages over DFT, for example, when dispersion forces or charge-transfer processes are important. On the other hand, MP2 is generally considered as less accurate compared to the best density functionals available (e.g., B3LYP,[13,14] for recent DFT computations of ΔH_f^0, see, e.g.,[15−20]) and, furthermore, not as robust when applied to complicated correlation problems occurring in, e.g., biradicals, transition states, or metal-containing compounds. There are, however, indications[16,17,20] that density functionals such as B3LYP do not perform as well for large systems as usually thought because they systematically underestimate the stability of molecules as their size increases.

Recently, it has been shown that a simple and logical correction to the MP2 scheme leads to significant improvements in cases where MP2 underperforms.[21] The correction is based on a different scaling of the same-spin (E_{SS}) and opposite-spin (E_{OS}) electron pair contributions to the correlation energy,

$$E_c = p_{OS}E_{OS}^{MP2} + p_{SS}E_{SS}^{MP2} \qquad (1)$$

where p_{OS} and p_{SS} are scaling factors of 6/5 and 1/3, respectively. This spin-component-scaled MP2 approach (SCS-MP2) differs from MP2 where both components contribute equally (i.e. $p_{OS} = p_{SS} = 1$). It was shown that this simple correction gives performances in reaction energies comparable to the QCISD(T) method.[21] This success is easily traced to the manner in which the dynamic (opposite-spin) and static (same-spin) correlation effects are handled. In the Hartree−Fock method (that actually is the first-order term of the MP series), the same-spin electron pairs are correlated (Fermi holes), while the

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* Author to whom correspondence should be addressed. E-mail: grimmes@uni-muenster.de.

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opposite-spin pairs remain uncorrelated. Low (second) order perturbation theory cannot fully correct for this unbalanced description. Hence, the non-HF-correlated pair contribution must be scaled up while the HF-correlated contribution must be scaled down.

Probably inspired by the remarkable improvement of SCS-MP2 over MP2 for various chemical problems,[22−27] Jung et al.[28] developed the SCS approach further. These authors completely neglect the same-spin contribution ($p_{SS} = 0$ and $p_{OS} = 1.3$), which leads (within some reasonable approximations) to a correlation method that computationally scales only with the fourth power on the size of the system. The accuracy of this method, that was termed SOS-MP2, is only slightly less than that of SCS-MP2 but (although much more efficient for large systems) still superior to standard MP2.[28]

The major aim of this paper is to test the newly developed MP2 methods for the prediction of thermodynamic properties of molecules against standard MP2 as well as the most popular (and probably most reliable) DFT-B3LYP method. For that purpose, a simple and well-defined standard protocol including large basis sets (polarized valence quadruple-ζ quality, QZV3P) and basis set extrapolation for the calculation of ΔH_f^0 (298) is developed. It ensures that basis set incompleteness effects are marginal so that the inherent performance of the underlying theoretical model can be extracted. The well-established G97/2 test set of molecules and a second set consisting of many larger and chemically relevant species are used to assess the performance of the methods.

The calculation of ΔH_f^0 is usually based on theoretical atomization enthalpies and subtracting the experimental atomization enthalpies of the elements in their standard states (see below). This implies that the theoretical reference point of energy are the isolated atoms which lead to serious computational problems. Accurate calculation of atomization energies (error <0.5 kcal/mol per atom) requires highly correlated treatments close to the basis set limit, inclusion of effects from (chemically not very relevant) core electrons, and consideration of relativistic corrections. However, atomization is of little relevance in chemistry where mostly *molecules near equilibrium* of different structure or composition are compared. In statistical assessments of quantum chemical methods, this standard procedure leads to a bias in favor of methods that energetically place the free atoms right with respect to the molecule. This, however, does not tell a lot about the chemically more important description of molecules relative to each other. Thus, in this work, the different strategy of atom equivalents is used (see below) that places the theoretical zero of energy close to commonly found chemical structures but retains all physically relevant parts that are needed to calculate ΔH_f^0.

After an outline of the theoretical procedure in section 2, the test sets of molecules are described (section 3). Section 4 contains a separate presentation, statistical analyses, and discussion of the results for the two sets. In some cases, the accurate theoretical data strongly indicate experimental errors, and these are cases discussed in more detail.

2. Theoretical Methods

The theoretical procedure to calculate ΔH_f^0 (298) consists of the following steps: (1) The molecular geometry is optimized at the B3LYP/TZV2P[29,30] level. Although this is not prerequisite and geometries from other sources can be used as well, it seems a very convenient way to obtain relatively accurate structures. They are used is all subsequent steps. Harmonic vibrational frequencies are also calculated at the B3LYP/TZV2P level and scaled by a factor of 0.97 similar to what has recently been recommended[31] to calculate the zero-point vibrational energy (ZPVE) and thermal corrections to the enthalpy.

(2) Single-point energy calculations employing two different AO basis sets are performed at the MP2-type levels. The valence electron[32] correlation energies as obtained from TZV2P[29,30] and QZV3P[29,33] treatments are used in the standard two-point extrapolation formula of Halkier et al.[34,35] to obtain an improved correlation energy E_c that is close to the basis set limit (denoted as $E_c[TQ]$). The total electronic energy is obtained by adding the SCF energy from the QZV3P calculation and a higher-level correction term *HLC* similar to that which is used in G1-3 theory,[4−6] i.e.,

$$E_e = E_{SCF}[\mathrm{QZV3P}] + E_c[TQ] + HLC \tag{2}$$

where for SCS-MP2

$$HLC = -6.3(mE_h)n_\alpha + 1.0(mE_h)n_\beta$$

and n_α and n_β are the number of correlated α and β electrons, respectively, with $n_\alpha > n_\beta$. The two coefficients have been obtained by fitting absolute SCS-MP2/cc-pVTZ to CCSD(T)/cc-pVTZ correlation energies for a subset of atoms and molecules of the G2/97 set. Note that the effect of *HLC* vanishes for reactions where the number of unpaired electrons remains the same. At the MP2 (SOS-MP2) level, the two coefficients are −5.2 (−6.8) mE_h and 0.6 (1.0) mE_h, respectively.

(3) The electronic energy at 0 K is obtained as

$$E_0 = E_e + E_{ZPVE} \tag{3}$$

where E_{ZPVE} is the zero-point vibrational energy from step 1. The energies E_0 of the molecule and its constituent atoms are used to calculate the atomization energy D_0 as

$$D_0 = \sum_{Z}^{\mathrm{atoms}} E_e'(Z) - E_0$$

where $E_e(Z)'$ is an empirically corrected electronic energy (see below) for atom Z. As outlined in detail in, e.g., ref 15, the molecular heat of formation ΔH_f^0 (0 K) is then obtained by adding the experimental heats of formation of the atoms. Our calculations are based on the values given in ref 15 and include atomic spin−orbit corrections. The enthalpies at 298 K are obtained by adding the difference H (298 K) − H (0 K) for the atoms from experiment[15] and for the molecule as obtained in step 1.

(4) The calculated atomic energies used to obtain D_0 are corrected by atom-specific empirical parameters $e(Z)$, leading to an atom equivalent (or atom additive) scheme that has been used before, e.g., in the framework of DFT,[17,20] i.e.,

$$E_e'(Z) = E_e(Z) + e(Z) \tag{4}$$

In the MP treatments, the correction parameters mainly account for neglected core−core and core−valence correlation effects that can reach about 0.5 kcal/mol per nonhydrogen atom for D_0 of first-row systems.[36] The parameters also account for nonharmonic vibrational, relativistic effects and remaining deficiencies of the theoretical treatment with respect to the differential electron correlation between the atoms and the molecule. The $e(Z)$ values have been obtained from least-squares optimizations on the G2/97′ training set (see below) and are listed for all methods in Table 1. Note that the $e(Z)$ parameters

TABLE 1: Optimized Corrections *e*(*Z*) for Atomic Ground State Energies (in kcal/mol)

atom	SCS-MP2	SOS-MP2	MP2	B3LYP
H	−1.99	−3.30	0.43	−0.29
Li	−0.10	−0.88	1.64	−0.15
Be	−7.72	−6.40	−9.65	−5.91
B	−1.34	1.97	−5.36	0.68
C	2.18	5.00	−3.22	2.16
N	1.04	1.55	0.24	−1.64
O	0.88	2.98	−2.74	0.62
F	1.59	3.37	−2.93	2.04
Na	0.55	−0.15	1.62	2.71
Mg	−6.75	−4.61	−8.28	5.12
Al	−0.78	0.89	−2.11	2.58
Si	4.15	3.90	2.54	4.01
P	5.62	5.37	5.88	1.71
S	3.42	4.66	0.66	2.51
Cl	2.55	4.16	−0.80	4.79

are model-dependent quantities that change slightly when other basis sets are used. They also do not belong to the SCS-MP2 model, which contains only two ($n_\alpha = n_\beta$ in a reaction) or four ($n_\alpha \neq n_\beta$) empirical parameters, respectively.

The entire procedure is much simpler than many other composite schemes. In addition to the process of geometry optimization and subsequent calculation of harmonic vibrational frequencies, it requires only two single-point energy calculations. To speed up these time-consuming steps for large systems, the SCF and MP2-type calculations are performed using the resolution-of-the-identity (RI) approximation[37−39] (also called "density fitting") for the two-electron integrals. The RI error for ΔH_f^0 is usually smaller than 0.01 kcal/mol per atom, and thus, completely negligible compared to AO basis incompleteness effects. The RI auxiliary basis sets were taken from refs[39−41] where they were optimized for the TZV[30] and Dunnings cc-pVXZ[42] AO basis sets, respectively. Even for large molecules, the two RI-SCF and RI-MP2 calculations are faster than the conventional generation of second derivatives, which thus, is the rate determining step of the entire treatment. The speedups due to the RI approximation are >10 and about 3−5 for RI-MP2 and RI-SCF treatments, respectively, for the larger systems with the QZV3P AO basis.

Comparative DFT calculations are carried out using the same geometries and ZPVE as that used for the MP2-type treatments. Atomic corrections *e*(*Z*) are obtained in analogous fitting procedures (a HLC correction is not applied). The large QZV3P AO basis set is used to obtain a conclusive picture about the performance also at the DFT level (although a smaller TZV-(2df,2pd) set gives very similar results). The GGA density functionals BP86[43−45] and PBE,[46] the hybrid functionals B3LYP[13,14] and PBE0,[47] and two meta GGAs (including terms of the kinetic energy density) either in pure form (TPSS[48]) or as a hybrid (TPSSh[49]) are employed. The results from B3LYP are presented in detail in direct comparison with those from the MP2 treatments. For the other density functionals, only statistical data are presented (for details, see Supporting Information) that should provide the reader an impression about the performance of DFT in general for the prediction of thermodynamic properties.

3. The Test Sets

The initial basis for the evaluation of theoretical methods is the G2/97 test set, consisting originally of 148 neutral molecules. From this set, the four radicals CN, CCH, ClO, and C_2H_3 were discarded because of large spin contamination ($\langle S^2\rangle > 0.9$). In such cases, low-order perturbation theory is not applicable. Note that this does not represent some attempt to polish the statistics in favor of the MP methods. The classification of the these molecules as outliers has a rigorous theoretical basis because the criterion ($\langle S^2\rangle$) can be obtained in advance without any reference to experiment, i.e., spin-contaminated open-shell species with $\langle S^2\rangle_{\mathrm{calc}} > \langle S^2\rangle_{\mathrm{expected}} + 0.05$ are outside the range of applicability of MP2-type theoretical models. When comparisons of the performance of different theoretical approaches (e.g., with G1-G3 or DFT) are made, however, this deficiency should be kept in mind because these methods may suffer less from the mentioned problem. Because metallic compounds are not very well represented in the G2/97 set and magnesium compounds are not included at all, it was decided to add some molecules involving the atoms Li−B and Na−Al, although we are aware that the experimental uncertainties for such molecules are larger than usual. The 12 additional species are listed in Table 2 as entries 149−160. We will refer to this modified test set in the following as G2/97′.

Although the G2/97′ test set covers a wide range of different chemical structures and bonding situations, it does not contain larger systems with more than six nonhydrogen atoms.[50] Furthermore, larger unsaturated compounds that are important in chemistry as well as charged systems are also not included. Because any empirical method that has been "trained" on a specific set of systems must be evaluated on a different set, we selected from the excellent compilation in ref 17 of 70 molecules for validation of the methods. This selection not only includes anions and cations, but also many systems with complicated structures, i.e., larger polyhalogenated, hypervalent, and strained organic systems. Larger unsaturated compounds are tested to cover the transition from insulator-like to semiconductor-type molecules. Note that, for obvious reasons, the average deviation from experiment for this set is expected to be larger than that for the G2/97′ test suite: (I) the theoretical errors for ΔH_f^0 per atom tend to accumulate in larger systems, (II) higher-order electron correlation effects that are difficult to account for increase as the number of electrons increases, and (III) the experimental data have larger errors or more often contain systematic errors resulting, e.g., from size (aggregation) effects. Furthermore, it should be mentioned that the ZPVE contribution that is calculated in the harmonic approximation becomes very large (>100 kcal/mol) for many systems in this set and, thus, even small errors for the high-energy frequencies may easily lead to errors of 5−10 kcal/mol for ΔH_f^0.

4. Results and Discussion

4.1. The G97/2′ Test Set. A comparison of calculated and experimental heats of formation for the 156 molecules in the modified G97/2′ test set is presented in Table 2. This table also includes the results of a statistical analyses of the performance for the four methods. Histograms of errors are graphically shown in Figure 1. According to these data, the SCS-MP2 model, including a HLC, is regarded as a very accurate quantum chemical model. The mean absolute deviation (MAD) is only 1.18 kcal/mol, which is close to that obtained from much more elaborate G3 computations (0.94 kcal/mol[6] for G97/2). This view is supported by a small maximum error of only 4.9 kcal/mol (for O_2 and Si_2, respectively) and that 90% (76%) of all cases have errors less than 3 (2) kcal/mol. Particularly impressive are the results for the organic molecules for which the MAD drops to about 0.9 kcal/mol. Except for the already mentioned problems with spin-contaminated open-shell species, there seem to be no systematic errors for particular compounds or bonding situations.

TABLE 2: Deviations of Calculated Heats of Formation ΔH_f^0 (298 K) (in kcal/mol) from Experiment[a] for the G2/97′ Neutral Test Set

			deviation[b]			
entry[c]	molecule	expt	SCS-MP2	SOS-MP2	MP2	B3LYP
1	H_2	0.0	−0.4	−0.6	−0.3	0.3
2	LiH	33.3	0.1	0.2	0.1	0.0
3	BeH	81.7	0.1	0.4	−0.1	2.4
4	CH	142.5	0.3	3.6	**−6.2**	3.1
5	$CH_2(^3B_1)$	93.7	0.7	0.6	0.7	3.4
6	$CH_2(^1A_1)$	102.8	−1.1	1.8	**−6.8**	1.1
7	CH_3	35.0	0.5	1.0	−0.6	3.5
8	CH_4	−17.9	−0.2	−0.2	−0.6	1.6
9	NH	85.2	−0.7	0.5	−3.0	2.1
10	NH_2	45.1	0.8	1.8	−1.3	3.3
11	NH_3	−11.0	0.3	−0.1	0.9	−0.1
12	OH	9.4	0.5	1.9	−1.8	1.7
13	H_2O	−57.8	0.7	0.1	2.4	−2.2
14	HF	−65.1	1.4	0.7	1.9	−0.8
15	$SiH_2(^1A_1)$	65.2	0.0	0.3	−2.9	2.9
16	$SiH_2(^3B_1)$	86.2	2.3	0.4	3.6	3.2
17	SiH_3	47.9	2.4	1.5	1.7	3.5
18	SiH_4	8.2	1.7	1.2	0.1	1.7
19	PH_2	33.1	2.1	2.7	0.3	**6.0**
20	PH_3	1.3	−0.4	0.1	−1.8	2.7
21	H_2S	−4.9	0.0	0.1	−0.7	0.0
22	HCl	−22.1	0.5	0.6	0.0	1.5
23	Li_2	51.6	−0.7	−0.7	−0.5	−3.9
24	LiF	−80.1	3.3	2.4	**4.5**	0.0
25	C_2H_2	54.2	0.9	2.4	−1.6	0.7
26	$H_2C{=}CH_2$	12.5	−0.9	0.1	−2.9	2.3
27	$H_3C{-}CH_3$	−20.1	0.0	0.1	−0.4	1.4
29	HCN	31.5	2.7	**4.5**	−0.2	−0.1
30	CO	−26.4	0.9	3.1	−2.2	−2.1
31	HCO	10.0	0.8	1.8	−0.4	3.3
32	$H_2C{=}O$	−26.0	0.8	1.9	−0.8	1.2
33	$CH_3{-}OH$	−48.0	0.7	0.7	1.1	−0.2
34	N_2	0.0	1.7	**4.0**	−1.9	−3.8
35	$H_2N{-}NH_2$	22.8	−0.3	−0.3	0.1	0.0
36	NO	21.6	−2.3	−0.7	**−4.3**	0.1
37	O_2	0.0	**−4.9**	**−6.7**	0.0	3.6
38	$HO{-}OH$	−32.5	−0.9	−0.6	−0.3	−2.0
39	F_2	0.0	−0.9	0.5	**−5.3**	1.4
40	CO_2	−94.0	2.4	3.0	3.1	0.4
41	Na_2	34.0	−0.2	−0.3	−0.7	**5.2**
42	Si_2	139.9	**−4.9**	**−7.3**	−3.9	−1.0
43	P_2	34.3	0.0	0.0	0.1	0.0
44	S_2	30.7	−1.6	−2.6	−0.1	3.0
45	Cl_2	0.0	−1.6	−0.5	−3.8	3.1
46	NaCl	−43.6	1.5	1.2	1.8	0.0
47	SiO	−24.6	−1.0	−2.0	−0.3	**−4.1**
48	CS	66.9	−2.2	−0.6	**−4.9**	−3.0
49	SO	1.2	−2.8	−3.8	−0.3	1.5
51	ClF	−13.2	0.0	1.1	−3.1	3.2
52	$H_3Si{-}SiH_3$	19.1	1.6	0.0	0.1	0.5
53	CH_3Cl	−19.6	0.4	0.8	−0.5	2.2
54	$H_3C{-}SH$	−5.5	−0.1	0.0	−0.7	−0.3
55	HOCl	−17.8	0.0	0.7	−0.7	1.0
56	SO_2	−71.0	−3.7	**−4.7**	−0.2	**−11.2**
57	BF_3	−271.4	0.2	0.1	0.5	−1.0
58	BCl_3	−96.3	−2.1	−1.8	0.0	0.0
59	AlF_3	−289.0	3.8	2.8	**5.4**	**−6.2**
60	$AlCl_3$	−139.7	0.1	−0.1	2.5	−1.9
61	CF_4	−223.0	1.0	−0.1	0.1	−0.7
62	CCl_4	−22.9	0.6	0.1	2.1	−3.6
63	COS	−33.1	2.1	2.3	2.9	2.0
64	CS_2	27.9	1.2	0.4	3.0	1.5
65	COF_2	−149.1	−3.5	−3.6	−3.8	−3.0
66	SiF_4	−386.0	−0.1	−3.2	0.8	**−14.5**
67	$SiCl_4$	−158.4	−1.5	**−4.3**	2.3	**−8.6**
68	N_2O	19.6	3.1	3.2	**4.5**	0.8
69	ClNO	12.4	−3.0	−1.9	−3.7	3.1
70	NF_3	−31.6	−2.5	−2.0	**−5.6**	**4.9**
71	PF_3	−229.1	−0.1	−1.0	−0.8	−3.0
72	O_3	34.1	0.5	0.1	3.6	**−6.2**
73	F_2O	5.9	−3.1	−1.5	**−7.3**	3.4

TABLE 2: (Continued)

			deviation^b			
entry^c	molecule	expt	SCS-MP2	SOS-MP2	MP2	B3LYP
74	ClF_3	−38.0	−2.1	−3.5	−1.8	**7.0**
75	C_2F_4	−157.4	2.7	2.9	−0.1	**8.2**
76	C_2Cl_4	−3.0	1.8	1.6	3.0	−0.3
77	CF_3CN	−118.4	3.3	**4.3**	0.0	−0.7
78	C_3H_4 (propyne)	44.2	1.0	2.2	−1.0	1.8
79	C_3H_4 (allene)	45.5	−1.8	−0.3	**−4.3**	**5.3**
80	C_3H_4 (cyclopropene)	66.2	−1.3	−0.5	−2.4	0.0
81	C_3H_6 (propylene)	4.8	−1.0	−0.2	−2.4	1.7
82	C_3H_6 (cyclopropane)	12.7	0.0	0.0	0.4	−0.1
83	C_3H_6 (propane)	−25.0	0.0	0.0	0.0	0.0
84	C_4H_6 (butadiene)	26.3	−2.2	−0.9	**−4.3**	2.3
85	C_4H_6 (2-butyne)	34.8	0.4	1.5	−1.1	1.8
86	C_4H_6 (methylenecyclopropane)	47.9	0.9	1.5	0.3	3.8
87	C_4H_6 (bicyclobutane)	51.9	−0.8	−1.3	0.8	−3.6
88	C_4H_6 (cyclobutene)	37.4	−1.1	−0.3	−1.9	−2.3
89	C_4H_8 (cyclobutane)	6.8	1.1	1.2	1.2	−2.4
90	C_4H_8 (isobutene)	−4.0	−1.2	−0.8	−1.8	−0.1
91	C_4H_{10} (butane)	−30.0	0.0	−0.2	0.3	−1.6
92	C_4H_{10} (isobutane)	−32.1	−0.3	−0.7	0.4	−2.8
93	C_5H_8 (spiropentane)	44.3	0.5	0.0	2.0	−1.4
94	C_6H_6 (benzene)	19.7	−0.7	−1.5	2.3	1.6
95	H_2CF_2	−107.7	1.8	1.8	0.2	2.3
96	CHF_3	−166.6	1.4	0.8	0.1	1.0
97	H_2CCl_2	−22.8	0.1	0.5	−0.6	1.2
98	$CHCl_3$	−24.7	0.0	0.1	0.2	−0.8
99	$CH_3{-}NH_2$	−5.5	0.0	0.0	0.0	0.2
100	$CH_3{-}CN$	18.0	2.0	3.7	−0.4	0.8
101	$CH_3{-}NO_2$	−17.8	0.0	−0.3	2.6	0.7
102	$CH_3{-}O{-}N{=}O$	−15.9	−3.4	−2.4	−3.3	−0.9
103	$CH_3{-}SiH_3$	−7.0	0.0	−0.9	−0.7	−0.8
104	$HCOOH$	−90.5	0.0	0.2	1.3	−0.9
105	$HCOOCH_3$	−85.0	0.6	1.1	1.2	0.1
106	CH_3CONH_2	−57.0	−1.4	−1.4	0.1	−0.6
107	$CH_2{-}NH{-}CH_2$	30.2	0.5	0.6	0.8	−0.7
108	$NC{-}CN$	73.3	**4.3**	**7.4**	−0.1	−0.2
109	$(CH_3)_2NH$	−4.4	−0.4	−0.4	−0.3	−0.3
110	$CH_3{-}CH_2{-}NH_2$	−11.3	0.8	0.7	1.3	−0.1
111	$H_2C{=}C{=}O$	−11.3	0.3	1.3	−0.4	**4.4**
112	$H_2C{-}O{-}CH_2$ (oxirane)	−12.6	1.0	1.4	1.3	−0.5
113	CH_3CHO	−39.7	−0.1	0.8	−0.9	1.0
114	$O{=}CH{-}CH{=}O$	−50.7	0.9	2.9	−1.1	0.2
115	$CH_3{-}CH_2OH$	−56.2	0.1	0.0	1.0	−1.6
116	$CH_3{-}O{-}CH_3$	−44.0	0.1	0.5	0.1	0.2
117	$CH_2{-}S{-}CH_2$ (thiirane)	19.6	1.6	1.3	2.2	−1.1
118	$CH_3{-}SO{-}CH_3$	−36.2	−3.2	**−4.2**	−0.8	**−7.0**
119	$CH_3{-}CH_2{-}SH$	−11.1	0.1	0.0	0.0	−1.5
120	$CH_3{-}S{-}CH_3$	−8.9	0.0	−0.1	−0.1	−1.1
121	$H_2C{=}CHF$	−33.2	0.3	1.1	−1.8	**4.2**
122	$CH_3{-}CH_2{-}Cl$	−26.8	0.1	0.3	−0.4	0.8
123	$H_2C{=}CH{-}Cl$	5.5	−0.6	0.3	−2.1	2.6
124	$H_2C{=}CH{-}CN$	43.2	−0.6	1.8	**−4.2**	−0.2
125	$CH_3{-}CO{-}CH_3$	−51.9	−0.6	0.0	−0.8	−0.4
126	CH_3COOH	−103.4	−0.8	−0.8	1.0	−2.2
127	CH_3COF	−105.7	−0.8	−0.6	−1.0	0.1
128	CH_3COCl	−58.0	−1.3	−0.9	−0.9	0.7
129	$CH_3CH_2CH_2{-}Cl$	−31.5	0.3	0.4	0.3	−0.5
130	$(CH_3)_2CH{-}OH$	−65.2	0.1	−0.3	1.7	−3.5
131	$C_2H_5{-}O{-}CH_3$	−51.7	0.4	0.5	0.7	−0.7
132	$(CH_3)_3N$	−5.7	−0.1	−0.3	0.6	−1.5
133	C_4H_4O (furan)	−8.3	−0.7	−1.0	1.7	−0.7
134	C_4H_4S (thiophene)	27.5	−0.4	−1.6	2.9	−3.3
135	C_4H_4NH (pyrrole)	25.9	0.0	−1.0	3.4	0.1
136	C_5H_5N (pyridine)	33.6	−0.5	−1.0	2.3	1.9
137	SH	34.2	0.9	1.9	−1.4	2.3
140	CH_3CO	−2.4	0.0	0.9	−0.8	3.6
141	H_2COH	−4.1	−0.2	−0.1	0.2	2.6
142	CH_3O	4.1	−3.5	−1.9	**−6.3**	4.0
143	CH_3CH_2O	−3.7	**−4.7**	−3.1	**−7.3**	1.9
144	CH_3S	29.8	1.1	1.9	−0.9	3.5
145	C_2H_5	28.9	−0.4	0.0	−1.4	3.8
146	$(CH_3)_2CH$	21.5	−1.5	−1.2	−2.2	2.5
147	$(CH_3)_3C$	12.3	−2.2	−2.2	−2.0	1.5

TABLE 2: (Continued)

			deviation[b]			
entry[c]	molecule	expt	SCS-MP2	SOS-MP2	MP2	B3LYP
148	NO_2	7.9	−1.8	−2.4	1.4	3.0
149	BeO	32.6	1.1	0.5	3.7	−0.3
150	BeF_2	−190.3	−0.4	−1.3	0.4	−0.6
151	AlF	−63.5	−0.7	0.0	−1.0	1.3
152	Na_2O	−8.6	2.3	0.2	**6.6**	**−6.6**
153	NaH	29.7	−3.3	−3.2	**−4.1**	−1.1
154	NaLi	43.4	0.0	0.0	−0.1	0.8
155	AlCl	−12.3	−2.4	−1.3	−2.5	2.3
156	BH_3	25.5	0.0	2.0	−1.9	3.9
157	MgO	36.0	2.3	2.7	**5.1**	−1.2
158	$MgCl_2$	−93.8	−3.3	−2.1	−2.9	3.3
159	$BeCl_2$	−86.1	−3.0	−3.0	−2.3	1.2
160	MgF_2	−173.7	0.0	0.0	1.0	0.0

	SCS-MP2	SOS-MP2	MP2	B3LYP
Mean deviation	−0.14	0.07	−0.38	0.33
Mean absolute deviation	1.18	1.36	1.74	2.12
Maximum deviation	4.9	7.4	7.3	14.5
<2 kcal/mol[d]	76%	76%	66%	58%
<3 kcal/mol[d]	90%	87%	80%	72%

[a] Experimental values are taken from the compilations in refs.[15,17] [b] Deviation = experiment-theory. Absolute deviations larger than 4 kcal/mol are indicated in bold. [c] For convenience the molecule numbering from the literature is used. The additional compounds start at entry 149. [d] Percentage of absolute deviations smaller than the specified value.

The SOS-MP2 method which completely neglects the same-spin correlation contribution is only slightly less accurate than SCS-MP2. This could be expected because already in the development of SCS-MP2 it was found that the contribution from the neglected same-spin part is small but still significant for a few molecules. The MAD and maximum errors increase to 1.36 and 7.4 kcal/mol, respectively. Still, more than 87% of all errors are smaller than 3 kcal/mol, which can be considered as very satisfactory. Systematic SOS-MP2 errors are only seen for triple bonds which are in general too stable by about 3−4 kcal/mol.

Comparison of these results with those from standard MP2 underlines the success of the SCS scheme. With standard MP2, the MAD increases to 1.74 kcal/mol and the distribution of errors becomes significantly larger (see Figure 1). There are 18 cases where MP2 predicts large errors >4 kcal/mol (compared to six for SCS-MP2 and 11 for SOS-MP2). For these, however, no structural similarities exist, and the reduced performance relative to SCS(SOS)-MP2 can be traced back to an unbalanced account of electron correlation effects. Note, however, that MP2 in this form (i.e., with a HLC and close to the basis set limit) performs much better than usually thought and that MAD below 2 kcal/mol can be considered as quite small.

To put these results on a more solid perspective, we want to compare the MP2-type results with those of a standard B3LYP treatment. As already mentioned in the Introduction, without the atom equivalent scheme, most density functionals outperform MP2 because they describe the process of atomization usually much better. As can be seen from Table 2 and Figure 1, however, this picture completely changes when the “real” accuracy for the different molecules in the G97/2′ set is considered. The MAD from B3LYP/QZV3P is 2.12 kcal/mol, which is almost doubled compared to SCS-MP2 and even larger than that for MP2. The maximum error increases to an unacceptably large value of 14.5 kcal/mol, and about a third of all systems have errors larger than 3 kcal/mol. Compared to all MP treatments, the B3LYP histogram in Figure 1 is much broader and also nonsymmetric, indicating systematic errors for parts of the test set (e.g., polyhalogenated compounds). Note also that even for simple hydrocarbons (entries 78−94), the range of B3LYP errors is very large (+5.3 to −3.6 kcal/mol), while it is only from +1.1 to −2.2 kcal/mol with SCS-MP2.

4.2. The Second Test Set. A comparison of calculated and experimental heats of formation for the 70 molecules in the second test set is presented in Table 3. This table also includes the results of the statistical analyses (excluding entries 26, 48, and 70 because of questionable experimental data, see below). A graphical presentation of the deviations is shown in Figure 2.

Although the errors are larger than for the G97/2′ set, the SCS-MP2 results again are very good. The MAD is only 2.8 kcal/mol, and there are only nine cases with errors larger than 5 kcal/mol. The largest deviation occurs for the P_4O_{10} molecule (−16.6 kcal/mol), which seems to be very difficult also for other methods except MP2. This rather large error should, however, be related to the very large enthalpy of −694.1 kcal/mol. Larger SCS-MP2 errors are also found for compounds containing multiply bonded sulfur (entries 32−33) and S_8. Note, however, that even the computationally much more expensive G3 theory produces sometimes large errors of about 6−7 kcal/mol for complicated structures of this kind (e.g., SF_6 or PF_5). The mean (signed) deviation of SCS-MP2 is −1.1 kcal/mol, indicating that some of the larger systems are predicted to be too unstable. Tentatively, this can be attributed to basis set incompleteness effects that are expected to show up mainly in more complicated bonding situations. Other systematic errors are not observed with SCS-MP2 and also the charged systems (including anions) are described very well. In general, SCS-MP2 seems to be as accurate for the larger molecules as for those in the G97/2′ set. This does not hold for standard MP2 and DFT-B3LYP (see below). Particularly striking is the good performance of SCS-MP2 for various types of polyhalogenated compounds (entries 19−21, 25, 37, 40). A notable exception is C_2Cl_6, where the origin of the SCS-MP2 error of 8.7 kcal/mol remains unclear (considering errors <1 kcal/mol for CCl_4 or C_6Cl_6) and is probably due to experimental problems. Surprisingly large errors are also found for the pure hydrocarbons C_{60} and cubane. Because the SCS-MP2 errors for all other hydrocarbons, including systems with similar structure that never exceed 3 kcal/mol, we strongly believe that the experimental values are

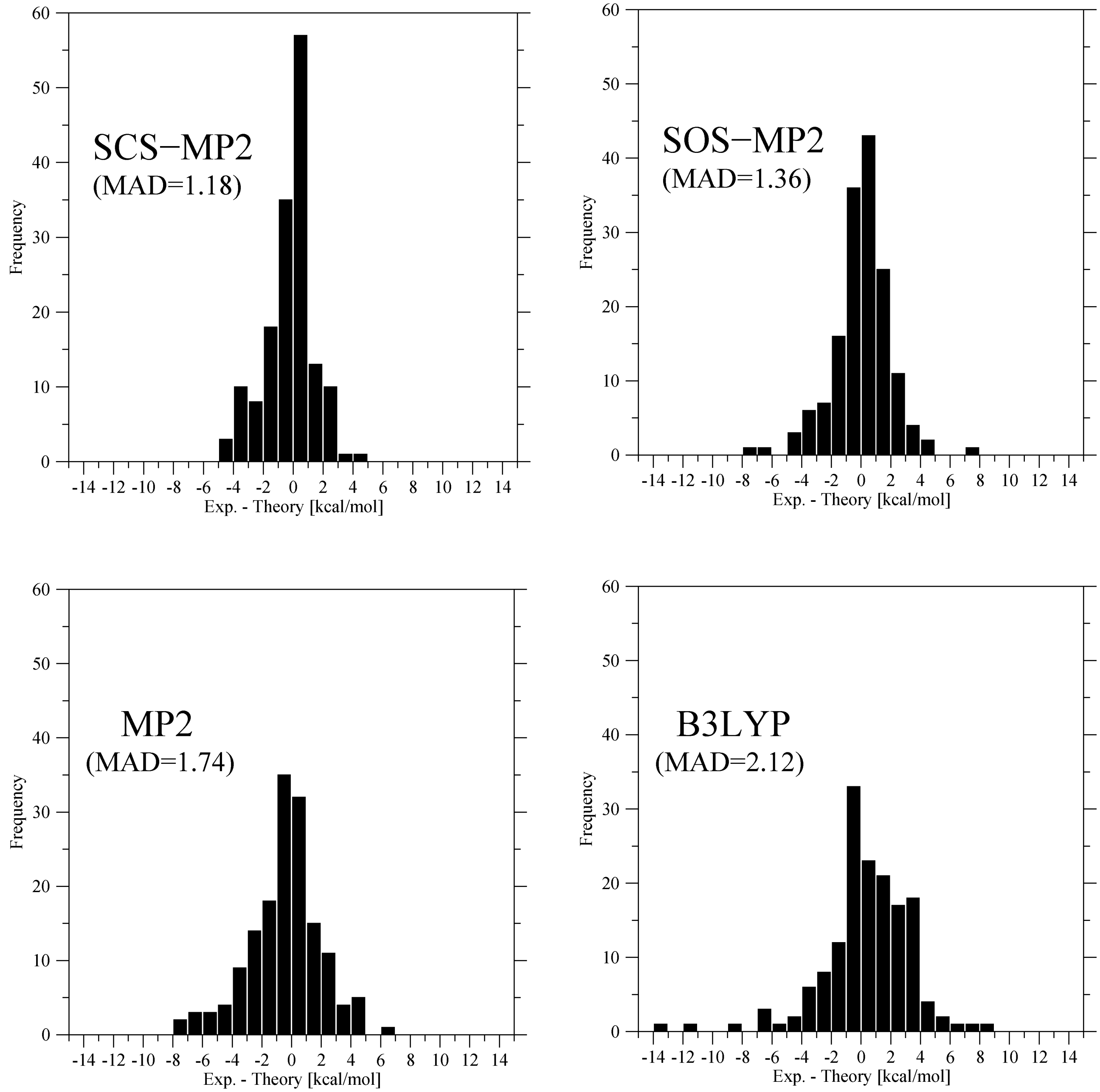

Figure 1. Histograms of deviations for the G2/97′ test set. Each vertical bar represents deviations in a 1 kcal/mol range.

wrong. In particular, the deviation for C_{60} of about 61 kcal/mol is not understandable because other large unsaturated systems such as perylene and also those with five-membered rings (entries 58 and 61) are described very accurately. Note that the experimental ΔH_f^0 of C_{60} is the average of two values,[51,52] differing by as much as 30 kcal/mol and that they correspond to crystal data corrected by the heat of sublimation.

Compared to SCS-MP2, the simplified SOS approach is less accurate but the SCS-MP2 and SOS-MP2 curves in Figure 2 are mostly close and also quite parallel. If one compares the SCS-MP2, SOS-MP2, and MP2 data, it is easily seen that SOS-MP2 slightly overcorrects the problematic MP2 cases. However, it is still much more reliable than MP2 and, in particular, DFT-B3LYP. The MAD are 3.7 (SOS-MP2), 4.6 (MP2), and 8.5 kcal/mol (B3LYP). The maximum deviations of SOS-MP2 and MP2 are almost the same (about 20 kcal/mol), but SOS-MP2 shows much less large errors >5 kcal/mol than MP2 (15 vs 26). The mean (signed) deviation of MP2 is positive, which mainly results from the unsaturated hydrocarbons that are systematically predicted to be too stable. The effect increases with the size of the π-system, which can be attributed to the increasing importance of static electron correlation that is overestimated by standard MP2. With SOS-MP2, this behavior is overcorrected, and the larger compounds thus become slightly too stable. All in all, however, the SOS-MP2 method especially should be regarded as relatively accurate, keeping the difficulty of the molecules in this test set in mind. On the other hand, the really bad performance of DFT-B3LYP is somehow surprising, considering its popularity and widespread use in all areas of chemistry. Note that the results obtained here for B3LYP more or less agree with those obtained by Cioslowski et al.[17] With DFT-B3LYP, there are more than 30 deviations >5 kcal/mol and many errors are even about 20 kcal/mol or larger. An obvious relation with composition or electronic structure is seen in some instances (e.g., polycyclic, strained, or sterically crowded hydrocarbons), but in other cases, the deviations cannot be classified. Particularly striking are the large errors for "simple" saturated systems (e.g., entries 54−55, 59, 64−65, and

TABLE 3: Deviations of Calculated Heats of Formation ΔH_f^0 (298 K) (in kcal/mol) from Experiment[a] for the Second Test Set

			deviation[b]			
entry	molecule	expt	SCS-MP2	SOS-MP2	MP2	B3LYP
1	H_3O^+	142.7	−1.6	−2.8	1.2	−2.3
2	SiH_3^+	14.7	−1.5	−2.2	−2.5	0.1
3	H_3S^+	192.3	−0.6	−0.7	−1.1	1.4
4	HN_3	70.3	2.7	3.0	3.4	4.0
5	$HCOO^-$	−110.9	1.8	1.9	3.5	0.3
6	H_2S_2	3.7	−1.5	−1.4	−2.1	−1.8
7	$COCl_2$	−52.6	1.3	1.7	1.9	2.0
8	$S{=}SF_2$	−71.0	3.7	1.6	**6.0**	3.6
9	P_4	−50.8	**−7.7**	**−8.8**	−4.6	**−5.4**
10	$SOCl_2$	14.1	**5.8**	0.9	**15.7**	**−9.0**
11	PCl_3	−69.0	−1.1	−1.7	0.3	1.1
11	PCl_3	−69.0	−1.1	−1.7	0.3	1.1
12	NH_4^+	150.7	−1.4	−2.2	−0.1	−0.3
13	$C_2H_3^-$	56.2	−0.6	0.5	−2.5	1.7
14	PH^+	179.4	0.1	0.5	−1.6	2.9
15	$O{=}C{=}C{=}C{=}O$	−22.4	4.1	4.6	**5.9**	**10.4**
16	Cl_3PO	−133.8	−0.9	−2.8	3.7	**−8.9**
17	$H_2Si{=}SiH_2$	65.7	−3.8	**−5.8**	−4.3	−1.6
18	N_2O_4	2.2	1.2	−1.3	**10.3**	3.2
19	PF_5	−381.1	−0.3	−3.5	1.8	**−14.6**
20	PCl_5	−89.9	−4.0	**−7.4**	2.7	**−9.5**
21	SF_6	−291.7	−4.2	**−9.3**	0.7	**−19.2**
22	B_2H_6	9.8	−4.3	−2.8	−2.9	2.1
23	$CH_2CHCH_2^-$	29.9	−1.2	−1.4	−0.6	2.9
24	$(COOH)_2$	−175.0	−4.0	−4.0	−0.4	**−8.6**
25	Al_2F_6	−629.5	3.6	1.2	**7.7**	**−20.2**
26	C_2Cl_6	−32.9	**8.7**	**6.6**	**13.6**	**−11.3**
27	S_8	24.0	**−7.6**	**−12.3**	1.2	**−17.5**
28	1,3,5-triazine	54.0	−1.0	−0.7	0.6	1.0
29	$B_3O_3F_3$	−565.3	−4.2	−3.3	1.9	**−8.5**
30	cyclo-$C_5H_5^-$	22.5	2.7	1.0	**7.3**	0.1
31	o-benzyne	105.9	−3.8	−4.6	−0.4	−4.6
32	1,3-dithiolane-2-thione	22.4	**−6.8**	**−8.6**	−2.8	**−16.0**
33	$(CH_3)_2SO_2$	−89.2	**−7.3**	**−9.6**	−1.5	**−17.7**
34	1,3,5-trioxane	−111.3	0.1	0.1	2.6	**−7.6**
35	$C_6H_5O^-$	−37.1	1.5	0.1	**6.7**	1.1
36	pyrazine-1,4-dioxide	44.6	−3.1	**−5.6**	**5.3**	2.5
37	C_6F_6	−228.5	−1.5	−3.2	−0.8	**6.0**
38	peruorocyclobutane	−369.5	1.4	−0.9	0.7	−2.0
39	tetrachloro-p-benzoquinone	−44.4	4.0	4.1	**7.9**	**−7.3**
40	C_6Cl_6[c]	−8.6	0.8	−3.0	**10.8**	**−12.6**
41	$N_3P_3Cl_6$	−175.9	**−10.5**	**−16.9**	3.9	**−42.6**
42	cyclo-$C_7H^+{}_7$	206.7	−4.0	−3.9	−2.6	4.9
43	benzotriazole	80.2	0.4	−1.8	**7.9**	−1.1
44	P_4O_{10}	−694.1	**−16.6**	**−23.6**	**5.2**	**−77.9**
45	quadricyclane	81.0	2.8	1.3	**7.2**	**−10.8**
46	$C_6H_5NH^+{}_3$	175.6	−1.7	−3.2	2.8	0.8
47	bicyclo[2:2:0]hexane	29.8	0.3	0.2	1.3	**−8.4**
48	cubane [c]	148.7	**7.0**	**7.2**	**8.6**	**−12.9**
49	1,3,5,7-cyclooctatetraene	70.7	−3.7	−2.2	−4.8	−3.1
50	$B(OCH_3)_3$	−214.6	−1.5	−0.6	1.3	**−5.3**
51	indole	37.4	−1.7	−4.1	**5.8**	−3.2
52	$P(OCH_3)_3$	−168.6	**−5.9**	**−6.4**	−2.8	**−13.9**
53	p$-O_2NC_6H_4NH_2$	13.2	−2.7	**−5.2**	**6.2**	−1.2
54	$C(CH_3)_4$	−40.3	−0.8	−1.7	1.0	**−6.9**
55	$Si(CH_3)_4$	−55.7	−3.8	**−6.2**	−1.5	**−10.9**
56	cyclohexane	−29.5	0.8	0.2	2.4	**−8.7**
57	naphthalene	36.1	0.3	−1.8	**7.4**	−0.4
58	azulene	69.1	−1.0	−3.6	**7.1**	−0.5
59	hexane	−39.9	0.0	−0.6	1.1	−4.7
60	biphenylene	99.9	0.8	−1.6	**9.2**	−2.3
61	acenaphthylene	62.1	0.3	−2.5	**9.4**	**−5.3**
62	$Mg(C_5H_5)_2$	32.9	−2.6	**−5.8**	**8.9**	**−13.6**
63	$Si(OCH_3)_4$	−281.8	2.4	0.6	**6.9**	**−14.3**
64	bicyclo[2:2:2]octane	−23.7	−0.3	−1.8	3.5	**−17.9**
65	urotropin	47.6	−0.6	−2.5	**5.7**	**−25.4**
66	anthracene	55.2	0.9	−2.5	**11.8**	−3.5
67	(E)-azobenzene	96.9	−1.8	−3.6	**6.0**	−1.5
68	adamantane	−31.8	3.2	1.0	**9.1**	**−25.4**
69	perylene	75.4	2.1	−4.6	**21.9**	**−11.6**
70	C_{60}[c]	618.1	**60.9**	**17.8**	**172.2**	**−119.1**

	SCS-MP2	SOS-MP2	MP2	B3LYP
Mean deviation	−1.14	−2.72	3.36	−6.91
Mean absolute deviation	2.84	3.65	4.56	8.46
Maximum deviation	16.6	23.6	21.9	77.9
<2 kcal/mol[d]	52%	43%	33%	27%
<3 kcal/mol[d]	63%	57%	49%	37%

[a] Experimental values are taken from ref.[17] [b] Deviation = experiment-theory. Absolute deviations larger than 5 kcal/mol are indicated in bold. [c] Data not included in the statistical evaluation, see text. [d] Percentage of absolute deviations smaller than the specified value.

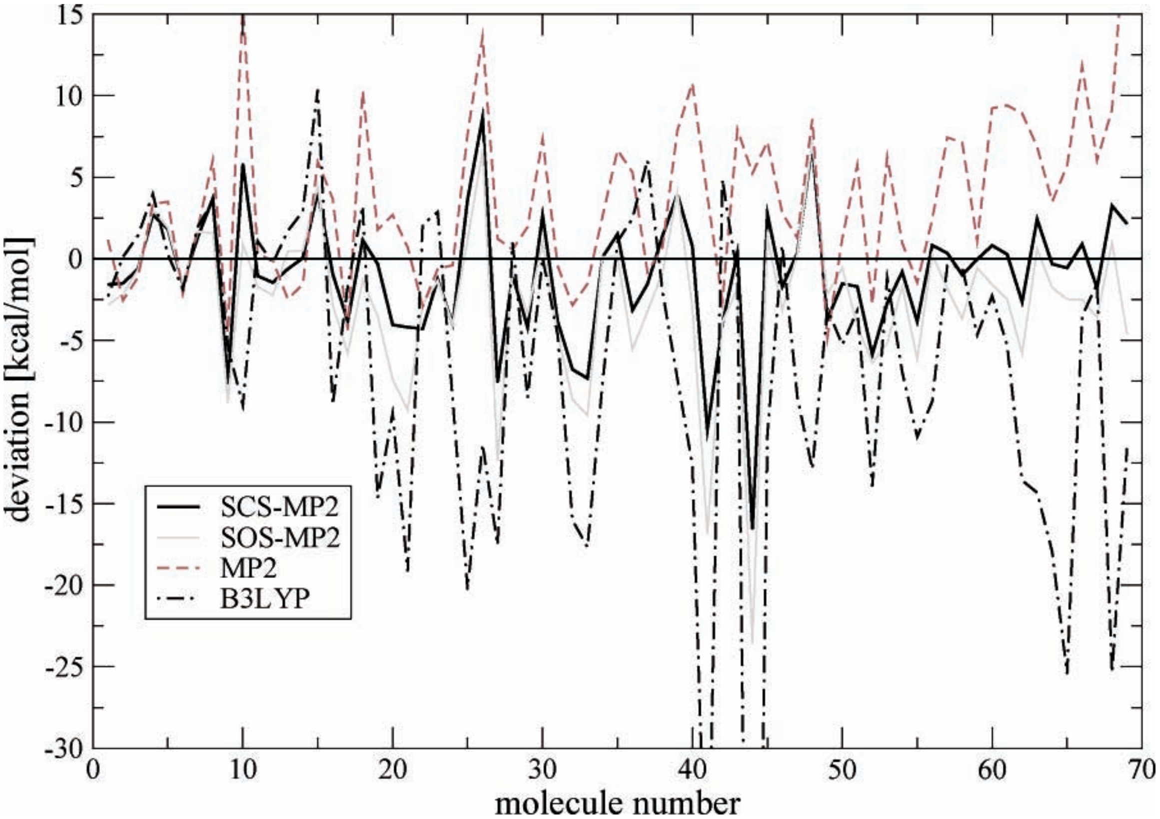

Figure 2. Deviations of ΔH_f^0 (298) (experiment-theory) for the second test set.

TABLE 4: Summary of Statistical Data (in kcal/mol) about the Performance of Different Density Functionals

	density functional					
	BP86	PBE	TPSS	TPSSH	B3LYP	PBE0
G2/97′ test set, $N = 156$						
Mean deviation	0.39	0.17	0.73	0.39	0.33	−0.25
Mean absolute deviation	2.79	2.87	3.06	2.74	2.12	2.28
Maximum deviation	24.2	25.9	21.7	19.8	14.5	14.7
<3 kcal/mol[a]	70	73	63	67	72	75
second test set, $N = 67$						
Mean deviation	−4.6	−2.66	−4.52	−3.55	−6.91	−0.88
Mean absolute deviation	8.77	7.74	8.45	7.02	8.46	4.63
Maximum deviation	87.4	79.0	70.3	52.9	77.9	36.9
<3 kcal/mol[a]	30	45	31	33	37	54

[a] Percentage of absolute deviations smaller than the specified value.

67), while unsaturated compounds of the same size are described much better. The mean (signed) deviation of DFT-B3LYP is −6.9 kcal/mol, indicating that most systems are predicted to be too unstable. Because the atomic equivalents $e(Z)$ have been obtained on "small" molecules, this confirms the results of ref 16 that the stability of molecules is increasingly underestimated by B3LYP as their size increases. This apparent "size inconsistency" represents a serious problem and is further discussed together with results for other functionals in the next section.

4.3. Performance of Other Density Functionals. Statistical evaluations of the performance of the other density functionals (DF) tested are given in Table 4. Inspection of these data reveal some interesting conclusions that mostly contradict previous claims in the literature. Having already pointed out the importance of the atomic corrections $e(Z)$ for the predictions of absolute ΔH_f^0 values, it comes as no surprise that our ranking of different quantum chemical methods (and various DF in particular) differs from those often cited.[53]

- The choice of the test set strongly influences the conclusions regarding the relative performance of different DF. For example, B3LYP is clearly the winner as long as only small molecules (e.g., G2/97′ set) are considered, but it is outperformed by TPSSh and especially by PBE0 for the second set.
- The "size inconsistency" problem is most severe for B3LYP, less pronounced for TPSSh, and almost absent for PBE0 (mean deviations are −6.9, −3.6, and −0.9 kcal/mol, respectively, for set two).
- The pure functionals BP86, PBE, and TPSS perform very similarly for both test sets. Thus, there seems to be no significant improvement for thermochemical predictions by recent inclusions of kinetic energy density terms.
- The hybrid functionals TPSSH and PBE0 perform very differently for the second test set, while the nonhybrid counterparts TPSS and PBE provide very similar results not only on the average but also for individual molecules. This underlines the importance of a larger fraction of nonlocal HF exchange (i.e., 25% in PBE0 vs 10% in TPSSH) for the investigated property[54] whose optimum value seems to be similar in GGA and meta-GGA functionals, respectively.
- If heats of formation as calculated here or reaction energies (except atomization) are considered, PBE0 seems to be the most accurate density functional available.

5. Summary and Conclusion

Three MP2-type correlation treatments employing large AO basis sets together with basis set extrapolation and standard DFT approaches have been used to calculate the heats of formation for a wide variety of different molecules. In addition to the standard G97/2 neutral test set of systems, a second compilation consisting of large and complex molecules is considered. Investigation of this second test set provides a more realistic picture about the accuracy of the methods, in particular for DFT, where small molecule test sets lead to overoptimistic conclusions. In all theoretical approaches, an empirical atom equivalent scheme is used to calculate the ΔH_f^0 values to extract the "real" accuracy of the methods for chemically relevant problems. No further bond or other parameters are applied, and thus, the present MP2-type approaches are very close to a "nonempirical model chemistry" that is applicable to really large molecules.

Relative to the parent method MP2, the spin-component scaled variants SCS-MP2 and SOS-MP2 both represent a significant improvement. The MAD from SCS-MP2 (SOS-MP2) are 1.2 (1.4) and 2.7 (3.6) kcal/mol for the two test sets, respectively, which is much better than MP2 (1.7 and 4.5 kcal/mol) and, in particular, DFT-B3LYP (2.1 and 8.5 kcal/mol). Perusing Table 3, one easily recognizes the remarkable accuracy of SCS-MP2 in particular for difficult systems and without any significant bias toward size or structure of the molecules. Especially for organic compounds, the method is so accurate that suspect experimental data can be identified. It may be speculated that the ΔH_f^0 compilations used in the theoretical community contain many significant experimental errors that should be corrected in the future.[55]

In summary, the SCS-MP2 method (that contains only two empirical parameters for closed-shell reactions) together with large AO basis sets turns out to be the most accurate quantum chemical model available that is routinely applicable to main group systems with about 50−100 atoms. By using the more efficient but only slightly less accurate SOS-MP2 method, the size of the systems that can be studied is further enlarged. The only serious limitation of the SCS/SOS approach in general seems to be the well-known sensitivity of the MPn perturbation series toward spin contamination in open-shell species.

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Supporting Information Available: Tables with deviations for all density functionals and B3LYP optimized coordinates of the molecules in the second test set. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) *Computational Thermochemistry;* Irikura, K. K., Frurip, D. J., Eds.; ACS Symposium Series 677; American Chemical Society: Washington, DC, 1998.

(2) *Quantum Mechanical Prediction of Thermochemical Data;* Cioslowski, J., Ed.; Kluwer: Dordrecht, 2001.

(3) Tajti, A.; Szalay, P. G.; Csaszar, A. G.; Kallay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vazquez, J.; Stanton, J. F. *J. Chem. Phys.* **2004**, *121,* 11599.

(4) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90,* 5622−5629.

(5) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94,* 7221−7230.

(6) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109,* 7764−7776.

(7) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110,* 2822.

(8) Boese, A. D.; Oren, M.; Atasolyu, O.; Martin, J. M. L.; Kallay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *120,* 4129.

(9) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules;* Oxford University Press: Oxford, 1989.

(10) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory;* Wiley-VCH: New York, 2001.

(11) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46,* 618.

(12) Cremer, D. In *Encyclopedia of Computational Chemisty*; von Rague-Schleyer, P., Ed.; J. Wiley: New York, 1998; Vol. 3, p 1706 .

(13) Becke, A. D. *J. Chem. Phys.* **1993**, *98,* 5648.

(14) Stephens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98,* 11623.

(15) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106,* 1063−1079.

(16) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112,* 7374.

(17) Cioslowski, J.; Schimeczek, M.; Liu, G.; Stoyanov, V. *J. Chem. Phys.* **2000**, *113,* 9377−3989.

(18) Xu, X.; Goddard, W. A. *J. Chem. Phys.* **2004**, *121,* 4068−4082.

(19) Duan, X.-M.; Song, G.-L.; Li, Z.-H.; Wang, X.-J.; Chen, G.-H.; Fan, K.-N. *J. Chem. Phys.* **2004**, *121,* 7086−7095.

(20) Winget, P.; Clark, T. *J. Comput. Chem.* **2004**, *25,* 725−733.

(21) Grimme, S. *J. Chem. Phys.* **2003**, *118,* 9095.

(22) Piacenza, M.; Grimme, S. *J. Comput. Chem.* **2004**, *25,* 83−99.

(23) Goumans, T. P. M.; Ehlers, A. W.; Lammertsma, K.; Würthwein, E.-U.; Grimme, S. *Chem. Eur. J.* **2004**, *10,* 6468.

(24) Gerenkamp, M.; Grimme, S. *Chem. Phys. Lett.* **2004**, *392,* 229−235.

(25) Grimme, S. *Chem. Eur. J.* **2004**, *10,* 3423−3429.

(26) Bulo, R. E.; Jansen, H.; Ehlers, A. W.; de Kanter, F. J. J.; Schakel, M.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Angew. Chem., Int. Ed.* **2004**, *43,* 714−717.

(27) Wannere, C. S.; Sattelmeyer, K. W.; Schaefer, H. F.; von R. Schleyer, P. *Angew. Chem., Int. Ed.* **2004**, *43,* 4200−4206.

(28) Jung, Y.; Lochan, R. C.; Dutoi, A. D.; Head-Gordon, M. *J. Chem. Phys.* **2004**, *121,* 9793.

(29) The TZV2P basis sets read in standard notation: H, [3s2p]; Li−F, [5s3p2d]; Na−Mg, [5s4p2d]; Al−Cl, [5s5p2d]. The QZV3P basis set contractions are: H, [4s3p2d]; Li, [6s4p3d2f]; Be−F, [7s4p3d2f]; Na−Mg, [9s5p3d2f]; Al−Cl, [9s6p3d2f]. The exponents of the polarization/correlation functions have been taken from Dunnings cc-pVTZ and cc-pVQZ basis sets, respectively.

(30) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100,* 5829−5835.

(31) Sinha, P.; Boesch, S. E.; Gu, C.; Wheeler, R. A.; Wilson, A. K. *J. Phys. Chem. A* **2004**, *108,* 9213−9217.

(32) All correlation energies are obtained in the frozen-core approximation. This also holds for systems with Li−Be and Na−Mg atoms for which only one and two electrons, respectively, are included in the MP2-type treatments.

(33) Weigend, F.; Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *119,* 12753−12762.

(34) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286,* 243.

(35) Although the TZV2P and QZV3P basis sets are not complete in a sense that the functions with highest angular momentum from the cc-pVTZ and cc-pVQZ sets have been discarded, we use as cardinal numbers X in the extrapolation procedure values of three and four, respectively, for TZV2P and QZV3P.

(36) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106,* 9639.

(37) Vahtras, O.; Almlöf, J.; Feyereisen, M. W. *Chem. Phys. Lett.* **1993**, *213,* 514.

(38) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97,* 331.

(39) Weigend, F. *Phys. Chem. Chem. Phys.* **2002**, *4,* 4285−4291.

(40) The basis sets are available from the TURBOMOLE homepage via the FTP server button (in the subdirectories basen, jbasen, and cbasen). See http://www.turbomole.com.

(41) Weigend, F.; Köhn, A.; Hättig, C. *J. Chem. Phys.* **2001**, *116,* 3175.

(42) Dunning, T. H. *J. Chem. Phys.* **1989**, *90,* 1007.

(43) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38,* 3098−3100.

(44) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33,* 8822−8824.

(45) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *34,* 7046.

(46) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77,* 3865.

(47) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110,* 6158.

(48) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91,* 146401.

(49) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119,* 12129.

(50) Most of the larger molecules in the new G3-3 set are saturated organics that provide not really new information about electronic or geometric structure. The interesting systems from the G3-3 set (e.g., P_4, SF_6, azulene, naphthalene) are included in our second test set.

(51) An, X. W.; Jun, H.; Zheng, B. *J. Chem. Thermodyn.* **1996**, *28,* 1115.

(52) Kolesov, V. P.; Pimenova, S. M.; Pavlovich, V. K.; Tamm, N. B.; Kurskaya, A. A. *J. Chem. Thermodyn.* **1996**, *28,* 1121.

(53) Without the atomic corrections, the MAD for the G2/97′ set are 4.2 (SCS-MP2), 6.7 (SOS-MP2), 6.3 (MP2), and 5.2 (B3LYP) kcal/mol, respectively. This supports the common (but misleading) view that DFT is more accurate than MP2 for energetic properties. The difference of our B3LYP value compared to the often cited MAD of about 3 kcal/mol results from error cancellation effects due to small AO basis sets, differently adjusted scaling factors for ZPVE, and the twelve additional molecules considered here.

(54) A hybrid functional on the basis of TPSS and including 25% HF exchange (instead of 10%) performs very similar to PBE0.

(55) Obvious and unexpected discrepancies (in light of the errors obtained for systems of similar structure) between SCS-MP2 and experimental ΔH_f^0 values (in kcal/mol) not discussed in detail are found during this study for perfluorocyclohexane (ΔH_f^0 (298, SCS-MP2) = −595.8, ΔH_f^0 (298, exp) = −566.2), B_5H_9 (ΔH_f^0 (298, SCS-MP2) = 36.8, ΔH_f^0 (298, exp) = 17.5), pyridine-*N*-oxide (ΔH_f^0 (298, SCS-MP2) = 31.9, ΔH_f^0 (298, exp) = 21.0), H_2PSiH_3 (ΔH_f^0 (298, SCS-MP2) = 7.7, ΔH_f^0 (298, exp) = 1.8), and HNCO (ΔH_f^0 (298, SCS-MP2) = −29.8, ΔH_f^0 (298, exp) = −24.3).