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Assessment of Basis Set and Functional Dependencies in Density Functional Theory: Studies of Atomization and Reaction Energies

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In search of the optimal combination of basis set and exchange-correlation potential, we have investigated the dependence of the atomization energies (D_0) and reaction enthalpies (ΔH) for a set of 44 molecules using gradient-corrected density functional theory. Of the six functionals tested, those that include a portion of the exact (Hartree−Fock) exchange perform best and yield D_0 values that generally lie within 3−5 kcal/mol of the experimental value. For the functionals in which pure DFT exchange is employed, the errors in D_0 are instead on the order of 8−10 kcal/mol. Conversely, reaction enthalpies show slightly better agreement with experimental results when pure DFT exchange is employed. For both D_0 and ΔH the four Gaussian basis sets 6-31G(d,p), 6-311G(d,p), cc-pVDZ, and cc-pVTZ show similar behavior. The most accurate predictions were obtained using the largest cc-pVTZ basis. There is a significant variation in these energies obtained with the various functionals depending on the basis set employed.

I. Introduction

The use of density functional theory (DFT) has increased tremendously as a serious and competitive alternative to more conventional *ab initio* approaches to molecular electronic structures. This increased interest in DFT has been stimulated by the formulation of a “Hartree−Fock type” formalism for DFT[1,2] by the development of accurate gradient correction schemes[3−10] and by the incorporation of DFT into widely used computational quantum chemistry programs.[11−13]

The performance of the various exchange and correlation functionals has been extensively tested, in particular with respect to molecular geometries and to atomization energies.[14−24] A number of books that review various applications of DFT have appeared recently.[25−28] The consensus at present appears to be that the so-called hybrid, or adiabatic connection method (ACM), functionals containing a mixture of different exchange terms and gradient-corrected correlation[8] constitute the most accurate forms of DFT currently at hand. The accuracy of predicted atomization energies is typically within 5−6 kcal/mol, and bond lengths and bond angles are within a few percent of experimental values. The basis sets employed have usually been the 6-31G(d) or the 6-31G(d,p) families by Pople *et al.*[29] A few larger bases were tested in a recent study[18] of the performance of the B3LYP functional.[8,9] In subsequent work[17] 6-31G(d) and 6-311+G(3df,2p) bases were employed together with a larger set of functionals. In a comparison, between the Becke−Wigner[3,30] (BW) and BLYP[3,9] functionals, the 6-31+G-(d) and 6-311+G(3df,2p) bases were used to study[21] the G2[31] set of molecules. The 6-31G(d,p) and a numerical DNP basis were employed to study the effects on geometries of different functional contributions.[22] The TZ2P basis set has been used[16,19] in studies of the BLYP and the “Becke−Roussel”[32] exchange functionals, respectively. Similar basis sets were employed[24] in a study of the performance of the B3 exchange[8] with different correlation corrections on the first row transition metal hydride cations. New exchange-correlation functional forms have recently been introduced.[23,33]

As yet, there seems to be no systematic approach for eliminating errors in the DFT approaches. For all functionals and basis sets tested, the mean absolute error in atomization energy appears to be at best within 4−5 kcal/mol (using B3 exchange). Some improvement is achieved with extremely large basis sets, in which case errors in atomization energies can be reduced to *ca.* 2 kcal/mol. Such basis set extensions become essentially computationally intractable for larger molecules. In addition, there exist few comparisons between the most popular functionals for a wide range of basis sets. Rather, one or two functionals are selected for study, together with one or two basis sets. It may be difficult to obtain an overview of the exchange-correlation functional and basis set that together are the most appropriate.

In the present work, we have chosen to investigate in detail a large subset of the “G2” molecules[31] consisting of 44 molecules. The molecules chosen include some from the standard set of 55 G2 molecules for which very accurate experimental data are known, as well as additional molecules for which experimental results are less accurate. This latter group of molecules also includes some species known to present problems for theoretical methods. Thus, it can be expected that the errors reported here would be larger than studies[34] that employ only the standard G2 data set. Atomization energies are calculated using 6 different frequently used exchange-correlation functionals and 4 readily available Gaussian basis sets for 24 levels of computation. We have employed the same 24 levels of theory in calculating reaction energies for 14 reactions involving reactants and products chosen from the set of 44 molecules. Our aim is to determine which functional and basis set combination is optimal for energetics before examining important reactions in atmospheric chemistry. These atmospheric reactions involve molecules containing only p-block elements but feature polar bonds, e.g., S═O. The systems to be studied will be much larger than those tested here, so the most computationally efficient method is required.

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II. Computational Methods

All calculations of atomization energies and reaction energies were performed using the Gaussian 94 program.[12] The default grid for the numerical integrations was employed. For open shell systems unrestricted wave functions were employed. The basis sets employed are the 6-31G(d,p)[29] and 6-311G(d,p)[35] bases by Pople *et al.* and the correlation-consistent polarized valence double and triple zeta (cc-pVDZ, cc-pVTZ)[36] bases of Dunning *et al.* For some calculations (see below) diffuse functions are also incorporated, resulting in the 6-311+G(d,p) and aug-cc-pVTZ bases, respectively.

Two sets of exchange functionals and three correlation functionals were used, yielding a total of six gradient-corrected combinations. The exchange functionals are those by Becke (B88)[3] and the three-parameter adiabatic connection exchange term (Becke3, or B3)[8] as implemented in the Gaussian program. The latter contains a linear combination of exact HF exchange, Slater exchange,[37] and B88 gradient-corrected exchange. For the correlation functionals, we used the Perdew 1986 (P86),[6] Perdew and Wang 1991 (PW91),[7] and the Lee, Yang, Parr (LYP)[9] functionals, as implemented in Gaussian 94. In the notation used in Gaussian 94 the six combinations are BLYP, B3LYP, BP86, B3P86, BPW91, and B3PW91.

All geometries were optimized using the 6-31G(d,p) or cc-pVDZ basis sets. The 6-31G(d,p) geometries are used for the 6-311G(d,p) single-point calculations and the cc-pVDZ for the cc-pVTZ single-point calculations. Zero-point vibrational energies and thermal corrections to enthalpies were taken directly from the vibrational frequency calculations, which were performed at the 6-31G(d,p) and cc-pVDZ levels. No scaling factor was employed for the vibrational frequencies.

III. Results and Discussion

A. Atomization Energies. Calculated atomic energies, along with the exact atomic energies as determined by Davidson *et al.*[38,39] are given in Table A of the Supporting Information. BLYP total atomic energies tend to be too high, with a few exceptions for carbon and heavier atoms with the two larger basis sets. In contrast, B3LYP energies are too low, except for nitrogen and heavier atoms with the two smaller basis sets. BP86 and BPW91 behave very similarly, giving energies that are either too high (smaller basis sets) or too low (larger basis sets). The latter energies tend to give results closest to the exact atomic energies[38,39] of the methods used. B3P86 consistently gives atomic energies that are much too low, with the discrepancy increasing with basis set size. Correspondingly, this functional gave much lower total molecular energies than other functionals. B3PW91 total energies are consistently too high for all atoms. The total energies of all species studied herein decrease significantly (on the order of a few millihartrees) when the B3 rather than the B88 exchange functional is employed. The PW91 correlation functional is exceptional and yields lower energies in combination with B88 exchange.

The total energies, zero-point vibrational energies, thermal corrections to the enthalpies, and atomization energies, D_0, are given in Tables B, C, D, and E, respectively, in the Supporting Information. Some general preliminary comments can be made on the atomization energies. For any given species, the basis set effect is nearly identical regardless of the exchange-correlation functional used. Similarly, the effect of switching from B88 to B3 exchange is essentially the same regardless of the correlation functional. The effects on atomization energies of the different correlation functionals are nearly constant regardless of the exchange functional. The consistency of these three trends indicates that the methods are well-behaved. Predictions made with the current data set of atoms and molecules should apply to similar species.

Deviations of the atomization energies from experimental values, and the experimental values as quoted in ref 31, are given in Table 1, and the mean and mean absolute deviations are presented in Table 2a−c. No one method consistently gives the best agreement with experimental results, or even good agreement for all molecules tested. Atomization energies are on average underestimated by B3LYP or B3PW91 and overestimated by the other functionals. When only mean deviations are considered, all functionals except BP86 give very satisfactory agreement with experimental results. For most functionals the results improve relatively when the basis set size is increased for the Pople basis sets, but the opposite is true for the correlation-consistent sets. There are exceptions for B3LYP and B3PW91 in both cases. The improved Pople basis set stabilizes the molecules relative to the atoms by some 3−4 kcal/mol on average, whereas with the cc-pVXZ (X = D or T) bases, the relative stability found for the atoms is increased by ca. 5 kcal/mol.

Results for mean deviations can be skewed by fortuitous cancellation of errors, whereby a method that gives an excellent mean deviation still may give highly positive or highly negative individual deviations. When mean absolute deviations are considered, B3LYP/cc-pVTZ//cc-pVDZ clearly gives the best results of the methods used here, and when all basis sets are considered, B3LYP is the most accurate functional followed closely by B3PW91. The poorest agreement with experimental data is given throughout by BP86. When the mean and mean absolute deviations are compared, little difference is seen between these for BP86. This indicates that this functional almost always overestimates atomization energies, whereas the remaining functionals show a greater spread in terms of over- and underestimations. This consistent behavior might allow an empirically adjusted BP86 method to yield accurate predictions.

The mean absolute deviations of the atomization energies seen in Table 2b are still skewed by three species with unusually large deviations from experimental results, SO_2, ClO_2 and CCl, all of which are hypervalent. For SO_2 and ClO_2, the poorest results are seen with methods that give good results for most other species. Note that the prediction of the atomization energy of SO_2 presents a problem for other theoretical methods, including the usually highly accurate G2 scheme. All methods used here have large deviations for CCl. The experimental value is quoted as 80 ± 5 kcal/mol, but G2 theory, which for most species gives atomization energies accurate to within 3 kcal/mol (and usually within 2 kcal/mol), predicts this value as 95.9 kcal/mol. We suspect that the true value for this quantity is much closer to 95 rather than 80 kcal/mol. When these three species are excluded from the mean absolute deviation calculation (Table 2c), the values improve, except for BP86.

For molecules containing CH_3 groups, atomization energies are about 10 kcal/mol higher with the cc-pVTZ versus the cc-pVDZ basis set and about 5 kcal/mol lower with the 6-311G-(d,p) in comparison to the 6-31G(d,p) basis set. As a result, agreement with experimental results improves for the cc-pVTZ basis set with the LYP and PW91 correlation functionals and for the 6-311G(d,p) basis set with the P86 correlation functional but worsens with the LYP and PW91/6-311G(d,p) and P86/cc-pVTZ combinations (see the discussion above). The same qualitative trends in atomization energies (but not necessarily agreement with experimental results) are noted for all species containing hydrogen. There are a few exceptions at certain levels of theory, usually involving the BLYP method with the Pople basis sets. For all species tested and for each functional,

TABLE 1: Experimental Atomization Energies and Deviations at Various Levels of Theory (kcal/mol)

species, expt[a]	basis set	BLYP	B3LYP	BP86	B3P86	BPW91	B3PW91
H_2, 103.3	6-31G(d,p)	1.5	8.4	3.9	3.9	−2.2	−1.0
	6-311G(d,p)	−0.4	0.3	1.8	2.1	−4.0	−2.6
	cc-pVDZ	−2.1	−2.2	−0.2	0.1	−6.0	−4.5
	cc-pVTZ	−0.1	0.6	2.1	2.3	−3.8	−2.4
$^3CH_2$, 179.6	6-31G(d,p)	0.2	1.9	8.8	10.0	3.0	4.1
	6-311G(d,p)	−1.4	0.7	7.2	8.7	1.5	2.6
	cc-pVDZ	−4.7	2.7	4.5	6.0	−1.2	0.0
	cc-pVTZ	−0.3	1.4	8.3	9.6	2.4	3.5
NH_2, 170.0	6-31G(d,p)	4.7	2.5	10.2	7.9	1.1	−0.8
	6-311G(d,p)	3.4	1.5	9.2	7.1	0.0	−1.8
	cc-pVDZ	−0.5	−2.3	5.8	4.3	−3.3	−5.0
	cc-pVTZ	6.5	4.5	12.0	10.5	2.8	1.1
OH, 101.3	6-31G(d,p)	1.7	−1.4	3.6	2.2	−0.9	−2.5
	6-311G(d,p)	−0.3	−1.8	3.3	1.8	−1.3	−2.8
	cc-pVDZ	−3.2	−4.6	0.6	−0.8	−3.9	−5.4
	cc-pVTZ	1.8	0.2	5.2	3.6	0.6	−1.0
H_2O, 219.3	6-31G(d,p)	−5.7	−7.7	1.8	−0.3	−6.7	−8.9
	6-311G(d,p)	−6.3	−8.2	1.3	−0.6	−7.2	−8.9
	cc-pVDZ	−11.4	−13.1	−3.3	−5.2	−11.9	−13.9
	cc-pVTZ	−2.4	−4.4	5.0	2.8	−3.7	−6.0
HF, 135.2	6-31G(d,p)	−6.6	−8.2	−2.4	−4.0	−6.6	−8.4
	6-311G(d,p)	−5.4	−6.9	−1.0	−2.6	−5.3	−7.1
	cc-pVDZ	−9.1	−10.6	−4.6	−6.1	−8.9	−10.6
	cc-pVTZ	−2.0	−3.8	2.0	0.1	−2.4	−4.4
CN, 176.6	6-31G(d,p)	9.4	−3.4	14.4	1.9	9.6	−3.8
	6-311G(d,p)	10.2	−2.6	16.7	2.4	10.0	−3.3
	cc-pVDZ	7.9	−5.0	12.8	0.2	8.0	−5.5
	cc-pVTZ	11.5	−0.7	16.2	4.4	11.5	−1.4
HCN, 301.8	6-31G(d,p)	5.7	−2.4	13.4	5.4	5.0	−4.0
	6-311G(d,p)	16.0	−1.4	13.9	6.2	5.5	−3.3
	cc-pVDZ	2.0	−6.0	10.0	2.0	1.6	−7.3
	cc-pVTZ	8.6	0.7	15.5	8.3	7.1	−1.4
CH_3NH_2, 542.7 ± 0.1	6-31G(d,p)	1.4	1.6	21.4	20.9	0.0	−0.7
	6-311G(d,p)	−4.1	−3.8	15.7	16.1	−5.2	−5.8
	cc-pVDZ	−11.8	−11.1	9.5	9.5	−11.6	−12.1
	cc-pVTZ	−0.7	0.0	19.5	19.7	−2.0	−2.4
CO, 256.2	6-31G(d,p)	1.2	−6.7	6.9	−0.9	2.7	−6.3
	6-311G(d,p)	2.3	−5.5	7.6	0.2	3.5	−5.2
	cc-pVDZ	0.2	−5.8	5.7	−2.0	1.5	−7.4
	cc-pVTZ	3.0	−4.2	8.4	1.6	4.2	−4.0
HCO, 270.3	6-31G(d,p)	9.0	0.6	17.3	8.9	10.3	0.9
	6-311G(d,p)	7.5	−0.5	15.9	8.2	9.1	0.1
	cc-pVDZ	5.2	−2.9	14.0	5.7	7.0	−2.2
	cc-pVTZ	9.1	1.6	17.5	10.2	10.5	2.0
H_2CO, 357.2	6-31G(d,p)	6.3	−0.1	17.3	10.9	6.9	−0.5
	6-311G(d,p)	2.5	−3.4	14.0	8.3	3.7	−3.2
	cc-pVDZ	−0.8	−6.9	11.0	4.9	0.8	−6.4
	cc-pVTZ	4.6	−0.8	15.9	10.7	5.5	−1.0
CH_3OH, 480.8	6-31G(d,p)	0.4	−1.0	17.6	15.8	0.5	−1.8
	6-311G(d,p)	−5.5	−6.4	12.3	11.2	−4.7	−6.7
	cc-pVDZ	−11.5	−12.3	7.0	5.7	−9.9	−11.9
	cc-pVTZ	−2.0	−2.6	15.7	14.7	−1.5	−3.3
N_2, 225.1	6-31G(d,p)	6.2	−5.8	10.1	−1.6	3.0	−9.5
	6-311G(d,p)	8.1	−3.6	11.8	0.4	4.7	−7.6
	cc-pVDZ	6.1	−5.8	10.1	−1.6	3.0	−9.5
	cc-pVTZ	11.1	0.1	14.9	4.2	7.7	−3.9
N_2H_4, 405.4	6-31G(d,p)	3.9	−2.1	19.8	13.6	−0.8	−6.9
	6-311G(d,p)	1.2	−4.6	17.1	11.3	−3.5	−9.5
	cc-pVDZ	−5.5	−11.1	11.3	5.4	−9.3	−15.2
	cc-pVTZ	5.6	0.1	21.6	16.0	0.9	−4.9
NO, 150.1	6-31G(d,p)	20.2	−0.4	17.4	4.4	11.7	6.3
	6-311G(d,p)	21.3	−0.7	16.6	4.1	11.0	−2.3
	cc-pVDZ	12.8	−0.3	17.4	4.5	11.6	−2.0
	cc-pVTZ	13.7	1.9	18.7	7.0	13.0	0.5
HNO, 198.7	6-31G(d,p)	10.1	−3.3	17.6	4.3	8.2	−5.6
	6-311G(d,p)	7.9	−4.9	15.7	2.9	6.3	−7.1
	cc-pVDZ	7.5	−5.7	15.3	2.0	5.9	−7.9
	cc-pVTZ	10.4	−1.7	18.3	6.2	8.9	−3.9
CF, 128.3 ± 2	6-31G(d,p)	12.2	4.8	16.0	8.8	12.9	5.0
	6-311G(d,p)	8.4	1.5	12.4	5.7	9.3	1.9
	cc-pVDZ	9.2	1.6	12.9	5.5	9.7	1.7
	cc-pVTZ	10.0	4.0	14.4	8.4	11.2	4.4
HCF, 210.2 ± 7	6-31G(d,p)	1.8	−5.0	8.0	1.1	1.2	−6.0
	6-311G(d,p)	2.7	−8.8	4.0	−2.0	−2.1	−9.3
	cc-pVDZ	−3.1	−9.9	3.4	−3.3	−3.2	−10.5
	cc-pVTZ	−0.6	−6.0	13.5	0.8	−0.7	−6.7

TABLE 1: (Continued)

species, expt[a]	basis set	BLYP	B3LYP	BP86	B3P86	BPW91	B3PW91
CH$_3$F, 397.4±8	6-31G(d,p)	3.7	1.9	16.3	14.2	3.6	1.0
	6-311G(d,p)	−2.5	−3.8	10.7	9.5	−1.9	−4.0
	cc-pVDZ	−6.5	−8.0	7.2	5.5	−5.3	−7.7
	cc-pVTZ	0.6	−0.3	13.8	12.9	1.0	−0.9
O$_2$, 118.0	6-31G(d,p)	18.8	4.4	24.0	9.8	20.0	5.0
	6-311G(d,p)	15.0	1.3	20.4	6.9	16.4	2.1
	cc-pVDZ	17.9	3.3	22.7	8.5	18.6	3.6
	cc-pVTZ	16.2	3.4	22.1	9.5	18.2	4.7
HO$_2$, 161.1 ± 2	6-31G(d,p)	20.0	7.3	27.7	15.2	19.5	6.5
	6-311G(d,p)	16.4	4.2	24.2	12.2	16.0	3.4
	cc-pVDZ	16.5	3.8	24.1	11.6	15.8	2.8
	cc-pVTZ	19.1	7.4	27.4	15.9	19.1	7.0
H$_2$O$_2$, 252.3	6-31G(d,p)	10.5	−4.4	16.7	6.2	4.9	−6.1
	6-311G(d,p)	3.1	−7.4	13.6	3.5	1.7	−9.0
	cc-pVDZ	0.0	−10.6	10.6	0.3	−1.3	−12.2
	cc-pVTZ	7.2	−3.0	18.0	8.2	6.0	−4.4
H$_2$S, 173.2	6-31G(d,p)	−3.7	−3.2	3.1	2.8	−4.5	−4.1
	6-311G(d,p)	−4.4	−3.5	2.9	2.9	−4.8	−4.2
	cc-pVDZ	−6.2	−5.5	1.2	1.1	−6.3	−5.9
	cc-pVTZ	−2.8	−2.0	4.4	4.4	−3.3	−2.8
HCl, 102.2	6-31G(d,p)	−3.6	−3.4	0.7	0.4	−3.0	−3.0
	6-311G(d,p)	−3.1	−2.8	1.4	1.3	−2.3	−2.3
	cc-pVDZ	−4.8	−4.9	−0.1	−0.2	−3.7	−3.7
	cc-pVTZ	−2.6	−2.2	2.0	1.9	−1.8	−1.7
HOF, 151.9 ± 1	6-31G(d,p)	9.1	−3.0	15.0	3.3	7.5	−4.6
	6-311G(d,p)	4.4	−7.4	10.4	−0.9	2.9	−8.9
	cc-pVDZ	4.5	−7.7	10.4	−1.4	2.9	−9.4
	cc-pVTZ	7.7	−3.5	14.3	3.5	6.7	−4.6
F$_2$, 36.9	6-31G(d,p)	17.6	3.8	19.3	6.0	16.2	2.6
	6-311G(d,p)	10.0	−3.7	11.8	−1.3	8.7	−4.8
	cc-pVDZ	13.8	−0.6	15.1	1.3	11.9	−2.2
	cc-pVTZ	12.3	−0.4	14.9	2.8	11.8	−0.9
CS, 169.5	6-31G(d,p)	−2.4	−9.4	3.7	−3.8	0.3	−7.9
	6-311G(d,p)	−2.9	−9.4	3.5	−3.4	0.2	−7.6
	cc-pVDZ	−2.7	−9.8	3.2	−4.2	−0.2	−8.3
	cc-pVTZ	−0.7	−7.0	5.4	−1.3	2.0	−5.5
CO$_2$, 381.9	6-31G(d,p)	21.7	−4.2	22.9	8.2	16.4	−1.1
	6-311G(d,p)	10.7	−3.8	22.6	8.8	16.3	−0.4
	cc-pVDZ	8.6	−6.7	20.4	5.8	14.0	−3.4
	cc-pVTZ	12.0	−1.4	24.1	11.4	17.6	1.9
SN, 110.7 ± 6	6-31G(d,p)	4.9	−6.3	8.8	−2.3	3.7	−8.0
	6-311G(d,p)	3.9	−7.1	7.9	−3.0	2.8	−8.7
	cc-pVDZ	3.8	−7.9	7.5	−4.2	2.4	−9.7
	cc-pVTZ	9.2	−1.3	13.3	2.9	8.2	−2.8
CCl, 80 ± 5	6-31G(d,p)	17.3	12.1	22.8	17.5	14.4	19.3
	6-311G(d,p)	15.2	10.6	21.3	16.4	13.5	19.1
	cc-pVDZ	17.6	19.4	23.2	17.7	14.8	20.8
	cc-pVTZ	18.8	14.4	25.0	20.3	17.3	22.7
SO, 123.5	6-31G(d,p)	2.5	−7.8	6.8	−3.2	3.4	−7.5
	6-311G(d,p)	−0.9	−11.0	3.7	−6.0	0.3	−10.5
	cc-pVDZ	0.1	−11.0	4.1	−6.7	0.6	−11.0
	cc-pVTZ	6.6	−2.5	11.5	2.6	8.0	−1.9
O$_3$, 142.2 ± 0.5	6-31G(d,p)	28.2	−5.9	38.3	4.7	29.9	−3.9
	6-311G(d,p)	21.0	−12.2	31.2	−1.4	23.0	−11.0
	cc-pVDZ	26.2	−8.4	35.5	1.5	27.1	−8.1
	cc-pVTZ	24.8	−6.5	36.2	5.3	27.9	−4.5
CH$_3$Cl, 371.0	6-31G(d,p)	−1.3	0.0	13.4	14.0	1.4	1.6
	6-311G(d,p)	−6.1	−4.5	9.1	10.2	−2.9	−2.4
	cc-pVDZ	−10.8	−9.0	5.1	6.1	−6.7	−6.2
	cc-pVTZ	−4.5	−2.6	11.0	12.2	−1.2	−0.6
SF, 81.2 ± 2.1	6-31G(d,p)	5.7	−1.9	8.0	0.9	5.1	−2.6
	6-311G(d,p)	0.3	−7.1	2.9	−4.1	0.0	−7.7
	cc-pVDZ	3.3	−5.0	5.3	−2.5	2.4	−6.0
	cc-pVTZ	7.3	0.8	9.8	4.0	7.1	0.4
ClO, 63.3	6-31G(d,p)	4.8	−4.6	8.9	−0.3	5.9	−4.0
	6-311G(d,p)	−0.1	−9.4	4.3	−4.7	1.4	−8.5
	cc-pVDZ	3.1	−6.9	6.9	−2.9	3.8	−6.5
	cc-pVTZ	7.6	−1.3	12.5	3.8	9.5	0.0
HOCl, 156.3	6-31G(d,p)	0.7	−6.6	8.0	0.9	1.2	−6.5
	6-311G(d,p)	−3.2	−10.4	3.0	0.3	−2.6	−10.2
	cc-pVDZ	−2.6	−10.1	4.8	−2.6	−2.1	−10.0
	cc-pVTZ	3.0	−3.5	11.4	4.6	4.2	−3.0
OCS, 327.7 ± 0.2	6-31G(d,p)	7.9	−4.8	19.7	6.9	14.0	−1.0
	6-311G(d,p)	6.0	−6.1	18.2	6.2	12.6	−1.8
	cc-pVDZ	6.4	−6.5	18.0	5.2	12.7	−2.7
	cc-pVTZ	9.2	−1.9	21.5	10.5	15.9	2.3

TABLE 1: (Continued)

species, expt[a]	basis set	BLYP	B3LYP	BP86	B3P86	BPW91	B3PW91
S_2, 100.7	6-31G(d,p)	0.1	−5.8	5.3	−0.7	2.7	−3.9
	6-311G(d,p)	3.2	−8.6	2.8	−2.8	0.4	−6.0
	cc-pVDZ	1.6	−4.3	6.9	0.7	4.3	−2.3
	cc-pVTZ	3.7	−1.0	9.9	4.9	7.4	1.8
SO_2, 254.0	6-31G(d,p)	−11.5	−31.6	−0.9	−20.4	−7.9	−29.5
	6-311G(d,p)	−17.1	−36.8	−6.1	−25.1	−13.1	−34.6
	cc-pVDZ	−22.3	−44.0	−11.9	−33.0	−18.8	−42.0
	cc-pVTZ	−2.6	−19.4	8.2	−7.5	1.8	−15.0
SCl, 57.1 ± 4	6-31G(d,p)	6.8	2.6	11.1	6.1	8.9	4.1
	6-311G(d,p)	3.8	−0.1	8.7	4.8	6.6	2.1
	cc-pVDZ	8.4	4.0	12.8	8.3	10.5	5.6
	cc-pVTZ	10.7	7.2	16.1	5.0	14.0	9.6
ClO_2, 121.5	6-31G(d,p)	0.2	−24.6	11.0	−13.1	4.8	−21.2
	6-311G(d,p)	−9.9	−34.6	1.3	−22.6	−4.8	−30.7
	cc-pVDZ	−7.1	−33.4	3.1	−22.5	−3.1	−30.4
	cc-pVTZ	9.3	−11.9	21.8	1.0	15.7	−7.2
Cl_2, 57.2	6-31G(d,p)	−5.4	−9.4	−1.2	−5.1	−3.0	−7.5
	6-311G(d,p)	−8.6	−12.2	−3.7	−7.2	−5.4	−9.6
	cc-pVDZ	−3.7	−7.8	0.6	−3.5	−1.3	−5.9
	cc-pVTZ	−1.3	−4.5	4.2	0.8	2.5	−1.6
CS_2, 273.5 ± 0.2	6-31G(d,p)	3.5	−6.4	15.9	5.5	11.1	−1.2
	6-311G(d,p)	1.4	−7.8	14.5	4.8	9.8	−2.1
	cc-pVDZ	1.1	−9.1	13.2	2.6	8.3	−4.1
	cc-pVTZ	4.4	−4.3	17.3	8.0	12.5	1.2

[a] Experimental uncertainties are ±1.0 kcal/mol unless otherwise specified.

TABLE 2

basis set	BLYP	B3LYP	BP86	B3P86	BPW91	B3PW91
(a) Mean Deviation in Atomization Energies (kcal/mol)						
6-31G(d,p)	5.7	−3.0	12.5	4.1	5.4	−3.0
6-311G(d,p)	2.9	−5.8	9.9	2.0	2.9	−5.5
cc-pVDZ	1.4	−6.9	8.9	0.5	1.8	−6.8
cc-pVTZ	6.2	−1.3	14.2	6.5	6.8	−0.9
(b) Mean Absolute Deviation in Atomization Energies (kcal/mol)						
6-31G(d,p)	7.6	5.6	12.7	6.7	7.0	5.6
6-311G(d,p)	6.8	6.8	10.4	6.2	6.1	6.9
cc-pVDZ	7.3	8.5	9.9	5.4	7.2	8.4
cc-pVTZ	7.2	3.1	14.2	6.9	7.8	3.8
(c) Mean Absolute Deviation in Atomization Energies (kcal/mol)[a]						
6-31G(d,p)	7.4	4.3	12.8	5.9	6.8	4.3
6-311G(d,p)	6.3	5.2	10.4	5.0	5.8	5.3
cc-pVDZ	6.7	6.6	9.7	3.9	6.8	6.7
cc-pVTZ	6.5	2.1	13.9	6.7	7.5	3.0

[a] Excluding CCl, SO_2, and ClO_2.

TABLE 3: C−O Bond Distance for CO_2[a]

basis set	BLYP	B3LYP	BP86	B3P86
6-31G(d)	1.183	1.169	1.181	1.169
6-311G(d)	1.174	1.160	1.173	1.158
cc-pVDZ	1.182	1.167	1.180	1.165
cc-pVTZ	1.174	1.160	1.172	1.158

[a] Experimental value is 1.162 Å (ref 40).

with very few exceptions the atomization energy increases when the basis set is increased to the triple zeta level for the correlation-consistent basis sets. This trend is very consistent for the B3LYP method, CN and CCl providing the only exceptions. For the majority of species, the atomization energy decreases when the basis set size is increased to triply split valence with the Pople basis sets.

By examination of the performance of the exchange-correlation functionals, BLYP tends to give more accurate energies for hydrogenated vs non-hydrogenated species, especially when hydrogen atoms number half or more of the atoms in the molecule. B3LYP gives at least satisfactory agreement with experimental results for most molecules tested, except for SO_2 and ClO_2 discussed above. There does not appear to be a distinct contrast in performance between different classes of molecules. Although BP86 in general gives the worst agreement with experimental results, it does provide accurate energies for most of the species containing sulfur atoms and those involving singly bonded oxygen atoms. B3P86 yields good agreement with experimental results for most non-carbon containing species except those that are hypervalent or that have NH_2 groups. For carbon-containing species, it tends to perform better when there are few or no hydrogens. BPW91 and B3PW91 behave very similarly to BLYP and B3LYP, respectively, in almost all instances.

Overall, computed atomization energies are more accurate when the hybrid B3 exchange functional is employed, regardless of which correlation functional is used, in particular for species with multiply bonded oxygen atoms. For a striking example, compare the results for O_3, especially for the P86 functional. The overall improved performance of the ACM functionals can be thought of as a "cancellation of errors". HF theory severely underestimates bond dissociation energies, whereas these are overestimated at the local density functional (LDA) theory level. The so-called nonlocal corrections to LDA in part, but not fully, correct for this tendency of overbinding. If we finally mix in a small contribution from a method that seriously underbinds (i.e., "exact" KS-exchange or HF) and then empirically adjust the balance between the various contributions, atomization energies fairly close to experimental values result. The effects of the ACM approach can be clearly seen in Table 2. Significant improvements in data are observed when going from B to B3 exchange, whereas the correlation functionals (in particular LYP and PW91) overall behave very similarly.

For the CO_2 molecule, we reoptimized the structure using the 6-311G(d) and cc-pVTZ basis sets for all six functionals. Using the larger basis set generally led to improved bond distances (see Table 3). Improved agreement with the experimental value[40] is noted when the hybrid B3 exchange is employed. The atomization energies (see Table 4) are essentially unaltered compared with single-point calculations on the geometries obtained with the smaller bases. If we add diffuse functions to the TZP optimized structures (i.e., 6-311+G(d) and aug-cc-pVTZ), the atomization energies drop by some 1−3 kcal/mol. Still, most functionals give deviations of between 10 and 20 kcal/mol compared with experimental results. Only

TABLE 4: Deviations in Atomization Energies for CO_2 at Triply Split Valence Basis Sets

basis set	BLYP	B3LYP	BP86	B3P86
6-311G(d)	9.7	−3.7	22.7	8.9
6-311+G(d)[a]	6.6	−6.5	19.5	6.9
cc-pVTZ	12.4	−1.3	24.3	11.5
aug-cc-pVTZ[b]	9.8	−2.7	22.6	10.6

[a] Single-point energy calculation at 6-311G(d) geometry. [b] Single-point energy calculation at cc-pVTZ geometry.

B3LYP lies close to the experimental value for all the basis set combinations described. There are significantly increased computational times associated with the triply split valence bases relative to the double valence sets. The addition of diffuse functions also increases the computational time by a factor of about 2−3.

B. Reaction Enthalpies. It has become almost standard to report atomization energies as the test for the accuracy of a theoretical method's energetics. However, this use of mixed "restricted" molecular and "unrestricted" atomic data may not be consistent with many problems of real chemical interest.[19] Therefore, further tests of the energetics of the DFT methods presently under consideration are presented. Reaction enthalpies, ΔH_{298}, are given in Table F of the Supporting Information. Experimental values and deviations of the calculated reaction enthalpies from them are given in Table 5, and the mean and mean absolute deviations are presented in Table 6a,b. All

TABLE 5: Experimental Reaction Enthalpies, ΔH_{298}, and Deviations at Various Levels of Theory (kcal/mol)

reaction, expt	basis set[a]	BLYP	B3LYP	BP86	B3P86	BPW91	B3PW91
$H_2 + CO \rightarrow H_2CO$, −1.3	6-31G(d,p)	−2.0	−2.8	−5.0	−6.3	−4.6	−5.0
	6-311G(d,p)	0.2	0.0	−2.7	−4.1	−2.3	−2.8
	cc-pVDZ	−0.3	−1.3	−3.7	−4.9	−3.4	−3.7
	cc-pVTZ	0.1	−1.0	−3.6	−4.9	−3.2	−3.6
$O_2 + H_2 \rightarrow H_2O_2$, −32.5	6-31G(d,p)	13.9	10.8	10.9	7.2	12.9	10.1
	6-311G(d,p)	11.7	9.0	8.7	5.5	10.8	8.5
	cc-pVDZ	14.8	11.7	11.9	8.3	14.0	11.3
	cc-pVTZ	8.9	6.9	6.2	3.6	8.4	6.7
$H_2 + S \rightarrow H_2S$, −71.1	6-31G(d,p)	5.2	5.2	0.5	0.8	2.3	3.1
	6-311G(d,p)	4.0	3.8	−1.1	−0.8	0.9	1.6
	cc-pVDZ	3.1	3.3	−1.4	−0.9	0.4	1.4
	cc-pVTZ	2.7	2.6	−2.3	−2.0	−0.4	1.9
$SO + 1/2\ O_2 \rightarrow SO_2$, −72.1	6-31G(d,p)	21.8	25.9	19.7	22.1	21.3	24.5
	6-311G(d,p)	22.1	26.5	20.0	22.5	21.7	25.2
	cc-pVDZ	31.3	34.6	27.4	30.5	28.7	32.8
	cc-pVTZ	17.3	18.6	13.7	14.8	15.3	17.4
$CO + S \rightarrow COS$, −72.9	6-31G(d,p)	−6.4	−1.7	−11.6	−7.6	−11.0	−5.1
	6-311G(d,p)	−3.5	0.9	−10.3	−5.8	−8.9	2.0
	cc-pVDZ	−6.0	−1.1	−12.1	−7.0	−10.6	−4.5
	cc-pVTZ	−6.0	−2.1	−12.8	−8.7	−11.5	−6.2
$2\ ClO_2 \rightarrow Cl_2 + 2\ O_2$, −-50.0	6-31G(d,p)	−31.0	−47.7	−23.9	−39.8	−26.4	−43.9
	6-311G(d,p)	−40.6	−58.7	−33.6	−50.9	−36.1	−55.1
	cc-pVDZ	−45.5	−64.7	−39.0	−57.4	−41.4	−61.2
	cc-pVTZ	−11.8	−25.2	−4.0	−16.8	−6.6	−24.2
$S_2 + F_2 \rightarrow 2\ SF$, −24.5	6-31G(d,p)	6.0	1.4	8.4	3.3	8.4	3.6
	6-311G(d,p)	5.9	1.5	8.6	3.7	8.8	4.2
	cc-pVDZ	8.5	4.8	11.1	6.8	11.1	7.1
	cc-pVTZ	1.1	−4.2	4.3	−0.7	4.7	−0.1
$HOF + O_2 \rightarrow HF + O_3$, −7.5	6-31G(d,p)	6.4	15.6	3.3	12.6	4.2	13.8
	6-311G(d,p)	4.1	13.1	0.8	10.0	1.8	11.3
	cc-pVDZ	5.5	14.7	2.3	11.7	3.3	13.0
	cc-pVTZ	1.3	10.3	−1.6	7.7	−0.4	8.9
$2\ OH + H_2S \rightarrow SO_2 + 2\ H_2$, −84.7	6-31G(d,p)	5.4	21.6	4.2	19.9	6.1	22.4
	6-311G(d,p)	12.9	29.2	11.9	27.4	13.8	30.0
	cc-pVDZ	15.5	33.4	14.9	32.2	16.6	34.4
	cc-pVTZ	3.3	16.4	1.9	14.4	3.7	17.0
$HCl + O_3 \rightarrow HOCl + O_2$, −29.8	6-31G(d,p)	4.9	7.2	6.8	5.8	5.7	−6.6
	6-311G(d,p)	5.6	−6.1	7.8	4.4	6.7	−5.3
	cc-pVDZ	5.8	−6.2	7.7	4.6	6.7	−5.5
	cc-pVTZ	2.9	8.7	4.8	−7.1	3.7	−8.0
$CH_2 + HCl \rightarrow CH_3Cl$, −90.3	6-31G(d,p)	−2.9	−2.3	−4.8	−4.5	−2.2	−1.5
	6-311G(d,p)	0.7	1.2	−1.3	−1.1	1.1	1.9
	cc-pVDZ	0.3	0.9	1.5	−1.2	0.9	−2.3
	cc-pVTZ	0.8	0.9	−1.4	−1.6	1.0	2.0
$CH_2 + H_2O \rightarrow CH_3OH$, −82.5	6-31G(d,p)	−7.3	−6.2	−8.4	−7.5	−5.7	−4.5
	6-311G(d,p)	−3.8	−3.0	−5.2	−4.6	−2.6	−1.6
	cc-pVDZ	−6.2	−5.0	−7.3	−6.4	−4.7	−2.8
	cc-pVTZ	−2.3	−1.9	−3.9	−3.8	−1.3	−0.1
$HNO + O_2 \rightarrow NO + HO_2$, −1.7	6-31G(d,p)	3.5	1.4	3.8	1.6	4.2	2.0
	6-311G(d,p)	2.0	0.2	2.5	0.6	2.9	1.0
	cc-pVDZ	3.4	1.3	3.7	1.6	4.2	2.0
	cc-pVTZ	1.0	−0.5	1.6	0.1	2.0	0.4
$NH_2 + HCO \rightarrow HCN + H_2O$, −81.4	6-31G(d,p)	14.1	13.6	12.8	12.2	13.5	13.4
	6-311G(d,p)	11.1	11.0	10.4	10.1	11.2	11.4
	cc-pVDZ	14.7	14.3	13.6	13.1	14.4	14.4
	cc-pVTZ	10.1	10.2	9.4	9.5	10.3	14.4

[a] 6-311G(d,p) energies are at the 6-31G(d,p) optimized geometries; cc-pVTZ energies are at the cc-pVDZ optimized geometries.

TABLE 6

basis set	BLYP	B3LYP	BP86	B3P86	BPW91	B3PW91
(a) Mean Deviation in Reaction Enthalpies (kcal/mol)						
6-31G(d,p)	2.3	3.0	1.2	1.4	2.0	1.9
6-311G(d,p)	2.9	2.0	1.2	1.2	2.1	1.9
cc-pVDZ	3.2	2.9	2.2	2.2	2.9	2.6
cc-pVTZ	2.1	2.8	0.9	0.3	1.8	1.6
(b) Mean Absolute Deviation in Reaction Enthalpies (kcal/mol)						
6-31G(d,p)	9.3	11.7	8.9	10.8	9.2	11.4
6-311G(d,p)	9.2	11.7	8.9	10.8	9.3	11.8
cc-pVDZ	11.5	14.1	11.3	13.3	11.5	14.0
cc-pVTZ	6.7	7.8	5.1	6.8	5.2	7.7
(c) Mean Absolute Deviation in Reaction Enthalpies (kcal/mol)[a]						
6-31G(d,p)	6.6	6.2	6.9	6.3	6.8	6.2
6-311G(d,p)	4.8	4.5	5.4	4.6	5.3	5.0
cc-pVDZ	8.6	5.9	6.9	6.0	6.7	6.3
cc-pVTZ	3.4	4.5	4.7	4.5	4.3	4.4

[a] Excluding reactions involving ClO_2 and SO_2.

reactions are written to be exothermic (according to the experimental enthalpies) in order to facilitate discussion.

Experimental values were derived from experimental heats of formation[41,42] and for this purpose only from species whose experimental uncertainty was ≤2.0 kcal/mol, since accurate experimental values are required for comparisons. As with the atomization energies discussed above, there is an internal consistency in the basis set and exchange-correlation functional effects for each reaction enthalpy, although the trends are not as quantitative. Unlike the atomization energies, more general qualitative trends are not so readily apparent.

When mean deviations are considered, all methods give excellent agreement with experimental results, especially when the P86 correlation functional is employed. The B3P86/cc-pVTZ//cc-pVDZ level of theory gives the best overall performance. In general, little variation is seen with basis sets, with all methods tending to underestimate reaction exothermicities on average.

The mean absolute deviations are considerably larger, and now there is no longer good agreement with experimental results. All methods give mean absolute deviations on the order of 10 kcal/mol. Little or no improvement is seen when basis set size is increased for the Pople basis sets, whereas a significant improvement (5−6 kcal/mol less error) is obtained by increasing the correlation-consistent basis set to the triple zeta level. In contrast to the atomization energies, there is no longer any significant difference in the reaction energies when including the HF component to the exchange term. In fact, the B3 exchange functionals perform slightly worse than the "pure" Becke 88 exchange. Regarding the correlation functionals, P86 gives very minor improvements in the ΔH values compared to LYP and PW91, which are virtually indistinguishable in their performance. The best overall agreement is found at the BP86/cc-pVTZ//cc-pVDZ level of theory.

As with atomization energies, unusually large deviations are seen for reactions involving SO_2 and ClO_2. In these cases the best results are for the BLYP, BPW91, and BP86 functionals with the 6-31G(d,p) and cc-pVTZ basis sets, even extending to very good agreement with experimental results for the reaction

$$2OH + H_2S \rightarrow SO_2 + 2H_2$$

If, by analogy with the data for the atomization energies listed in Tables 2, the three reactions involving SO_2 and ClO_2 are removed, a dramatic improvement in mean absolute deviations is noted at all levels of theory. The mean deviations remain more or less unaltered. This is caused by a substantial underestimation in exothermicity for

$$2ClO_2 \rightarrow Cl_2 + 2O_2$$

being roughly the same as the overestimated exothermicities of the two reactions involving SO_2 (*vide infra*). The revised data for the mean absolute deviations are shown in Table 6c. A striking feature of this table is the small range in the numbers. For each basis set, there is almost no variation with the different functionals. Small improvements are seen when larger basis sets are employed, with the best overall performance given by BLYP/cc-pVTZ. Satisfactory performance can be obtained with either of the larger basis sets in combination with any of the functionals.

We further note that all methods give very good agreement with experimental results for reactions involving C−H or S−H bond formation. Agreement is poorer when there is formation or breakage of bonds to oxygen, and in these cases the B88 exchange functional usually outperforms B3.

Compared to the atomization energies, there tends to be a more even performance of the various methods for individual reaction enthalpies. For a given reaction, the differences in performance for the various functionals and basis sets are usually small.

IV. Conclusions

Atomization energies and reaction enthalpies have been investigated for 44 small molecules containing atoms of the first and second row and 14 reactions involving these molecules. Six different gradient-corrected DFT functionals (BLYP, B3LYP, BP86, B3P86, BPW91, and B3PW91) and four basis sets (6-31G(d,p), 6-311G(d,p), cc-pVDZ, and cc-pVTZ) have been employed.

For atomization energies, the best overall performance is found with the B3LYP functional closely followed by B3PW91. The B3LYP/cc-PVTZ (B3PW91/cc-PVTZ) mean and mean absolute deviations are −1.4 (0.9) kcal/mol and 3.2 (3.8) kcal/mol, respectively. The poorest overall agreement is observed with the BP86 functional, with both mean and mean absolute deviations in the 9−14 kcal/mol range. The remaining functionals and basis sets fall in an intermediate 6 ± 2 kcal/mol range for both the mean and mean absolute deviations. Overall, the correlation-consistent basis sets yield better agreement with experimental results relative to the Pople basis sets but at the expense of significantly increased computational times. The hybrid B3 exchange outperforms the pure B88 exchange, and of the correlation corrections the LYP and PW91 functionals yield essentially identical statistics.

For reaction enthalpies, all methods and basis sets are found to give excellent agreement for mean deviations (within 3 kcal/mol), whereas mean absolute deviations are considerably larger (up to 14 kcal/mol). In contrast to the atomization energies, the B88 exchange functional consistently gives more accurate data than does the B3 hybrid method. Of the three correlation corrections, P86 gives slightly better performance than LYP and PW91, which are virtually identical in performance.

For both groups of basis sets, a clear trend is observed in improved statistics when going from a DZP to a TZP quality basis. The improvement is in most cases in the 1−2 kcal/mol range, although for some functionals larger improvements occur, or, in a few cases, agreement even becomes worse. A large spread in terms of over- and underestimated energy differences is noted irrespective of functional and/or basis set for both the atomization energies and reaction enthalpies.

The largest deviations are observed for the hypervalent species SO_2, ClO_2 and CCl. These systems are known to be the major sources of deviation in the highly accurate G2 scheme of calculations, and for CCl it is likely that the experimental data are in error. Hence, when these systems (or reactions containing these as reactants or products) are removed from the statistics, mean absolute deviations in atomization energies improve by up to 1.5 kcal/mol and in reaction enthalpies by 3−8 kcal/mol. For the atomization energies, all methods but BP86 now lie in the 2−7 kcal/mol range in mean absolute deviations. B3LYP/cc-pVTZ is the most accurate with a deviation of only 2.2 kcal/mol. For the reaction enthalpies all methods generate mean absolute deviations of the improved set in the 3−9 kcal/mol range, with the best overall agreement at the BLYP/cc-pVTZ level (3.4 kcal/mol).

For the calculation of atomization energies, using the B3 hybrid exchange method is recommended in combination with either the LYP or PW91 correlation functional. For the calculation of reaction enthalpies, none of the correlation functionals can be ruled out, while for exchange a small advantage can be realized by choosing B88. For either quantity, of the basis sets tested here, the correlation-consistent sets preferably at the triple zeta level are recommended. If computational time is a concern, the smaller Pople type basis sets will also give satisfactory performance.

There are still unresolved problems in the use of DFT for energetics calculations. In particular, the issue of problems in the case of hypervalent compounds needs exploration. It is also apparent that if results of chemical accuracy are desired, the use of either larger, more flexible basis sets or those specifically optimized for use with DFT should be considered fully.

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Supporting Information Available: Tables A−F listing atomic energies, total energies, zero-point vibrational energies, thermal corrections to enthalpy, atomization energies, and reaction enthalpies (36 pages). Ordering information is given on any current masthead page.

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