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New Empirical Procedures for Improving ab Initio Energetics[†]

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Empirical schemes are developed for correcting the energies resulting from a moderately high-level ab initio calculation. Each method involves only a few adjustable parameters, which are determined by fitting a set of 31 high-spin atomization energies. Parameters are developed only for elements through the 2*p* block. The methods are based upon (1) bond lengths, (2) the electron densities at mid-bond critical points, (3) correlation energy scaling, (4) basis-set extrapolation, and (5) the number and spin of the valence electrons. A hybrid method, in which correlation energy is scaled by a factor that depends on the mid-bond electron densities, is also investigated. Each type of correction achieves a marked improvement over ab initio atomization energies; the first two are especially effective. Additional expressions are developed to represent the expected (1σ) uncertainties for predicted atomization energies.

Introduction

Ab initio calculations have become commonplace throughout physical chemistry. They are sufficiently reliable and inexpensive to be useful in experimental laboratories. One of the most successful areas of application has been molecular thermochemistry.[1] Nonetheless, routine calculations still do not offer accuracy competitive with good experimental measurements. Empirical corrections, in which one quantitative model describes the deficiencies of another, more fundamental model, have been useful in this area for some time.[2−5] As better fundamental (viz., ab initio) models are developed and popularized, new opportunities arise for developing empirical corrections to them. Furthermore, there are many alternative concepts upon which to build corrective models.

An earlier study investigated three empirical schemes for correcting ab initio bond dissociation energies.[6] All were found to be effective. In the present work, each of the three schemes is refined into a prescriptive method for computing the energies of chemical reactions. A fourth scheme, based upon parametric basis set extrapolation, a fifth, based upon the number and spin of electrons, and a sixth, hybrid scheme are also investigated. Attention is restricted to the light elements (up to the "first" row, or 2*p* block) because of problems identified for the heavier elements.[6] The six models are compared here on an equal footing, since they are parameterized and tested using the same set of reference data.

The first empirical method is based upon bond lengths, as in the successful BAC-MP4 method (bond-additive corrections to energetics from fourth-order perturbation theory) developed by Melius and co-workers.[3,7,8] The present model is much simpler than the original BAC-MP4 procedure because the base calculation that is reasonable today [CCSD(T)/cc-pVTZ] is much better than it could be at that time [MP4/6-31G(d,p)].

The second method is based upon the values of the electron density at the midbond critical points. It may be termed a "bond-density corrected" (BDC) procedure. This study is the first to use electron densities as the basis for a corrective model.

The third method is based upon the observation that correlated ab initio calculations generally recover a constant fraction of the contribution of dynamic electron correlation to the bond strengths. This has been systematized in the "scaling-all-correlation" (SAC) methods of Truhlar, Gordon, and co-workers[4,9,10] and the "parameterized configuration-interaction" (PCI) methods of Siegbahn, Blomberg, and co-workers.[11,12] As evident from the references, scaling methods have been developed to correct many choices of base calculation; the present study represents yet another such parameterization. Although not novel, it is included here for comparison.

The fourth method is based upon discrete basis set extrapolation using the series of basis sets developed by Dunning and co-workers.[13,14] For reasons of computational cost, only the smallest members of the series are considered, as suggested by Truhlar.[15] As for the third method, the present parameterization is undertaken for comparison with the first two methods.

The fifth method is based upon the number and spin of the valence electrons, as in the successful G2 family of corrective methods.[16]

The sixth method involves scaling of the correlation contribution, as in the SAC and PCI methods described above (method 3). However, the scaling factor is not taken as a constant, but as a linear function of the electron densities in the bonds, as in method 2.

Computational Details

The molecules used for method parameterization, which are intended to be representative of common 2*p*-block compounds, are listed in Table 1 along with their reference enthalpies of formation at zero temperature. The reference data were not thoroughly evaluated but are believed to be sufficiently reliable, at least in the aggregate, for developing useful parameters. The quality of the final models is tested using a different set of molecules. No attempt has been made to optimize or vary the partitioning between the training set and the testing set. Atomization energies are used as the target quantities for parameterization because they are challenging for ab initio theory. Thus, they are presumed to be relatively sensitive to

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TABLE 1: Reference Data (ideal gas) for the Training Set of Molecules[a]

molecule	$\Delta_f H_0^\circ$ (kJ/mol)	ref	molecule	$\Delta_f H_0^\circ$ (kJ/mol)	ref
H	216.035(6)	37	OH	37.14(06)	43
C	711.19(45)	37	H_2O	−238.92(4)	37
C (^{5}S)	1114.75(45)	37,31	CO	−113.81(17)	37
N	470.82(40)	37	CO_2	−393.15(13)	37
O	246.8(1)	37	N_2	0	37
F	77.27(30)	37	NH_3	−38.95(35)	37
HCN	129.9(5)	44	NO	90.77(22)	45
NO_2	37.00(25)	45	F_2	0	37
CF_4	−927.23(38)	45	HF	−273.3(7)	37
CH	594.03(65)	45	CH_3	150.04(15)	46
CH ($^4\Sigma^-$)	665.63(65)	45,32	CH_4	−66.63(15)	45
CH_2	389.9(4)	46	C_2H_4	60.92(25)	45
C_2H_2	228.0(4)	45	C_3H_4 (allene)	198.0(6)	47,48,37
C_2H_6	−68.4(2)	45	cy-C_3H_6	70.40(25)	47,48,37
C_3H_5 (allyl)	184.5(21)	49	O_2	0	37
C_6H_6 (benzene)	100.10(35)	47,48,37	$B(OH)_3$	−991.0(12)	45
O_3	144.5(10)	45	HOOH	−129.89(11)	45
B (^{4}P)	915.2(4)	50,51	BF_3	−1133.2(8)	37
NF_3	−125.9(5)	45	CH_3OH	−190.1(3)	45
CH_2O	−104.86(25)	45			

[a] Reported uncertainties in the least significant digits (in parentheses) are assumed to represent the standard uncertainty (1σ).

TABLE 2: Spin−Orbit Corrections to Computed Energies

molecule	E_{SO} (kJ mol^{-1})	ref
B (^{4}P)	−0.09	31
C	−0.35	31
CH	−0.17	32
F	−1.61	31
NO	−0.74	32
O	−0.93	31
O_2	−0.03	32
OH	−0.83	32

the values of the adjustable parameters. To avoid biasing the fit in favor of large molecules, the target quantity for each molecule is its atomization energy (at zero temperature) divided by the number of bonds, i.e., its average bond dissociation energy, denoted $\bar{D}_0$. Parameter values (see below) were determined by unweighted least-squares fitting.

Wherever reasonable, the high-spin dissociated limit was used for calculating atomization energies. This procedure is intended to isolate most of the correlation error in the bonded, molecular calculation and not to reflect spin recoupling in the isolated atoms. For example, the BF_3 molecule is dissociated to three F atoms and a B atom in its excited ^{4}P state.

Some of the empirical corrections considered here involve a sum over all chemical bonds in the molecule. Each adjustable parameter, say X_{ij}, carries one index for each atom involved in the bond in question. However, atoms are not distinguished by atomic number but by the value of their valence principal quantum number, n. For example, a parameter for bonds between carbon or oxygen ($n = 2$) and hydrogen ($n = 1$) may be called X_{12}. This coarse distinction among elements avoids the proliferation of adjustable parameters. Each empirical correction, ΔE, is applied to the zero-point adjusted coupled-cluster energy, E_C, to provide a total molecular energy, E. This is shown by eq 1, where E_{SO} is the spin−orbit contribution missed by our nonrelativistic calculations. E_{SO} is the difference between the mean energy of a term and the energy of its lowest level; values are collected in Table 2.

$$E = E_C + E_{SO} + \Delta E \tag{1}$$

The first procedure is based upon bond lengths and may be termed BLC-CCSD(T), where the prefix indicates "bond-length corrected." The form of the correction for a molecular energy is given by eq 2, where i and j refer to the types of atoms involved in the bond, A_{ij} and α_{ij} are parameters, and r_{ij} is the length of the bond. A_{ij} has a negative value and α_{ij} has a positive value.

$$\Delta E_{BLC} = \sum_{\text{bonds}} A_{ij} \exp(-\alpha_{ij} r_{ij}) \tag{2}$$

The second procedure is based upon electron density and may be denoted BDC-CCSD(T), meaning "bond-density corrected." It has the form given by eq 3, where a_{ij} and b_{ij} are parameters and ρ_{ij} is the electron density at the bond critical point. In this case, b_{ij} has a negative value but a_{ij} may have any value near zero.

$$\Delta E_{BDC} = \sum_{\text{bonds}} (a_{ij} + b_{ij}\rho_{ij}) \tag{3}$$

The third procedure, termed SAC-CCSD(T), is based upon the assumption that a particular type of correlated calculation will always recover the same fraction, F, of the correlation energy, regardless of the molecule. The correction has the form given by eq 4, where F is a parameter and E_{HF} and E_C are Hartree−Fock and coupled-cluster energies, respectively. No structural information is included.

$$\Delta E_{SAC} = \left(\frac{1 - F}{F}\right)(E_C - E_{HF}) \tag{4}$$

The fourth correction scheme involves basis-set extrapolation, with independent parameters for the Hartree−Fock and the correlated contributions to the energy. The method is labeled DLE-CCSD(T), where the prefix indicates "dual-level extrapolation."[15] The correction is given by eq 5, where the energy subscripts denote either Hartree−Fock (HF) or CCSD(T) (C) energies combined with either cc-pVDZ (DZ) or cc-pVTZ (TZ) basis sets. The adjustable parameters are α and β, which were chosen for compatibility with the literature. However, the expression is simplified by using the alternative parameters a and b, as shown in eq 5. No structural information is included.

$$\Delta E_{\mathrm{DLE}} = (a - b)(E_{\mathrm{HF/TZ}} - E_{\mathrm{HF/DZ}}) + (b - 1)(E_{\mathrm{C/TZ}} - E_{\mathrm{C/DZ}})$$

$$a \equiv \frac{3^{\alpha}}{3^{\alpha} - 2^{\alpha}}$$

$$b \equiv \frac{3^{\beta}}{3^{\beta} - 2^{\beta}} \qquad (5)$$

The fifth correction is based upon the numbers of paired and unpaired valence electrons, as in the G2 and related methods.[16] It is denoted here ECC-CCSD(T), meaning “electron-count corrected.” Equation 6 shows the form of the correction, where N_{α} and N_{β} are the numbers of valence up- and down-spin electrons, respectively, under the convention $N_{\alpha} \geq N_{\beta}$. The adjustable parameters are A and B. No structural information is included.

$$\Delta E_{\mathrm{ECC}} = A(N_{\alpha} - N_{\beta}) + BN_{\beta} \qquad (6)$$

The sixth correction scheme is a hybrid. All correlation energy is scaled, as in the third procedure, but the scaling factor depends on weighted, averaged electron densities at the bond critical points. So the correction involves eq 4, but where F depends on the densities as shown in eq 7, where N_{bonds} is the total number of bonds of all types. The adjustable parameters are F_0 and F_{ij}. This formulation is independent of the chemical reaction under study, that is, the correction is intrinsic to the molecule. This density-dependent procedure is termed DDSAC-CCSD(T).

$$F = F_0 + \sum_{ij} F_{ij} d_{ij}$$

$$d_{ij} = N_{\mathrm{bonds}}^{-1} \sum_{ij\text{-bonds}} \rho_{ij} \qquad (7)$$

Molecular geometries were computed using the B3LYP hybrid DFT method[17,18] and 6-31G(d) basis sets. Harmonic vibrational frequencies were also calculated at this level; their sum was scaled by 0.9806 and divided by 2 to obtain vibrational zero-point energies (ZPE).[19] All vibrational frequencies were real-valued. Electron densities were computed using the BLYP functional[20,21] and 6-311+G(d,p) basis sets. Densities were analyzed using the “atoms-in-molecules” (AIM) topological approach developed by Bader and co-workers,[22] as implemented in the Gaussian program package.[23−25] BLYP was used instead of B3LYP because of a weak preference for “pure” DFT densities.[26] The AIM analysis was used to identify the bonds in each molecule, and also to compute the density at the corresponding bond critical points. Electronic energies were computed using the coupled-cluster CCSD(T) theory[27] and the cc-pVTZ basis sets.[28] The ACES II program suite[29,30] was used for the larger coupled-cluster calculations and Gaussian 94[23] or Gaussian 98[24] was used for all other calculations.[25] Core electrons (K-shell) were uncorrelated in the coupled-cluster calculations. Thus, core correlation effects are absorbed into the fitting constants for each empirical correction procedure. All DFT computations employed the default integration grid. All open-shell calculations were spin-unrestricted. Spin−orbit corrections were taken from compilations of experimental data.[31,32]

The atomization energy, including spin−orbit corrections, was computed for each of the molecules in Table 1. Experimental and uncorrected values [HF and CCSD(T) using both cc-pVDZ and cc-pVTZ basis sets, with B3LYP/6-31G(d) ZPEs included] are listed in Table S1 of the Supporting Information. Bond lengths and electron densities, which are needed for some of the correction procedures, are collected in Table S2 (Supporting Information). As described above, the target quantity, $\bar{D}_0$, is the atomization energy divided by the number of bonds in the molecule. Accepting the experimental values as correct, the error in the theoretical quantity for each molecule is listed in Table 3. Parameter values for the various correction schemes are determined by minimizing the sum of the squares of these errors.

Parameter Values and Estimated Uncertainties. *BLC-CCSD(T).* When restricted to light atoms of $Z \leq 10$, as here, this method has four adjustable parameters (eq 2). The optimized value of each (A_{ij},α_{ij}) pair is insensitive to the value of the other pair, but within each pair the parameter values show a strong interdependence. Although the minimization process reveals a shallow minimum, the parameter values $A_{12} = -210$ kJ mol^{-1}, $\alpha_{12} = 2.62$ Å^{-1}, $A_{22} = -2100$ kJ mol^{-1}, and $\alpha_{22} = 3.45$ Å^{-1} can be recommended. The resulting errors in $\bar{D}_0$ are listed in Table 3 for each molecule, along with the mean error, the mean unsigned error (that is, the mean of the absolute values of the errors), and the rms error (that is, the square root of the mean of the squares of the errors).

The uncertainty is an essential part of any prediction or measurement. It is reasonable to estimate the uncertainty based upon fitting statistics. For example, one might estimate the standard uncertainty as the rms error of the fit. However, the errors frequently exhibit trends that allow an uncertainty estimate to be tailored to the chemical reaction of interest, which should yield a more reliable value.

For example, the BLC-CCSD(T) errors may be plotted against the corresponding corrections. This graph does show a trend (correlation coefficient = 0.61), which suggests adopting the estimated standard uncertainty given in eq 8. The term σ_{BLC} is the estimated standard uncertainty of an arbitrary prediction and ΔE_{BLC} is the corresponding correction from eq 2 (used to obtain the corresponding BLC value in Table 3). The coefficient (0.12) was chosen so that about two-thirds of the errors in Table 3 would be in the range $(-\sigma, \sigma)$ and about 95% would be in $(-2\sigma, 2\sigma)$. Of the 31 molecules in the training set (Table 1), 20 errors are less than $1\sigma_{\mathrm{BLC}}$ and 31 are less than $2\sigma_{\mathrm{BLC}}$. The two largest errors, with 2σ uncertainties estimated by eq 8, are (7.8 ± 10.0) kJ mol^{-1} (for CO) and (−5.6 ± 6.4) kJ mol^{-1} (for O_3).

$$\sigma_{\mathrm{BLC}} = 0.12|\Delta E_{\mathrm{BLC}}| \qquad (8)$$

The errors also show some correlation (correlation coefficient = 0.25) with the T_1 diagnostic proposed by Lee and co-workers.[33−35] Thus, an alternative choice is $\sigma_{\mathrm{BLC}} = 200T_1$ kJ mol^{-1}, for which 21 errors are less than $1\sigma_{\mathrm{BLC}}$ and 29 are less than $2\sigma_{\mathrm{BLC}}$.

One desirable feature of any parameterized method is the ability to estimate the values of missing parameters.[36] In addition to extending the domain of the method, it increases confidence that there is a sound physical basis for the corrective procedure. For each method in this study, parameters are estimated for H_2 for this reason only. For a parameter X_{ij}, the appropriate value in the H_2 molecule ($i = j = 1$) is X_{11}. It is estimated here either by linear extrapolation ($X_{11} = 2X_{12} - X_{22}$) or by geometric extrapolation ($X_{11} = X_{12}^2/X_{22}$). For reference, the experimental[37] and uncorrected CCSD(T)/cc-pVTZ//B3LYP/6-31G(d) values of $\bar{D}_0$ for H_2 are 432.1 and 427.4 kJ mol^{-1}, respectively.

TABLE 3: Errors in Computed Values of $\bar{D}_0$ for the Training Set[a]

molecule	uncert	CCSD(T)	BLC	BDC	SAC	DLE	DDSAC	ECC	G2
BF_3	0.4	−17.7	4.6	−3.9	−0.4	10.7	−1.0	−1.4	3.3
C_2H_2	0.3	−23.1	−3.6	−5.3	−0.2	1.6	−1.5	4.1	−0.8
C_2H_4	0.2	−14.3	−0.3	0.1	1.3	1.8	0.4	5.3	0.6
C_2H_6	0.1	−10.7	1.0	1.7	1.9	2.2	1.1	5.6	0.9
C_3H_4	0.2	−17.4	−1.6	−1.5	0.7	1.1	−0.4	4.3	0.4
C_3H_5	0.2	−14.5	−0.8	0.2	0.7	1.5	−0.2	4.1	0.5
C_6H_6	0.2	−17.2	−2.7	−0.6	0.1	−0.3	−1.0	3.1	−0.4
CF_4	0.3	−17.2	4.2	3.1	1.5	4.9	1.4	−0.9	6.4
CH	0.8	−9.2	1.6	2.2	1.0	5.7	1.4	7.1	3.6
CH_2	0.3	−13.4	−1.0	−1.3	0.1	2.5	−0.5	2.9	−2.0
CH_2O	0.2	−17.7	0.8	−0.3	1.4	0.6	0.9	4.0	3.5
CH_3	0.2	−11.1	1.2	1.1	1.6	3.7	0.9	5.2	0.8
CH_3OH	0.1	−12.7	0.9	1.4	0.8	2.6	0.4	3.6	1.5
CH_4	0.1	−10.0	1.9	1.7	2.1	3.0	1.4	6.2	1.3
CO	0.5	−33.6	7.8	−0.2	−1.9	−7.5	−1.5	−1.1	7.7
CO_2	0.3	−33.9	3.3	−2.6	−0.4	−5.2	−1.1	−1.3	6.7
cy-C_3H_6	0.2	−12.1	−0.1	1.2	1.1	1.3	0.2	4.2	0.3
F_2	0.6	−18.8	−2.2	−0.3	9.9	3.1	9.9	−2.5	−1.4
H_2O	0.1	−16.0	0.6	0.7	−1.6	4.5	−1.0	0.3	0.6
$B(OH)_3$	0.2	−15.6	1.9	−0.5	−0.7	2.9	−0.9	0.6	1.3
HCN	0.4	−30.0	−4.2	−7.1	−2.1	−2.7	−3.1	2.6	0.5
HF	0.8	−19.4	−1.2	−2.8	−2.6	8.0	−0.1	−3.1	3.7
HOOH	0.1	−15.4	0.1	1.9	1.4	3.2	1.7	0.8	−0.3
N_2	0.8	−51.5	−5.2	−4.7	−10.0	−10.7	−8.9	−2.7	−5.1
NF_3	0.4	−20.5	−2.8	1.1	0.5	4.0	0.5	−4.2	5.3
NH_3	0.2	−13.9	0.6	1.2	−1.9	3.4	−2.0	2.4	−0.3
NO	0.5	−39.8	−1.3	0.4	−3.1	−10.4	−2.0	−7.3	3.2
NO_2	0.3	−32.8	0.2	3.0	−0.6	−7.4	−0.3	−8.4	2.1
O_2	0.2	−29.6	2.2	7.1	3.5	−4.3	4.9	−13.4	−10.1
O_3	0.5	−32.4	−5.6	−0.5	6.0	−6.3	5.6	−7.9	1.9
OH	0.1	−15.0	1.0	1.2	−0.6	6.9	1.1	1.2	1.3
mean		−20.5	0.1	−0.1	0.3	0.8	0.2	0.4	1.2
MUE		20.5	2.1	2.0	2.0	4.3	1.9	3.9	2.5
rms		22.8	2.8	2.7	3.1	5.2	3.0	4.8	3.5

[a] Uncertainties are for the experimental quantities and are believed to represent the standard uncertainty (1σ). Mean errors, mean unsigned errors ("MUE"), and root-mean-square errors ("rms") are included. Values are in kJ mol^{-1}.

For example, for the BLC−CCSD(T) method, geometric parameter extrapolation suggests $A_{11} = -21$ kJ mol^{-1} and $\alpha_{11} = 2.0$ Å^{-1}. The corresponding BLC ($r_{calc} = 0.743$ Å) prediction of (432.2 ± 1.1) kJ mol^{-1} (est. 2σ) is surprisingly good. Linear extrapolation of parameters must be dismissed because it yields an unreasonable, positive value for A_{11}.

BDC-CCSD(T). This procedure also has four adjustable parameters (eq 3). As for the BLC correction, parameters are interdependent within an (a_{ij},b_{ij}) pair but not across pairs. The minimum in parameter space is, again, rather shallow. Recommended parameter values are $a_{12} = 3.1$ kJ mol^{-1}, $b_{12} = -55$ kJ mol^{-1} a$_0^3$, $a_{22} = 0.9$ kJ mol^{-1}, and $b_{22} = -72$ kJ mol^{-1} a$_0^3$ (a$_0 \approx 5.291772 \times 10^{-11}$ m). Graphing the errors (Table 3) against the corrections, as before, shows only a weak correlation, suggesting a constant value for the estimated standard uncertainty of $\sigma_{BDC} = 2.5$ kJ mol^{-1}. Of the 31 molecules in the training set, 22 errors are less than $1\sigma_{BDC}$ and 28 are less than $2\sigma_{BDC}$. Alternatively, the same results are obtained using the estimate given in eq 9 (correlation coefficient = 0.32), which is analogous to that for the BLC procedure. The two largest errors ($\pm 2\sigma$ estimated by eq 9) are (7.1 ± 8.8) kJ mol^{-1} (for O_2) and (-7.1 ± 5.4) kJ mol^{-1} (for HCN).

$$\sigma_{BDC} = 0.12|\Delta E_{BDC}| \qquad (9)$$

For H_2, the mid-bond electron density $\rho = 0.262$ a$_0^{-3}$. Linear parameter extrapolation yields good results for H_2: (432.0 kJ $\pm$ 1.1) mol^{-1} (est. 2σ) for $a_{11} = 5.3$ kJ mol^{-1} and $b_{11} = -38$ kJ mol^{-1} a$_0^3$. A poorer prediction of (427.7 ± 0.1) kJ mol^{-1} is obtained from geometric extrapolation of parameters.

SAC-CCSD(T). The sum of the squared errors is very sensitive to the single adjustable parameter F (eq 4). The value $F = 0.912$ is recommended. Graphing the errors (Table 3) as before suggests adopting an estimated standard uncertainty as given in eq 10 (correlation coefficient = 0.58). Of the 31 molecules in the training set, 23 errors are less than $1\sigma_{SAC}$ and 30 are less than $2\sigma_{SAC}$. The two largest (± est. 2σ from eq 10) are (-10.0 ± 10.0) kJ mol^{-1} (for N_2) and (9.9 ± 6.8) kJ mol^{-1} (for F_2).

$$\sigma_{SAC} = 0.12|\Delta E_{SAC}| \qquad (10)$$

In the case of H_2, using $F = 0.912$ overcorrects by about 100%, leading to a poor prediction of $\bar{D}_0 = (437.3 \pm 2.4)$ kJ mol^{-1} (est. 2σ). The value $F = 0.956$ yields the correct result for H_2.

DLE-CCSD(T). There are two adjustable parameters (eq 5). Minimizing the squared errors shows a moderately shallow minimum and that α and β are mutually dependent. Recommended values are $\alpha = 2.18$ and $\beta = 2.55$. The errors (Table 3) can be estimated using eq 11 (correlation coefficient = 0.74), for which 18 molecules of the training set are less than $1\sigma_{DLE}$ and 31 are less than $2\sigma_{DLE}$. The three largest errors (± est. 2σ from eq 11) are (-10.7 ± 16.4), (10.7 ± 11.4), and (-10.4 ± 11.8) kJ mol^{-1} for N_2, BF_3, and NO, respectively.

$$\sigma_{DLE} = 0.20|\Delta E_{DLE}| \qquad (11)$$

For H_2, these parameter values lead to a prediction of $\bar{D}_0 = (438.5 \pm 4.5)$ kJ mol^{-1} (est. 2σ), overshooting by more than 100%.

ECC-CCSD(T). Although there are two adjustable parameters (eq 6), least-squares optimization reveals that they are redundant.

TABLE 4: Reference Data (ideal gas) for the Atomization Test Set of Molecules[a]

molecule	$\Delta_f H_0^\circ$ (kJ/mol)	ref	molecule	$\Delta_f H_0^\circ$ (kJ/mol)	ref
B_2H_6	52.4(10)	45	CH_2CO	−46.40(45)	46
cy-C_2H_4O	40.1(3)	51	CH_3NO_2	−60.8(3)	47,48
CH_3CHO	−155.40(25)	47,52	F_2O	26.75(80)	45
CHOCHO	−206.40(25)	53	N_2H_4	109.34(25)	45
furan	−21.80(35)	47,54	NO_3	79.0(7)	55
N_2O	85.03(25)	45			

[a] Reported uncertainties in the least significant digits (in parentheses) are believed to represent the standard uncertainty (1σ).

That is, the same quality of fit can be obtained even when one parameter is fixed arbitrarily. As done in the G2 method,[16] the first parameter is chosen here such that the correct energy (−1/2 hartree) is obtained for the H atom: $A = -0.00019$ hartree. Optimization of the second parameter then gives $B = -0.00658$ hartee. The errors show no obvious trends. They can be estimated as $\sigma_{ECC} = 4.2$ kJ mol^{-1} for $\bar{D}_0$ for all molecules. This choice places 20 of the molecules within $1\sigma_{ECC}$ and 29 within $2\sigma_{ECC}$ of the experimental values. The largest error is for O_2: (−13.4 ± 8.4) kJ mol^{-1} (est. $\pm 2\sigma$). In the case of H_2, these values of A and B lead to $\bar{D}_0 = (443.6 \pm 8.4)$ kJ mol^{-1} (est. 2σ), which overshoots by more than 200%.

DDSAC-CCSD(T). There are three adjustable parameters (eq 7) for this set of molecules. Parameter optimization shows fair sensitivity to the parameter values and that those values are interdependent. Recommended values are $F_0 = 0.921$, $F_{12} = -0.014$, and $F_{22} = -0.007$. The errors, listed in Table 3, can be estimated using eq 12 (correlation coefficient = 0.62), for which 23 molecules of the training set are less than $1\sigma_{DDSAC}$ and 30 are less than $2\sigma_{DDSAC}$. The largest errors (± est. 2σ) are (9.9 ± 6.3) and (−8.9 ± 9.4) kJ mol^{-1} for F_2 and N_2, respectively.

$$\sigma_{DDSAC} = 0.11|\Delta E_{DDSAC}| \qquad (12)$$

For H_2, linear parameter extrapolation ($F_{11} = -0.021$) predicts $\bar{D}_0 = (436.9 \pm 2.1)$ kJ mol^{-1} (est. 2σ), again overshooting by about 100%. The value $F_{11} = 0.135$ yields the correct dissociation energy for H_2.

Test Sets. *Atomization Energies*. The parameterization process described above involves fitting the various parametric corrections to a "training set" of accepted data (Table 1). A test of predictive ability must involve different molecules; the present "test set" is listed in Table 4 along with reference thermochemical data. As for the training set, the target quantity, $\bar{D}_0$, is the atomization energy divided by the number of bonds in the molecule (as identified from topological analysis of the electron density). The results of the test are collected in Table 5, which may be compared with the training results in Table 3. Inspecting Table 5 suggests that the uncertainty estimates are too conservative, since more than two-thirds of the values lie within $\pm 1\sigma$. On the other hand, the BDC-CCSD(T) prediction for B_2H_6 lies 3.9σ from the experimental value, primarily because the estimated uncertainty ($\sigma = 0.6$ kJ mol^{-1}) is unrealistically small. This suggests that a small constant should be added to the uncertainty estimates. Unfortunately, the present data set is too small for developing meaningful parameters at this level of detail.

Isogyric Reactions. As mentioned earlier, atomization reactions are useful for parameterization because they exacerbate systematic errors in the underlying theory. Conversely, atomization reactions should be avoided when accurate thermochemistry is desired.[38,39] Isogyric reactions, which conserve total electron spin, are preferred. Isodesmic reactions, in which the number of bonds of each chemical type is preserved, are even better, but are often precluded by a lack of auxiliary reference data. A set of isogyric reactions, some of which are also isodesmic, is listed in Table 6 along with experimental enthalpy changes. Even from this limited set of reactions, it is apparent that (1) the empirical corrections improve the results most of the time, and (2) the errors are much larger than would be expected from the estimates for atomization (eqs 8−12), except for the ECC scheme. Specifically, the number of errors within the atomization 2σ uncertainties is 0, 1, 2, 1, 0, and 9 for the BLC, BDC, SAC, DLE, DDSAC, and ECC corrections, respectively. However, the uncorrected results are quite good, the improvements are small, and the corrections sometimes increase the error relative to experiment. Thus, correcting the energetics of such reactions does not appear to be particularly worthwhile.

Adiabatic Ionization Energies. Ionization involves changing the total number of electrons without breaking any bonds, thus testing the various correction methods in a way for which they were not designed. A set of experimental adiabatic ionization energies, IE_a, is collected in Table 7. Most of the corrections perform poorly, frequently making the results worse. Only two

TABLE 5: Errors in Computed Values of $\bar{D}_0$ for the Atomization Test Set[a]

molecule	uncert	CCSD(T)	BLC	BDC	SAC	DLE	DDSAC	ECC	G2
B_2H_6	0.2	−7.7	0.2	−2.5	1.0	1.3	0.3	4.5	1.0
C_2H_4O	0.1	−13.3	−0.2	1.1	0.8	1.5	0.0	3.0	1.3
CH_2CO	0.3	−22.0	−1.0	−2.8	−0.1	−1.0	−1.1	2.4	1.3
CH_3CHO	0.2	−15.2	−0.1	0.2	0.9	0.6	0.1	3.7	1.6
CH_3NO_2	0.1	−18.4	−0.2	2.0	0.0	−0.7	−0.5	0.6	2.4
CHOCHO	0.2	−20.4	−0.7	−0.8	0.8	−1.2	0.0	2.3	3.2
F_2O	0.5	−19.8	−3.6	−0.1	5.6	3.1	5.2	−3.5	1.0
furan	0.2	−17.5	−1.8	−0.6	0.3	−0.1	−0.7	2.4	0.4
N_2H_4	0.2	−15.1	−0.5	1.3	−2.6	1.7	−2.7	1.2	−0.9
N_2O	0.4	−36.5	1.6	1.1	−2.3	−6.7	−2.3	−4.0	−1.4
NO_3	0.3	−31.0	−1.8	2.9	0.5	−6.3	0.4	−9.3	−3.9
mean		−19.7	−0.7	0.2	0.4	−0.7	−0.1	0.3	0.5
MUE		19.7	1.1	1.4	1.4	2.2	1.2	3.4	1.7
rms		21.2	1.5	1.7	2.1	3.1	2.0	4.0	2.0
$n_{1\sigma}$			10	9	9	9	9	9	
$n_{2\sigma}$			11	10	11	11	11	10	

[a] Uncertainties are from the experimental quantities and are believed to represent the standard uncertainty (1σ). Mean errors, mean unsigned errors ("MUE"), and root-mean-square errors ("rms") are included. Compared with the estimated standard uncertainty for each prediction, σ, the number of predictions within $\pm 1\sigma$ is given by $n_{1\sigma}$ and the number within $\pm 2\sigma$ is given by $n_{2\sigma}$. Values are in kJ mol^{-1}.

TABLE 6: Isogyric Reaction Test Set

reaction	uncert	CCSD(T)	BLC	BDC	SAC	DLE	DDSAC	ECC	G2
$C_2H_4O \rightarrow CH_3CHO$	0.4	−1.4	−0.5	6.6	0.1	6.9	−0.6	−1.4	−0.1
$CH_2CO + CH_4 \rightarrow C_2H_4 + CH_2O$	0.6	−3.7	2.7	−4.3	−3.1	−2.9	−3.5	−3.7	−3.0
$CH_3CHO + CH_4 \rightarrow C_2H_6 + CH_2O$	0.4	−3.8	−2.7	−3.3	−3.8	−1.9	−4.0	−3.8	−1.6
$CH_3NO_2 + H \rightarrow CH_4 + NO_2$	0.4	−4.6	−9.5	−0.6	−7.1	−1.0	−7.6	−4.6	4.9
$CHOCHO + 2CH_4 \rightarrow C_2H_6 + 2CH_2O$	0.7	−1.7	−0.5	−1.1	−1.1	−1.2	−1.9	−1.7	−0.3
$F_2O + O \rightarrow F_2 + O_2$	0.8	8.8	−7.0	−7.0	−2.2	7.6	−4.4	8.8	13.5
furan + $4CH_4 + H_2O \rightarrow 2C_2H_4 + C_2H_6 + 2CH_3OH$	1.1	−5.2	3.0	−3.8	−1.5	−3.9	−2.0	−5.2	−1.5
$N_2H_4 \rightarrow (4/3)NH_3 + (1/3)N_2$	0.5	−2.7	−3.4	3.4	−1.8	−1.5	−2.5	−2.7	−1.4
$N_2O + NO \rightarrow N_2 + NO_2$	0.4	4.3	6.6	1.2	3.3	1.6	3.0	4.3	1.2
$NF_3 \rightarrow (1/2)N_2 + (3/2)F_2$	0.5	−7.6	−2.4	6.0	−8.2	12.7	−8.9	−7.6	20.4
mean		−1.8	−1.4	−0.3	−2.5	1.6	−3.2	−1.8	3.2
MUE		4.4	3.8	3.7	3.2	4.1	3.8	4.4	4.8
rms		4.9	4.7	4.3	4.1	5.5	4.6	4.9	8.0
number improved			7	7	7	8	6	0	

[a] Uncertainties are from the experimental quantities and are believed to represent the standard uncertainty (1σ). Mean errors, mean unsigned errors ("MUE"), root-mean-square errors ("rms"), and the number of errors reduced by each empirical correction ("Number improved") are included. Energies are in kJ mol^{-1}.

TABLE 7: Experimental Ionization Energies and Theoretical Deviations Therefrom[a]

molecule	expt	uncert	CCSD(T)	BLC	BDC	SAC	DLE	DDSAC	ECC	G2
C_2H_2	1099.9	0.096	−13.2	−7.2	−11.7	0.6	3.1	−0.2	3.5	2.1
C_2H_4	1014.4	0.029	−12.7	−6.7	−12.1	2.7	1.7	1.7	4.1	6.1
C_3H_4	935.1	0.193	−9.5	−6.7	14.8	3.4	3.9	3.1	7.3	4.0
CH_2	1003.1	0.145	−10.2	−9.1	−34.7	−4.4	−0.2	−5.2	−9.7	−8.1
CH_2CO	927.9	0.145	−17.2	−16.9	−18.7	−6.0	2.3	−6.9	−0.5	−2.5
CH_3CHO	986.9	0.034	−15.2	−15.1	−13.3	−2.2	3.2	−3.0	1.6	7.7
CO_2	1329.3	0.048	−21.2	−18.2	−20.2	−9.4	0.8	−10.1	−4.4	−6.7
H_2O	1217.7	0.096	−29.3	−10.9	−23.9	−15.1	2.4	−15.3	−12.5	0.8
N_2	1503.3	0.386	−16.7	−14.9	−9.5	−18.9	3.5	−17.9	0.1	−1.6
N_2O	1243.6	0.193	−19.0	−16.6	−18.6	−3.1	0.7	−4.1	−2.2	3.3
NO	893.9	0.001	−15.9	−29.2	−26.3	−15.9	−1.8	−17.3	−15.4	1.7
NO_2	924.9	0.096	−22.4	−41.7	−35.8	−24.2	−9.3	−25.5	−21.9	1.0
O_2	1164.5	0.010	−16.7	−28.7	−28.4	−19.8	−3.3	−21.3	−16.2	9.7
OH	1255.9	0.010	−28.7	−26.3	−25.2	−15.3	1.7	−15.5	−11.9	−3.9
mean			−17.7	−17.7	−18.8	−9.1	0.6	−9.8	−5.6	1.0
MUE			17.7	17.7	20.9	10.1	2.7	10.5	8.0	4.2
rms			18.6	20.3	22.5	12.6	3.4	13.1	10.3	5.1
improved				11	8	10	14	10	14	

[a] Uncertainties are for the experimental quantities and are believed to represent the standard uncertainty (1σ). Mean errors, mean unsigned errors ("MUE"), root-mean-square errors ("rms"), and the number of errors reduced by each empirical correction ("improved") are included. Energies are in kJ mol^{-1}.

methods consistently improve the CCSD(T) results: dual-level basis-set extrapolation (DLE) and electron-count (ECC). Of these two, the DLE correction is better, reducing the rms error from 18.6 kJ mol^{-1} to only 3.4 kJ mol^{-1}.

Discussion

These six correction schemes have been parameterized for mean, high-spin bond dissociation energies. Tables 3 and 5 show that all six schemes are effective in improving ab initio energetics for such processes. When the largest errors are considered, the BLC and BDC methods appear slightly better than the other methods. Furthermore, when parameters for H_2 are guessed by extrapolation of the other parameters, results are good only for those two methods. Thus, the BLC and BDC procedures are preferred for bond dissociation reactions.

The BLC correction is based upon the BAC-MP4 method developed by Melius and co-workers.[3,8] However, many fewer parameters are needed here because the present CCSD(T)/cc-pVTZ calculations are much more accurate (and expensive) than are the MP4/6-31G(d,p) calculations underlying BAC-MP4. The success of parameter extrapolation for H_2 suggests that the number of parameters might be limited further by expressing two-index parameters in terms of single-index parameters (e.g., $A_{ij} = A_iA_j$ and $b_{ij} = b_i + b_j$).[40] However, results for heavier elements ($n \geq 3$) are needed before this simplification can be evaluated.[41]

For isogyric or isodesmic reactions, Table 6 shows that the uncorrected CCSD(T)/cc-pVTZ results are already quite good. Note that the rms errors in Table 6 are for the total reaction enthalpy, whereas those in Tables 3 and 5 are on a per-bond basis. Improvements due to empirical corrections are minor and somewhat inconsistent, so they cannot be recommended for isogyric reactions. For isogyric reactions, the empirical correction is zero in both the ECC and G2 procedures ($\Delta N_\alpha = \Delta N_\beta = 0$).

For ionization energies, Table 7 shows that only the basis-set extrapolation (DLE) and electron-count (ECC) corrections consistently improve the ab initio results. The DLE correction is clearly the most effective. The poor performance of the BLC, BDC, and DDSAC methods can be rationalized by their formulation in terms of chemical bonds. Since molecular ionization usually involves a nonbonding orbital, the bonds are not usually relevant. The relatively good results from the BLC correction for C_2H_2, C_2H_4, and C_3H_4 are consistent with this interpretation, since those are the only molecules in Table 7 that are ionized from bonding orbitals. Likewise, the BLC correction is a disaster for NO, O_2, and NO_2, for which ionization is from antibonding orbitals.

The ECC correction is of the same form used in the G2 procedure.[16] However, the ECC ionization energies are much worse than the G2 results (Table 7). This is probably because the ECC procedure lacks diffuse basis functions, which are important for the ionization energy of molecules with polar bonding.[42] Diffuse functions are included economically in the G2 procedure by estimating their effects using low-level theory. Moreover, ionization energies were included in the parameterization of the G2 procedure.

Conclusions

All the empirical corrections considered here are effective in reducing the errors in ab initio [CCSD(T)/cc-pVTZ] thermochemistry for high-spin atomization or dissociation reactions. The BLC (based upon bond lengths) and BDC (based upon bond electron densities) procedures provide the best results for such reactions. For well-balanced, isogyric reactions, the empirical corrections offer little benefit. For adiabatic ionization energies, only the DLE (basis-set extrapolation) correction is recommended. Each empirical method is accompanied by a means for estimating the standard uncertainty of its predictions for bond dissociation.

In the correction procedures, atoms are distinguished only by their valence principal quantum number (n), or not at all. Avoiding fine distinctions (e.g., by element) serves to avoid a proliferation of fitting parameters, thus increasing the predictive domain and reducing the size of the experimental database required. As more complicated methods are developed, it will be increasingly challenging to limit the number of adjustable parameters.[40]

Supporting Information Available: Uncorrected HF and CCSD(T) atomization energies (cc-pVDZ and cc-pVTZ basis sets); calculated bond lengths; calculated electron densities at bond critical points; a worked example of each correction (7 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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