Computationally Inexpensive Theoretical Thermochemistry

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An approach to converting HF and DFT energies of molecules, ions, and radicals to standard enthalpies of formation (ΔH_f°) is presented. Employing a combination of atomic equivalents, bond density functions, and corrections for molecular charge and spin multiplicity, this new approach is capable of producing accurate enthalpy estimates for most organic and inorganic compounds of the first- and second-row elements. At the B3LYP/6-311G** level of theory, the average absolute errors in the computed values of (ΔH_f°) amount to 1.6, 2.4, and 3.4 kcal/mol for the sets of 61 CH, 156 CHNOS, and 300 H...Cl species that include systems as small as the Cl^- anion and as large as the C_{60} fullerene. Computationally inexpensive theoretical predictions of molecular thermochemistry with accuracy rivaling that of calorimetric measurements are now possible for compounds of interest to the broad audience of experimental chemists.

Introduction

Accurate prediction of thermodynamic properties of molecules constitutes the primary objective of many electronic structure calculations. Among those properties, the standard enthalpy of formation ΔH_f°, which measures thermodynamic stability, is most commonly employed in chemical research. For a given chemical system X, $\Delta H_f^\circ(X)$ is given by the expression

$$\Delta H_f^\circ(X) = H(X) + \sum_I n_I(X)[\Delta H_f^\circ(I) - H(I)] \qquad (1)$$

where $n_I(X)$ is the number of atoms of the element I present in X and $\Delta H_f^\circ(I)$ is the standard enthalpy of formation of I. The enthalpies $H(X)$ and $H(I)$ of X and I at $T = 298.15$ K are sums of three terms:

$$H(A) = E(A) + E_{ZP}(A) + E_{therm}(A), \quad A = X \text{ or } I \qquad (2)$$

where E and E_{ZP} are the total and zero-point energies, respectively, and E_{therm} is the difference between the enthalpy at $T = 298.15$ K and the energy at $T = 0$ K. Within the harmonic approximation, both $E_{ZP}(X)$ and $E_{therm}(X)$ are explicit functions of vibrational frequencies and moments of inertia of X. Consequently, approximate values of both $H(X)$ and $H(I)$ are readily available from quantum-chemical calculations. On the other hand, although in principle obtainable from theoretical considerations, the values of $\Delta H_f^\circ(I)$ are usually taken from experiment.

The aforedescribed atomization energy scheme requires very accurate estimates of $H(A)$ and $H(I)$. Several contemporary electronic structure methods are capable of providing such estimates for small molecules, radicals, and ions. The G2[1] and G2MP2[2] approaches rely on the additivity of electron correlation contributions to the total energy computed at escalating levels of theory. The complete basis set (CBS) methods, such as CBS-Q, CBS-q, CBS-4,[3] or CBS-APNO,[4] employ a different formalism that is somewhat more empirical in nature. When applied to the G2 neutral test set of 148 species,[5] these extrapolative scheme yield standard enthalpies of formations with mean absolute deviations of 1.6 (G2), 2.0 (G2MP2), 1.6 (CBS-Q), 2.1 (CBS-q), and 3.1 kcal/mol (CBS-4) from reliable experimental values.[5,6] Similar results are obtained with a test set of 166 molecules, radicals, anions, and cations.[7]

The steep computational cost and the accumulation of errors (which, like the enthalpies themselves, are size-extensive) limits the usefulness of the atomization energy methodology to small chemical systems. Larger species, which are of much more interest to experimentalists, can be treated only with less involved formalisms, such as the Hartree−Fock (HF) approximation or the density functional theory (DFT). Since the enthalpies afforded by these methods are not accurate enough to be used in conjunction with eq 1, indirect approaches to the estimation of ΔH_f° have to be employed. These approaches, which take the advantage of the approximate conservation of electron correlation energy in certain types of chemical transformations, usually invoke isodesmic[8] or homodesmotic reactions.[9] Bond separation reactions,[8] which can be uniquely defined for species with classical Lewis structures, are particularly useful in this context, sharply increasing the accuracy of standard enthalpies of formation computed with extrapolative schemes[6,10] and DFT-based methods.[1]

Combining the atomic quantities that enter eq 1 yields an expression

$$\Delta H_f^\circ(X) = H(X) + \sum_I n_I(X) h_I \qquad (3)$$

from which another procedure for the estimation of ΔH_f°, based upon least-squares fitting of the atomic enthalpy equivalents h_I, follows. An even more expedient scheme is obtained by absorbing the zero-point energies and thermal corrections into atomic equivalents e_I

$$\Delta H_f^\circ(X) = E(X) + \sum_I n_I(X) e_I \qquad (4)$$

thus obviating the expensive calculations of vibrational frequen-

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TABLE 1: Experimental Standard Enthalpies of Formation (kcal/mol) of the 300 Molecules, Radicals, and Ions Comprising the Training Set Employed in the Present Implementation of the BDF Scheme

species	ΔH_f°	species	ΔH_f°	species	ΔH_f°
LiH	33.3^a	CH_3ONO	-15.9^a	$HCOCH_2^\bullet$	2.5^e
$BeH^\bullet$	81.7^a	CH_3SiH_3	-7.0^a	HCO^-	2.7^e
$CH^\bullet$	142.5^a	$HCOOH$	-90.5^a	$HCOCH_2^-$	-39.6^e
$CH_2\ (^3B_1)$	93.7^a	$HCOOCH_3$	-85.0^a	CH_3^-	33.2^e
$CH_2\ (^1A_1)$	102.8^a	CH_3CONH_2	-57.0^a	NH_2^-	27.3^e
$CH_3^\bullet$	35.0^a	aziridine	30.2^a	OH^-	-32.8^e
CH_4	-17.9^a	$(CN)_2$	73.3^a	F^-	-59.3^e
$NH\ (^3\Sigma)$	85.2^a	$(CH_3)_2NH$	-4.4^a	SiH_3^-	14.7^e
$NH_2^\bullet$	45.1^a	$(E)-CH_3CH_2NH_2$	-11.3^a	PH_2^-	6.4^e
NH_3	-11.0^a	ketene	-11.4^a	SH^-	-19.1^e
$OH^\bullet$	9.4^a	oxirane	-12.6^a	Cl^-	-53.4^e
H_2O	-57.8^a	CH_3CHO	-39.7^a	CH_3O^-	-32.4^e
HF	-65.1^a	glyoxal	-50.7^a	CH_3S^-	-14.3^e
$SiH_2\ (^1A_1)$	65.2^a	CH_3CH_2OH	-56.2^a	CN^-	18.0^e
$SiH_2\ (^3B_1)$	86.2^a	$(CH_3)_2O$	-44.0^a	$C_2H_5^-$	35.1^e
$SiH_3^\bullet$	47.9^a	thiooxirane	19.6^a	$H_2C{=}CH^-$	56.2^e
SiH_4	8.2^a	$(CH_3)_2SO$	-36.2^a	$HC{\equiv}C^-$	66.8^e
$PH_2^\bullet$	33.1^a	CH_3CH_2SH	-11.1^a	$(CH_3)_2CH^-$	28.2^e
PH_3	1.3^a	$(CH_3)_2S$	-8.9^a	$cyclo-C_3H_5^-$	59.0^e
H_2S	-4.9^a	CH_2CHF	-33.2^a	$CH_2CH{=}CH_2^-$	30.4^e
HCl	-22.1^a	C_2H_5Cl	-26.8^a	H_2Cl^+	207.0^e
Li_2	51.6^a	$CH_2{=}CHCl$	8.9^a	$H_2C{=}CH^+$	266.0^e
LiF	-80.1^a	$CH_2{=}CHCN$	43.2^a	NH_4^+	151.0^e
C_2H_2	54.2^a	CH_3COCH_3	-51.9^a	H_3O^+	141.0^e
C_2H_4	12.5^a	CH_3COOH	-103.4^a	H_2F^+	184.0^e
C_2H_6	-20.1^a	CH_3COF	-105.7^a	PH_4^+	178.0^e
$CN^\bullet$	104.9^a	CH_3COCl	-58.0^a	H_3S^+	190.0^e
HCN	31.5^a	$CH_3CH_2CH_2Cl$	-31.5^a	$CH_3CHClCH_2Cl$	-38.9^f
CO	-26.4^a	$(CH_3)_2CHOH$	-65.2^a	$(CH_3)_2CHCl$	-34.6^f
$HCO^\bullet$	10.0^a	$CH_3CH_2OCH_3$	-51.7^a	$(CH_3)_3CCl$	-43.5^f
H_2CO	-26.0^a	$(CH_3)_3N$	-5.7^a	$CFCl_3$	-64.0^f
CH_3OH	-48.0^a	furan	-8.3^a	CF_2Cl_2	-114.1^f
N_2	0.0^a	thiophene	27.5^a	CF_3Cl	-168.7^f
N_2H_4	22.8^a	pyrrole	25.9^a	CH_2FCl	-62.6^f
$NO^\bullet$	21.6^a	pyridine	33.6^a	CHF_2Cl	-115.1^f
O_2	0.0^a	H_2	0.0^a	$CHFCl_2$	-67.6^f
H_2O_2	-32.5^a	$HS^\bullet$	34.2^a	$CHCl_2CH_3$	-30.5^f
F_2	0.0^a	$HC{\equiv}C^\bullet$	135.1^a	CH_2ClCH_2Cl	-30.3^f
CO_2	-94.1^a	$CH_2{=}CH^\bullet\ (^2A')$	71.6^a	CH_3CCl_3	-34.6^f
Na_2	34.0^a	$CH_3CO^\bullet\ (^2A')$	-2.4^a	$CHCl_2CH_2Cl$	-36.1^f
$Si_2\ (^3\Sigma_g^-)$	139.9^a	$HOCH_2^\bullet\ (^2A)$	-4.1^a	$CHCl_2CCl_3$	-33.9^f
P_2	34.3^a	$CH_3O^\bullet\ (^2A')$	4.1^a	C_2Cl_6	-34.3^f
S_2	30.7^a	$CH_3CH_2O^\bullet\ (^2A'')$	-3.7^a	$CH_2{=}CCl_2$	0.6^f
Cl_2	0.0^a	$CH_3S^\bullet\ (^2A')$	29.8^a	$(E)-CHC{=}CHCl$	1.1^f
$NaCl$	-43.6^a	$C_2H_5^\bullet\ (^2A')$	28.9^a	$(Z)-CHCl{=}CHCl$	1.2^f
SiO	-24.6^a	$(CH_3)_2CH^\bullet\ (^2A')$	21.5^a	$CHCl{=}CCl_2$	-1.9^f
CS	66.9^a	$(CH_3)_3C^\bullet$	12.3^a	$CFCl{=}CF_2$	-132.7^f
$SO\ (^3\Sigma)$	1.2^a	$NO_2^\bullet$	7.9^a	$H-C{\equiv}C-Cl$	51.0^f
$ClO^\bullet$	24.2^a	$HC{\equiv}C-C{\equiv}CH$	113.0^c	$Cl-C{\equiv}C-Cl$	50.0^f
FCl	-13.2^a	cyclopentadiene	32.1^c	C_6H_5Cl	12.4^f
Si_2H_6	19.1^a	$(CH_3)_4C$	-40.3^c	C_6F_5Cl	-194.1^f
CH_3Cl	-19.6^a	fulvene	47.5^c	CCl_3CHO	-47.0^f
CH_3SH	-5.5^a	bicyclopropyl	30.9^c	$ClCN$	32.9^f
$HOCl$	-17.8^a	norbornadiene	59.7^c	$NClF_2$	4.4^f
SO_2	-71.0^a	toluene	12.0^c	$ClNO_2$	2.9^f
BF_3	-271.4^a	cubane	148.7^c	$FOCl$	12.9^f
BCl_3	-96.3^a	naphthalene	36.1^c	Cl_2O	21.0^f
AlF_3	-289.0^a	adamantane	-31.9^c	$ClO_2^\bullet$	25.0^f
$AlCl_3$	-139.7^a	phenanthrene	49.5^c	$ClO^-{}_4$	-81.0^f
CF_4	-223.0^a	tetrahydrofuran	-44.0^c	$BeCl_2$	-86.1^g
CCl_4	-22.9^a	phenol	-23.0^c	BeF_2	-189.7^g
COS	-33.1^a	$O{=}C{=}C{=}C{=}O$	-22.4^c	BeH_2	30.0^g
CS_2	28.0^a	*p*−benzoquinone	-29.3^c	BeO	32.6^g
COF_2	-152.7^a	C_6H_5CN	51.5^c	$Be_2\ (^3\Sigma_g)$	152.3^g
SiF_4	-386.0^a	H_2NCHO	-44.5^c	$MgCl_2$	-93.8^g
$SiCl_4$	-158.4^a	HNO_3	-32.1^c	MgF_2	-173.0^g
N_2O	19.6^a	N_2O_3	19.8^c	NaH	29.7^h
$ClNO$	12.4^a	N_2O_4	2.2^c	$NaCH_3$	26.3^h
NF_3	-31.6^a	HN_3	70.3^c	Na_2O	-8.6^h
PF_3	-229.1^a	1*H*−tetrazole	79.9^c	$NaOH$	-47.3^h
O_3	34.1^a	H_2S_2	3.7^c	NaF	-69.4^h

TABLE 1. (continued)

species	ΔH_f°	species	ΔH_f°	species	ΔH_f°
F_2O	5.9[a]	S_8	24.0[c]	MgH_2	37.5[h]
ClF_3	−38.0[a]	HOF	−23.5[c]	CH_3MgH	28.4[h]
C_2F_4	−157.4[a]	CNF	8.6[c]	$Mg(CH_3)_2$	15.3[h]
C_2Cl_4	−3.0[a]	NOF	−15.7[c]	$Mg(CN)_2$	60.5[h]
CF_3CN	−118.4[a]	C_6F_6	−228.5[c]	MgO	36.0[h]
$CH_3C{\equiv}CH$	44.2[a]	SF_6	−291.4[c]	CH_3MgF	−74.6[h]
$CH_2{=}C{=}CH_2$	45.5[a]	C_4F_8[d]	−369.5[c]	MgS	49.3[h]
cyclopropene	66.2[a]	$COCl_2$	−52.6[c]	AlH_3	29.1[h]
$CH_3CH{=}CH_2$	4.8[a]	SCl_2	−4.2[c]	Al_2H_6	24.6[h]
cyclopropane	12.7[a]	S_2Cl_2	−4.0[c]	AlCl	−12.3[h]
propane	−25.0[a]	C_6Cl_6	−8.6[c]	P_4	14.1[h]
$CH_2{=}CHCH{=}CH_2$	26.3[a]	$(CH_3)_3Al$	−20.9[c]	P_2H_4	5.0[h]
2−butyne	34.8[a]	AlF	−63.5[c]	HCP	52.7[h]
C_4H_6[b]	47.9[a]	Al_2 ($^2\Pi_u$)	116.4[c]	PN	42.8[h]
bicyclobutane	51.9[a]	Al_2Cl_6	−309.7[c]	PCl_3	−68.4[h]
cyclobutene	37.4[a]	$(CH_3)_4Si$	−55.7[c]	PF_5	−381.1[h]
cyclobutane	6.8[a]	$(CH_3)_3P$	−22.5[c]	PCl_5	−89.6[h]
isobutene	−4.0[a]	SO_3	−94.6[c]	C_8H_8[i]	70.3[j]
(*E*)−butane	−30.0[a]	SOF_2	−130.0[c]	triphenylene	66.5[j]
isobutane	−32.1[a]	SO_2F_2	−181.3[c]	$C_{18}H_{12}$[k]	69.6[j]
spiropentane	44.3[a]	SF_4	−182.4[c]	pyrene	54.0[j]
benzene	19.7[a]	$SOCl_2$	−50.8[c]	perylene	78.4[j]
CH_2F_2	−107.7[a]	SO_2Cl_2	−86.2[c]	acenaphthene	37.2[j]
CHF_3	−166.6[a]	H_2SO_4	−175.7[c]	biphenylene	99.8[j]
CH_2Cl_2	−22.8[a]	BH_3	25.5[e]	acenaphthylene	62.2[j]
$CHCl_3$	−24.7[a]	$CH_2{=}CHOH$	−29.8[e]	biphenyl	43.3[j]
CH_3NH_2	−5.5[a]	CH_3COSH	−41.8[e]	$CCl_3^\bullet$	17.5[l]
CH_3CN	18.0[a]	$CH_2{=}CHC{\equiv}CH$	72.8[e]	$C_2Cl_5^\bullet$	8.1[l]
CH_3NO_2	−17.8[a]	$HSCH_2^\bullet$	36.3[e]	C_{60}	618.0[m]

[a] Reference 5. [b] Methylenecyclopropane. [c] Reference 27. [d] Perfluorocyclobutane. [e] Reference 7. [f] Reference 28. [g] Reference 29. [h] Reference 30. [i] Cyclooctatetraene. [j] Reference 31. [k] Benzo[*c*]phenanthrene. [l] Reference 32. [m] Reference 33.

cies. A partial justification for the approximate validity of eq 4 is furnished by the observation that E_{ZP} is to a large extent atomic additive.[12] Since replacing the differences $\Delta H_f^\circ(I) - H(I)$ with the fitted equivalents h_I or e_I eliminates the large errors associated with the neglect of electron correlation in atoms with open-shell configurations, eq 4 is capable of producing reasonably accurate (average errors of 10.7, 6.9, and 6.1 kcal/mol for 45 CHNO molecules treated at the HF/STO-3G, HF/3-21G, and HF/6-31G* levels of theory, respectively) predictions for ΔH_f° even from Hartree−Fock energies.[13] However, much better results (standard deviations of 0.8, 1.2, and 2.1 kcal/mol for the values of ΔH_f° computed for 23 hydrocarbons at the B3LYP/6-311G**, B3LYP/6-31G*, and BLYP/6-311G** level of theory,[14] respectively) are obtained when the energies calculated with DFT-based methods that approximately account for electron correlation effects are employed.

The realization that the use of homodesmotic reactions in the estimation of standard enthalpies of formation is equivalent to invoking eq 3 or 4 with the index I pertaining to groups rather than atoms[15] has prompted the development of several group-equivalent schemes.[15−20] Although some of these schemes (especially those based upon energies corrected for the effects of populating higher-energy conformations and low-lying vibrational/rotational states,[16] and those tailored to specific classes of molecules[17] are remarkably accurate, their applicability is limited to chemical systems with the "usual" bonds employed in the parametrization process. Because of their reliance on large numbers of parameters (almost 40 for CHNOS molecules[16] and over 50 for CHNOFCl species[18]), such methods are in fact procedures for augmenting primitive bond contribution schemes with *ab initio* energies rather than approaches to correcting the latter quantities for electron correlation effects.

The need for a new formalism capable of converting the data produced by electronic structure calculations to standard enthalpies of formation clearly emerges from the above discussion. Such formalism should be universally applicable to all molecules, radicals, and ions composed from a given set of elements without regard to the types of bonds present or the existence of a classical Lewis structure. Moreover, it should produce reasonably accurate predictions of ΔH_f° at diverse levels of theory, including those employed in calculations on large systems, from formulas involving as few fitted parameters as possible. A formalism that satisfies these requirements is described in this paper.

The Bond Density Function Scheme

Among the aforedescribed four distinct approaches to converting *ab initio* energies/enthalpies of molecules at equilibrium geometries to standard enthalpies of formation, only the atom-equivalent scheme satisfies the requirement of universal applicability.[13] However, the crude implementation of such a scheme (eq 3 and 4) lacks sufficient accuracy when applied in conjunction with HF or DFT energies/enthalpies. It is therefore necessary to augment the computed energies/enthalpies with a correction that accounts for the electron correlation effects associated with bond formation that are not reproduced at a given level of theory. In order to obviate the use of bond-specific formulas, such a correction must be an explicit function of only the electron and spin densities, and the positions and atomic numbers of nuclei.

The total number of electrons $N(X)$ and the number of unpaired electrons $N_S(X)$

$$N(X) = \int \rho(X,\vec{r})\, d\vec{r}, \quad N_S(X) = \int \rho_S(X,\vec{r})\, d\vec{r} \qquad (5)$$

are the simplest quantities directly derivable from the electron and spin densities, $\rho(X,\vec{r})$ and $\rho_S(X,\vec{r})$, of the system X. Both $N(X)$ and $N_S(X)$ enter the expressions for the "higher-level

TABLE 2: Error Statistics for the Standard Enthalpies of Formation Derived from the Computed Total Energies at T = 0 K of 300 Test Molecules[a]

level of theory	no. of terms in BDF	av abs error	std dev	max abs error[b]
HF/6-31G*	0	8.87	12.62	52.95 (ClO_4^-)
	1	6.66	9.72	37.16 (H_2Cl^+)
	2	5.95	8.74	35.54 (Be_2)
	3	5.70	8.51	35.49 (Be_2)
	4	5.51	8.21	34.45 (H_2Cl^+)
	5	5.42	8.16	34.27 (H_2Cl^+)
HF/6-31G**	0	8.83	12.44	53.60 (ClO_4^-)
	1	6.29	9.16	32.77 (H_2Cl^+)
	2	5.74	8.32	33.90 (Be_2)
	3	5.44	8.04	33.81 (Be_2)
	4	5.30	7.89	32.51 (F^-)
	5	5.22	7.59	33.17 (F^-)
HF/6-311G**	0	9.72	14.04	65.93 (ClO_4^-)
	1	6.51	9.34	30.76 (NH_2^-)
	2	5.79	8.26	31.48 (Be_2)
	3	5.53	8.03	33.31 (Be_2)
	4	5.30	7.78	31.80 (Be_2)
	5	5.19	7.69	29.93 (Be_2)
BLYP/6-311G**	0	7.01	10.77	59.69 (ClO_4^-)
	1	5.28	8.07	37.71 (F^-)
	2	4.12	6.56	40.03 (F^-)
	3	3.88	6.21	41.61 (F^-)
	4	3.73	6.00	40.59 (F^-)
	5	3.63	5.95	39.85 (F^-)
B3LYP/6-311G**	0	6.63	10.09	58.48 (ClO_4^-)
	1	4.95	7.62	37.13 (ClO_4^-)
	2	3.90	6.20	31.10 (OH^-)
	3	3.73	5.99	33.02 (OH^-)
	4	3.49	5.66	31.28 (OH^-)
	5	3.36	5.58	31.64 (OH^-)

[a] All values in kcal/mol. [b] The system with the maximum absolute error given in parentheses.

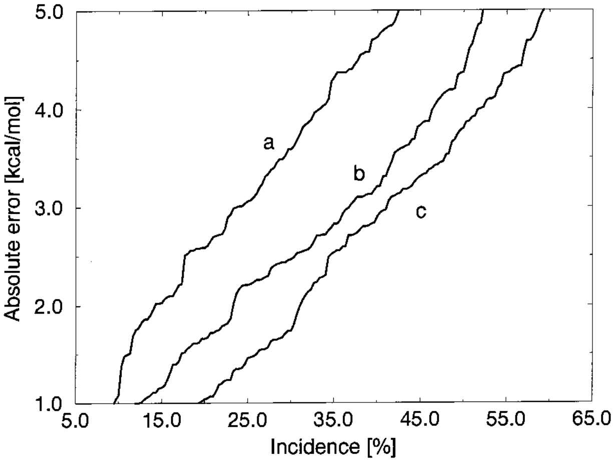

Figure 1. Incidence of molecules with the absolute error in ΔH_f° below a given threshold for the standard enthalpies of formation computed from HF/6-31G* energies at $T = 0$ K with (a) a scheme with the BDF set to zero, (b) a one-term BDF scheme, (c) a five-term BDF scheme.

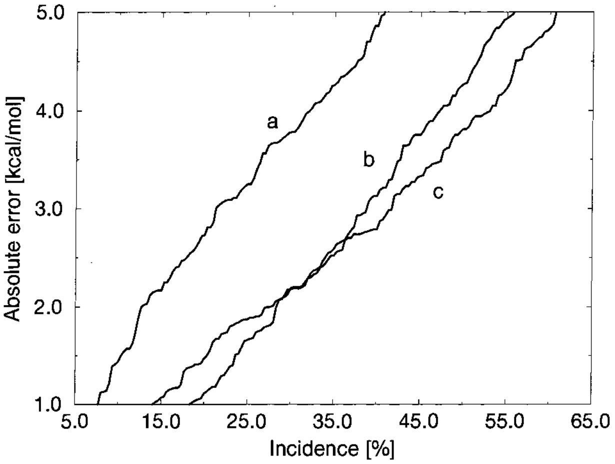

Figure 2. Incidence of molecules with the absolute error in ΔH_f° below a given threshold for the standard enthalpies of formation computed from HF/6-31G** energies at $T = 0$ K with (a) a scheme with the BDF set to zero, (b) a one-term BDF scheme, (c) a give-term BDF scheme.

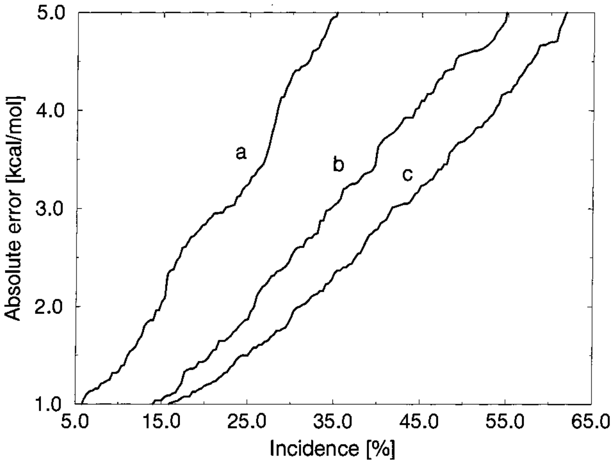

Figure 3. Incidence of molecules with the absolute error in ΔH_f° below a given threshold for the standard enthalpies of formation computed from HF/6-311G** energies at $T = 0$ K with (a) a scheme with the BDF set to zero, (b) a one-term BDF scheme, (c) a five-term BDF scheme.

corrections” employed in the extrapolative methods of the G2 family.[1,2] It is therefore reasonable to include a linear combination of these two quantities in the energy/enthalpy correction. For neutral species, the term proportional to N(X) can be conveniently absorbed into the atomic equivalents, leaving a contribution proportional to the molecular charge Q(X) that comes into play only for ions. Both this contribution (which also partially alleviates the inadequacies of basis sets lacking diffuse functions) and the term proportional to N_S(X) are expected to be more important for HF energies/enthalpies than for those obtained with DFT methods.

A rigorous quantum-mechanical definition of chemical bonds in molecules is provided by the theory of atoms in molecules.[21] According to this theory, lines of steepest descent in $\rho(X,\vec{r})$ that connect nuclei present in X delineate all major chemical interactions (“bonds”) in that system.[21,22] Each of these attractor interaction lines is associated with a bond critical point in $\rho(X,\vec{r})$ at which $\nabla\rho(X,\vec{r})$ vanishes. Thus, each bond I−J is characterized by, among other quantities, the arc length R_{IJ} of the corresponding attractor interaction line, the atomic numbers Z_I and Z_J of the nuclei linked by it, the magnitude ρ_{IJ} of the density at the bond critical point, and the eigenvalues $\lambda_{IJ}^{(1)}$, $\lambda_{IJ}^{(2)}$, $\lambda_{IJ}^{(3)}$ of the corresponding electron density Hessian. The simplest expression for the bond contribution to the energy/enthalpy correction that depends on these observables and exhibits proper invariance with respect to the permutation of the nuclei I and J and the rotation about the I−J axis involves ρ_{IJ}, R_{IJ}, $Z_{IJ} \equiv (Z_I Z_J)^{1/2}$, $\alpha_{IJ} \equiv [\lambda_{IJ}^{(1)}\lambda_{IJ}^{(2)}]^{1/2}$, and $\beta_{IJ} \equiv \lambda_{IJ}^{(3)}$, where $\lambda_{IJ}^{(1)}$ and $\lambda_{IJ}^{(2)}$ are assumed to be the two negative eigenvalues of the electron density Hessian.[23]

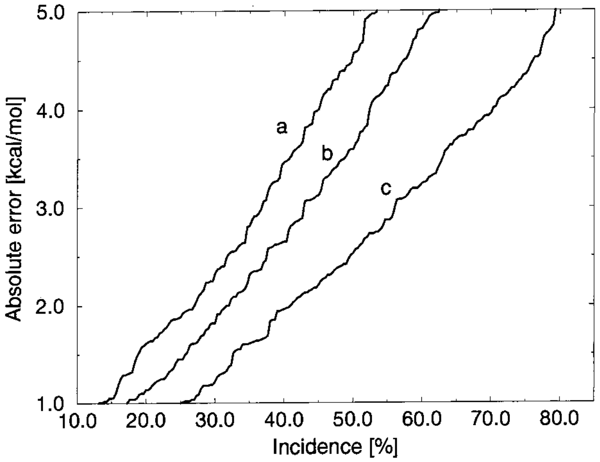

Figure 4. Incidence of molecules with the absolute error in ΔH_f° below a given threshold for the standard enthalpies of formation computed from BLYP/6-311G** energies at $T = 0$ K with (a) a scheme with the BDF set to zero, (b) a one-term BDF scheme, (c) a five-term BDF scheme.

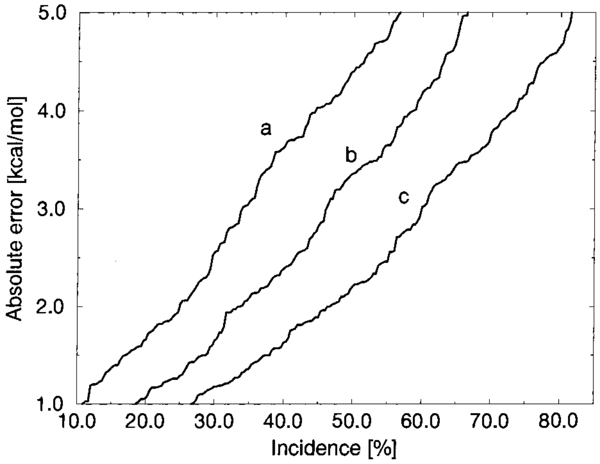

Figure 5. Incidence of molecules with the absolute error in ΔH_f° below a given threshold for the standard enthalpies of formation computed from B3LYP/6-311G** energies at $T = 0$ K with (a) a scheme with the BDF set to zero, (b) a one-term BDF scheme, (c) a five-term BDF scheme.

In light of these considerations, the expressions

$$\Delta H_f^\circ(X) = E(X) + e_Q Q(X) + e_S N_S(X) + \sum_I e_1(Z_I) + \sum_{I-J} e_2(\rho_{IJ},R_{IJ},Z_{IJ},\alpha_{IJ},\beta_{IJ}) \quad (6)$$

$$\Delta H_f^\circ(X) = H(X) + h_Q Q(X) + h_S N_S(X) + \sum_I h_1(Z_I) + \sum_{I-J} h_2(\rho_{IJ},R_{IJ},Z_{IJ},\alpha_{IJ},\beta_{IJ}) \quad (7)$$

emerge as viable candidates for the formulas enabling approximate conversion of $E(X)$ or $H(X)$ to $\Delta H_f^\circ(X)$. In eqs 6 and 7, the first sums run over all the nuclei present in X, whereas the second summations encompass all the atomic interaction lines between nuclear attractors. In systems with nonnuclear attractors,[24] the interaction lines linked to each such attractor are combined, yielding nuclei-connecting lines with multiple bond critical points. In such cases, the quantities ρ_{IJ}, α_{IJ}, and β_{IJ} are obtained from electron densities and Hessian eigenvalues averaged over all the bond critical points lying on a given combined line I−J.

TABLE 3: Error Statistics for the Standard Enthalpies of Formation Derived from the Computed Enthalpies at T = 298 K of 300 Test Molecules[a]

level of theory	no. of terms in BDF	av abs, error	std dev	max abs error[b]
HF/6-31G*	0	8.78	12.50	54.14 (ClO_4^-)
	1	6.39	9.26	34.69 (F^-)
	2	5.89	8.71	36.30 (Be_2)
	3	5.64	8.44	36.76 (Be_2)
	4	5.46	8.09	35.34 (Be_2)
	5	5.34	8.00	36.12 (Be_2)
HF/6-31G**	0	8.73	12.34	54.73 (ClO_4^-)
	1	6.01	8.71	33.80 (F^-)
	2	5.63	8.27	34.39 (F^-)
	3	5.43	8.01	32.43 (F^-)
	4	5.24	7.82	32.71 (F^-)
	5	5.14	7.67	32.56 (F^-)
HF/6-311G**	0	9.72	14.11	67.01 (ClO_4^-)
	1	6.32	8.97	29.59 (MgO)
	2	5.81	8.22	31.70 (Be_2)
	3	5.51	7.92	33.43 (Be_2)
	4	5.28	7.70	32.36 (Be_2)
	5	5.17	7.59	32.01 (Be_2)
BLYP/6-311G**	0	7.22	11.04	60.97 (ClO_4^-)
	1	5.08	7.92	39.09 (ClO_4^-)
	2	4.52	6.89	38.48 (F^-)
	3	4.09	6.23	38.98 (F^-)
	4	3.81	6.05	38.10 (F^-)
	5	3.67	5.93	38.58 (F^-)
B3LYP/6-311G**	0	6.53	10.16	59.73 (ClO_4^-)
	1	4.72	7.29	39.65 (ClO_4^-)
	2	4.02	6.31	30.92 (ClO_4^-)
	3	3.70	5.90	32.31 (F^-)
	4	3.53	5.70	31.54 (F^-)
	5	3.41	5.61	31.48 (OH^-)

[a] All values in kcal/mol. [b] The system with the maximum absolute error given in parentheses.

TABLE 4: Error Statistics for the Standard Enthalpies of Formation Derived (with e_Q Set to Zero) from the Computed Total Energies at T = 0 K of 300 Test Molecules[a]

level of theory	no. of terms in BDF	av abs error	std dev	max abs error[b]
HF/6-31G*	0	10.04	15.35	77.92 (ClO_4^-)
	1	8.23	13.49	62.70 (F^-)
	2	7.39	11.85	57.20 (F^-)
	3	7.16	11.73	57.62 (F^-)
	4	7.04	11.64	57.65 (F^-)
	5	6.87	11.35	58.73 (F^-)
HF/6-31G**	0	10.17	15.41	79.58 (ClO_4^-)
	1	8.02	13.32	62.13 (F^-)
	2	7.19	11.68	55.31 (F^-)
	3	6.92	11.53	55.80 (F^-)
	4	6.71	11.13	55.85 (F^-)
	5	6.62	11.08	55.84 (F^-)
HF/6-311G**	0	10.71	15.91	87.42 (ClO_4^-)
	1	7.96	12.49	58.53 (NH_2^-)
	2	6.94	10.46	47.27 (NH_2^-)
	3	6.67	10.15	46.69 (NH_2^-)
	4	6.43	9.83	49.59 (NH_2^-)
	5	6.22	9.67	48.25 (NH_2^-)
BLYP/6-311G**	0	7.14	11.33	69.85 (ClO_4^-)
	1	5.70	9.22	44.05 (ClO_4^-)
	2	4.56	7.51	47.70 (F^-)
	3	4.24	7.08	47.38 (F^-)
	4	4.09	6.92	48.58 (F^-)
	5	3.95	6.85	48.27 (F^-)
B3LYP/6-311G**	0	6.74	10.43	66.15 (ClO_4^-)
	1	5.14	7.88	41.57 (OH^-)
	2	4.06	6.39	35.62 (OH^-)
	3	3.79	6.09	36.66 (OH^-)
	4	3.61	5.97	36.74 (OH^-)
	5	3.41	5.84	36.70 (OH^-)

[a] All values in kcal/mol. [b] The system with the maximum absolute error given in parentheses.

The atomic equivalents $e_1(Z_I)$ and $h_1(Z_I)$ are functions defined only for integer arguments. Obtained by least-squares fitting, these quantities incorporate errors in energy/enthalpy due to the approximate description of core orbitals by finite basis sets of

TABLE 5: Error Statistics for the Standard Enthalpies of Formation Derived (with h_Q Set to Zero) from the Computed Enthalpies at T = 298 K of 300 Test Molecules[a]

level of theory	no. of terms in BDF	av abs error	std dev	max abs error[b]
HF/6-31G*	0	9.85	14.91	77.37 (ClO_4^-)
	1	7.98	12.89	62.14 (F^-)
	2	7.25	11.56	55.26 (F^-)
	3	7.07	11.45	55.39 (F^-)
	4	6.90	11.17	54.06 (F^-)
	5	6.75	10.97	52.43 (F^-)
HF/6-31G**	0	10.01	14.97	78.98 (ClO_4^-)
	1	7.81	12.66	62.17 (F^-)
	2	7.11	11.40	54.79 (F^-)
	3	6.85	11.26	55.31 (F^-)
	4	6.69	10.87	54.98 (F^-)
	5	6.58	10.80	55.09 (F^-)
HF/6-311G**	0	10.64	15.70	86.72 (ClO_4^-)
	1	7.89	11.89	54.17 (NH_2^-)
	2	6.91	10.35	44.43 (NH_2^-)
	3	6.65	10.26	45.58 (NH_2^-)
	4	6.40	9.92	47.96 (NH_2^-)
	5	6.19	9.59	45.71 (NH_2^-)
BLYP/6-311G**	0	7.30	11.41	69.43 (ClO_4^-)
	1	5.43	8.95	51.82 (F^-)
	2	4.40	7.57	48.94 (F^-)
	3	4.20	7.31	52.21 (F^-)
	4	4.11	7.27	51.28 (F^-)
	5	4.00	7.24	50.56 (F^-)
B3LYP/6-311G**	0	6.57	10.36	65.72 (ClO_4^-)
	1	4.85	7.96	53.35 (ClO_4^-)
	2	4.02	6.64	38.00 (ClO_4^-)
	3	3.67	6.20	38.82 (F^-)
	4	3.49	6.03	38.08 (F^-)
	5	3.37	5.94	38.77 (F^-)

[a] All values in kcal/mol. [b] The system with the maximum absolute error given in parentheses.

TABLE 6: Error Statistics for the Standard Enthalpies of Formation Derived from the Computed Total Energies at T = 0 K of 156 CHNOS Species[a]

level of theory	no. of terms in BDF	av abs error	std dev	max abs error[b]
HF/6-31G*	0	8.13	10.62	29.91 (C_{60})
	1	6.42	8.96	32.26 (H_3S^+)
	2	5.35	7.35	28.60 (O_3)
	3	4.59	6.66	24.38 (OH^-)
	4	4.32	6.35	23.39 (OH^-)
	5	4.08	6.15	23.69 (OH^-)
HF/6-31G**	0	7.94	10.31	28.95 (C_{60})
	1	5.96	8.37	29.17 (H_3S^+)
	2	4.68	6.73	26.82 (O_3)
	3	4.26	6.47	23.65 (O_3)
	4	4.06	6.34	24.03 (O_3)
	5	3.80	6.04	24.19 (O_3)
HF/6-311G**	0	8.46	11.06	31.58 (SO_3)
	1	5.77	8.00	26.69 (NH_2^-)
	2	4.51	6.62	27.09 (O_3)
	3	4.18	6.37	27.01 (OH^-)
	4	3.98	6.22	26.83 (OH^-)
	5	3.83	5.85	24.65 (O_3)
BLYP/6-311G**	0	6.09	9.61	49.97 (H_2SO_4)
	1	4.15	6.95	34.27 (H_2SO_4)
	2	3.76	6.26	31.49 (OH^-)
	3	3.17	5.33	34.45 (OH^-)
	4	2.91	5.02	33.09 (OH^-)
	5	2.65	4.52	31.26 (OH^-)
B3LYP/6-311G**	0	5.22	8.18	40.51 (H_2SO_4)
	1	4.10	6.08	28.97 (OH^-)
	2	3.28	5.43	32.46 (OH^-)
	3	2.70	4.58	31.15 (OH^-)
	4	2.48	4.43	30.75 (OH^-)
	5	2.36	4.28	30.19 (OH^-)

[a] All values in kcal/mol. [b] The system with the maximum absolute error given in parentheses.

TABLE 7: Error Statistics for the Standard Enthalpies of Formation Derived from the Computed Total Energies at T = 0 K of 61 CH Species[a]

level of theory	no. of terms in BDF	av abs error	std dev	max abs error[b]
HF/6-31G*	0	6.54	8.41	22.07 ($CH_2{=}CH^+$)
	1	3.04	4.23	12.02 (H_2)
	2	2.37	3.31	7.40 (fulvene)
	3	2.30	3.27	7.81 (cubane)
	4	2.22	3.23	7.11 (cubane)
	5	2.16	3.00	5.56 (pyrene)
HF/6-31G**	0	6.70	8.62	21.60 (C_{60})
	1	3.16	4.46	15.39 (H_2)
	2	2.45	3.39	7.48 (fulvene)
	3	2.28	3.25	6.95 (fulvene)
	4	2.22	3.18	6.94 (pyrene)
	5	2.14	3.14	6.87 (fulvene)
HF/6-311G**	0	7.31	9.20	23.48 (C_{60})
	1	2.97	4.33	13.78 (H_2)
	2	2.53	3.61	9.61 (cubane)
	3	2.33	3.34	8.33 (fulvene)
	4	2.13	3.23	8.07 (fulvene)
	5	2.10	3.26	8.19 (fulvene)
BLYP/6-311G**	0	5.08	7.15	25.73 (adamantane)
	1	2.03	3.17	10.71 (cubane)
	2	1.96	3.15	10.88 (cubane)
	3	1.95	3.17	11.06 (cubane)
	4	1.88	3.11	11.42 (cubane)
	5	1.87	3.14	11.59 (cubane)
B3LYP/6-311G**	0	4.24	5.91	15.82 ($CH_2{=}CH^+$)
	1	1.89	2.73	7.84 (cubane)
	2	1.82	2.67	7.91 (adamantane)
	3	1.73	2.59	7.18 (adamantane)
	4	1.62	2.41	6.57 (CH_3^-)
	5	1.56	2.35	6.73 (CH_3^-)

[a] All values in kcal/mol. [b] The system with the maximum absolute error given in parentheses.

Gaussian functions and the corrections to atomic energies due to the spin−orbit coupling effects (note that in atomization schemes, these corrections have to be added to the computed nonrelativistic energies[5,25]). The energy equivalents $e_1(Z_I)$ also include average atomic contributions to E_{ZP} and E_{therm}.

Dual interpretation is possible for the *bond density functions* (BDFs) $e_2(\rho_{IJ},R_{IJ},Z_{IJ},\alpha_{IJ},\beta_{IJ})$ and $h_2(\rho_{IJ},R_{IJ},Z_{IJ},\alpha_{IJ},\beta_{IJ})$. On the one hand, these quantities may be regarded as generalizations of empirical bond equivalents. On the other hand, since the BDFs depend only on the electron density (note that, thanks to the cusp condition,[26] the atomic numbers and positions of nuclei are inferable from the electron density alone), they are in fact density functionals. However, unlike their conventional counterparts, which depend on the magnitudes of electron density and its derivatives over the entire Cartesian space, the BDFs are not derivable from the properties of homogeneous electron gas. For this reason, the BDFs adopted in the present implementation of eqs 6 and 7 are completely empirical, being given by linear combinations of terms of the form $\rho_{IJ}^p\, R_{IJ}^q\, Z_{IJ}^r\, \alpha_{IJ}^s\, \beta_{IJ}^t$, where the exponents p, q, r, s, and t are rational numbers taken from the set $\{0, \pm1/3, \pm1/2, \pm2/3, \pm1, \pm4/3, \pm3/2, \pm5/3, \pm2, \pm5/2, \pm3\}$.

The BDF scheme described above requires a training set of chemical systems. Judicious selection of the constituents of this set is of paramount importance to the practical usefulness of the resulting parametrization. Adequate diversity with respect to types and numbers of bonds, molecular sizes and charges, and spin multiplicities has to be balanced against the accuracy of the available experimental values of ΔH_f°. With these considerations in mind, a set of 300 molecules, radicals, and ions composed of the elements H−Cl (except for the noble gases) has been assembled (Table 1). At the core of this collection of chemical species lies the 148-member G2 neutral set[5] augmented with 47 larger molecules (including many hypervalent systems) taken from the compilation of standard enthalpies of formation employed in the development of the PM3 semiempirical method.[27] The values of ΔH_f° for ad-

TABLE 8: Recommended BDF Schemes for Converting Total Energies at $T = 0$ K of Species Containing the First- and Second-Row Elements to Standard Enthalpies of Formation[a]

level of theory	e_Q (kcal/mol)	e_S (kcal/mol)	$e_1(1)$ (au)	$e_1(3)$ (au)
HF/6-31G*	31.278	9.353	0.566 186	7.458 415
HF/6-31G**	29.511	10.558	0.569 298	7.462 005
HF/6-311G**	24.581	8.728	0.569 060	7.462 544
BLYP/6-311G**	14.336	−1.856	0.580 896	7.534 836
B3LYP/6-311G**	8.522	−0.682	0.587 172	7.548 379

level of theory	$e_1(4)$ (au)	$e_1(5)$ (au)	$e_1(6)$ (au)	$e_1(7)$ (au)	$e_1(8)$ (au)
HF/6-31G*	14.660 206	24.721 150	37.894 947	54.470 859	74.796 964
HF/6-31G**	14.673 495	24.719 659	37.892 554	54.466 717	74.791 539
HF/6-311G**	14.664 680	24.723 524	37.904 703	54.482 771	74.817 642
BLYP/6-311G**	14.782 528	24.870 879	38.118 980	54.781 380	75.193 069
B3LYP/6-311G**	14.781 368	24.876 865	38.123 796	54.775 330	75.180 571

level of theory	$e_1(9)$ (au)	$e_1(11)$ (au)	$e_1(12)$ (au)	$e_1(13)$ (au)
HF/6-31G*	99.359 058	161.840 393	199.625 371	241.955 746
HF/6-31G**	99.355 871	161.840 307	199.625 533	241.956 992
HF/6-311G**	99.387 597	161.847 663	199.636 928	241.972 438
BLYP/6-311G**	99.797 830	162.307 237	200.130 812	242.495 981
B3LYP/6-311G**	99.790 250	162.321 835	200.144 733	242.508 489

level of theory	$e_1(14)$ (au)	$e_1(15)$ (au)	$e_1(16)$ (au)	$e_1(17)$ (au)
HF/6-31G*	288.973 363	340.760 716	397.543 353	459.474 494
HF/6-31G**	288.973 111	340.764 755	397.544 151	459.473 098
HF/6-311G**	288.994 607	340.788 379	397.573 008	459.502 892
BLYP/6-311G**	289.564 313	341.402 633	398.239 227	460.206 056
B3LYP/6-311G**	289.570 606	341.407 477	398.243 634	460.216 640

level of theory	$e_2(\rho,R,Z,\alpha,\beta)$ (kcal/mol)
HF/6-31G*	$-7.75990 \times 10^{0}\rho^{5/3}R^{-1/3}Z^{2/3}\alpha^{-2/3} + 1.09575 \times 10^{2}\rho^{5/2}R^{4/3}Z^{-1/3}\alpha^{-1/3}\beta^{1/3} + 1.78331 \times 10^{-3}\rho^{-5/3}R^{-2/3}Z^{1/3}\alpha^{-2/3}\beta^{1/3} - 1.08198 \times 10^{-2}\rho^{-3}R^{-3}Z^{4/3}\alpha^{3} + 3.14392 \times 10^{-1}\rho^{3}R^{5/2}Z^{1/2}\alpha^{-3/2}$
HF/6-31G**	$-5.82883 \times 10^{0}\rho^{5/3}R^{-1/3}Z^{2/3}\alpha^{-2/3} + 1.06996 \times 10^{2}\rho^{5/2}R^{4/3}Z^{-1/3}\alpha^{-1/3}\beta^{1/3} + 2.90953 \times 10^{-3}\rho^{-5/3}R^{-2/3}Z^{1/3}\alpha^{-2/3}\beta^{1/3} - 2.39154 \times 10^{-3}\rho^{-3}R^{-3}Z^{5/3}\alpha^{3} - 2.69972 \times 10^{2}\rho^{3}R^{-3}Z^{-1/3}\alpha^{-3}$
HF/6-311G**	$-7.32028 \times 10^{0}\rho^{5/3}R^{-1/3}Z^{2/3}\alpha^{-2/3} + 2.62520 \times 10^{2}\rho^{5/2}R^{1/2}Z^{-1/3}\alpha^{-1/2}\beta^{1/3} + 1.54489 \times 10^{0}\rho^{1/2}R^{-1/3}\alpha^{-1} - 1.74776 \times 10^{-3}\rho^{-3}R^{-2}Z^{5/3}\alpha^{3} - 1.31122 \times 10^{2}\rho^{5/3}R^{-5/3}Z^{-1/3}\alpha^{-4/3}$
BLYP/6-311G**	$-3.73040 \times 10^{0}\rho^{-1/2}R^{-3}Z\alpha^{1/3} + 4.19892 \times 10^{2}\rho^{3}R^{2/3}Z^{-1/3}\alpha^{-1/2} + 9.89486 \times 10^{-2}\rho^{-1/3}R^{1/2}Z^{1/3}\alpha^{-1/2}\beta^{1/2} - 3.19413 \times 10^{2}\rho^{3}R^{-3}Z^{-1/3}\alpha^{3}\beta^{-5/3} - 4.97012 \times 10^{-4}\rho^{3}R^{-3}Z^{3}\alpha^{-1}\beta$
B3LYP/6-311G**	$-6.31175 \times 10^{-1}\rho^{3/2}R^{2/3}Z\alpha^{-1/2}\beta^{1/3} + 3.08666 \times 10^{2}\rho^{3}RZ^{-1/3}\alpha^{-2/3}\beta^{1/3} + 8.74260 \times 10^{-2}\rho^{3}R^{3}Z\alpha^{-3/2}\beta^{2/3} - 1.37406 \times 10^{2}\rho^{5/3}R^{-5/2}Z^{-1/3}\alpha^{4/3}\beta^{2/3} - 2.90703 \times 10^{-1}\rho^{5/2}R^{-3}Z^{5/3}\alpha^{-5/3}\beta^{1/3}$

[a] ρ, R, α, β in au; 1 au = 627.5095 kcal/mol.

ditional 32 molecules, radicals, anions, and cations orginate from another test set.[7] Three recent publications are the source of the data on compounds of chlorine (32 species[28]), and of beryllium, magnesium, aluminum, and phosphorus (29 species[29,30]). Standard enthalpies of formation of 9 polycyclic benzenoid hydrocarbons come from ref 31 and those of the $CCl_3^{\bullet}$ and $C_2Cl_5^{\bullet}$ radicals from the data cited in ref 32. An average of two recent experimental values of ΔH_f°[33] is used for the C_{60} fullerene molecule.

In the present work, BDF schemes are developed for the conversion of HF/6-31G*, HF/6-31G**, HF/6-311G**, BLYP/6-311G**, and B3LYP/6-311G** energies and enthalpies of compounds containing the first- and second-row elements (other than noble gases) to standard enthalpies of formation. The values of $E(X)$ and $H(X)$ required for the parametrization of these schemes were computed for all the members of the training set at each of the five levels of theory. Full geometry optimizations and unscaled vibrational frequencies were used except for the HF/6-311G**, BLYP/6-311G**, and B3LYP/6-311G** values of $H(C_{60})$, which were calculated with E_{ZP} and E_{therm} extrapolated from the respective HF/6-31G* data (the error introduced by such extrapolation is estimated at less than 1.5 kcal/mol). The GAUSSIAN 94 suite of programs[34] was employed in all the calculations. The attractor interaction lines were located with a previously published algorithm.[35,36]

For a scheme with an K-term BDF, there are two parameters that multiply $N(X)$ and $N_S(X)$, 15 atomic equivalents $e_1(Z)$ or $h_1(Z)$, and K linear combination coefficients that enter the BDF itself. These $K + 17$ parameters were obtained by least-squares fitting of the 300 standard enthalpies of formation predicted from eq 6 or 7 to their experimental counterparts. Initially, the exponents p, q, r, s, and t were determined for the single-term BDF by minimizing the average absolute error in the computed values of ΔH_f°. As the second set of exponents was being determined, these exponents were retained in the two-term BDF and then used together with the second set in the three-term BDF, etc. In each case, the linear combination coefficients were computed *de novo*.

Results

Because of its empirical nature, parameterization of BDF schemes entails extensive numerical testing. The main objective of such testing is to quantify the relationship between the number of terms in the bond density function $e_2(\rho_{IJ},R_{IJ},Z_{IJ},\alpha_{IJ},\beta_{IJ})$and the accuracy of the resulting ΔH_f° estimates. In this context, the results obtained with the BDFs set to zero serve as a useful reference point. Inspection of Table 2 reveals the poor performance of such BDF schemes (which can also be regarded as atom-equivalent schemes augmented with the number of unpaired electrons and molecular charge corrections) employed in conjunction with Hartree−Fock energies. For example, the average absolute error in the computed values of ΔH_f° amounts to almost 9 kcal/mol at the HF/6-31G* level of theory. Enthalpy predictions for diverse classes of compounds, including hypervalent species (ClF_3, SF_6, SO_2Cl_2, $ClO_2^\bullet$, and ClO_4^-), beryllium-containing molecules ($BeCl_2$ and Be_2), the H_2Cl^+ cation, and the C_{60} fullerene, suffer from errors in excess of 30 kcal/mol that make them virtually useless for experimental research. The addition of polarization functions at hydrogen nuclei has very little effect on both the average and maximum absolute errors. Interestingly, the enthalpy estimates obtained from the HF/6-311G** energies are even less accurate.

As expected, the BLYP/6-311G** and B3LYP/6-311G** energies fare much better than their Hartree−Fock counterparts. However, while the average absolute error in ΔH_f° decreases from 9.72 kcal/mol (HF/6-311G**) to 7.01 (BLYP/6-311G**) and 6.63 kcal/mol (B3LYP/6-311G**), the accuracy gains are far from uniform. Thus, although substantial error reductions are seen for some species (e.g., *p*-benzoquinone: −12.3 kcal/mol at B3LYP/6-311G** vs −31.0 kcal/mol at HF/6-311G**), small improvements (e.g., SO_2Cl_2: 28.2 vs 34.5 kcal/mol) and large error increases (e.g., H_2SO_4: 31.1 vs 13.2 kcal/mol) are observed as well.

The inclusion of even a single-term bond density function in eq 6 has a dramatic effect on the accuracy of BDF schemes. The average absolute errors in the standard enthalpies of formation derived from the HF/6-31G* and HF/6-31G** energies decline by over 2 kcal/mol. Even more impressive is the 3.21 kcal/mol reduction in the average absolute error that makes the HF/6-311G** single-term BDF method more accurate than both the BLYP/6-311G** and B3LYP/6-311G** schemes without BDFs. This improvement is broad-based, with the enthalpy estimates for *p*-benzoquinone, SO_2Cl_2, and H_2SO_4 deviating by −9.3, 6.6, and 0.8 kcal/mol, respectively, from the experimental data. However, as indicated by the presence of 16 species ($BeH^\bullet$, Na_2, SO_2, ClF_3, C_4F_8, NH_2^-, OH^-, F^-, H_2F^+, H_2Cl^+, Be_2, MgO, P_4, PN, PF_5, and C_{60}) with the absolute errors in ΔH_f° exceeding 20 kcal/mol among the members of the training set, some pockets of poor performance remain.

The addition of a single-term BDF has also a profound effect on the enthalpy predictions obtained at the BLYP/6-311G** and B3LYP/6-311G** levels of theory. In the latter case, the average absolute error amounts to less than 5 kcal/mol. However, there are still nine species (N_2O_4, NH^-_2, OH^-, F^-, H_3S^+, H_2Cl^+, ClO^-_4, Be_2, and C_{60}) with the computed standard enthalpies of formation that are off by more than 20 kcal/mol.

At all the five levels of theory, the error statistics steadily improve with the number of terms in the BDFs. This across-the-spectrum improvement is nicely illustrated by the data displayed in Figures 1−5. For example, the incidence of the absolute error not greater than 3.0 kcal/mol among the values of ΔH_f° derived from the HF/6-311G** energies, is ca. 22%, 33%, and 41% for $K = 0$, 1, and 5, respectively (Figure 3). At the B3LYP/6-311G** level of theory, the impressive 60% of the 300 standard enthalpies of formation computed with the five-term BDF scheme are accurate within 3.0 kcal/mol (Figure 5), only 10 (those of $BeH^\bullet$, C_3O_2, PH_2^-, PH_4^+, H_3S^+, H_2Cl^+, $C_2H_3^+$, ClO_4^-, $BeCl_2$, and BeO) deviate by between 10 and 20 kcal/mol from the experimental values, and only 4 (those of NH_2^-, OH^-, F^-, and Be_2) deviate by more than 20 kcal/mol.

Analysis of the data compiled in Table 2 reveals that the gains in accuracy become marginal beyond $K = 5$. Thus, 5.0 kcal/mol appears to constitute the limit of accuracy achievable within the Hartree−Fock approximation for compounds of the first- and second-row elements. The analogous figure for the currently used DFT-based approaches is 3.0−3.5 kcal/mol.

BDF schemes utilizing enthalpies at $T = 298$ K rather than energies at $T = 0$ K were also investigated. The error statistics for these schemes (Table 3) convincingly prove that, while computationally expensive, the quantum-mechanical estimation of E_{ZP} and E_{therm} offers no real advantage over the inclusion of these quantities in the fitted parameters. On the other hand, the results of test calculations with the charge-dependent terms in eqs 6 and 7 set to zero (and the other parameters reoptimized) demonstrate the importance of these contributions, especially for energies and enthalpies calculated within the Hartree−Fock approximation (Tables 4 and 5).

The training set employed in the present work contains 156 CHNOS species. Minimization of the average error in the standard enthalpies of formation computed for these species produces a set of BDF schemes tailored to electronic structure calculations on systems of biological importance. As expected, restricting the number of elements improves the accuracy of the ΔH_f° estimates (Table 6). On average, the estimates derived from Hartree−Fock energies possess absolute errors as small as 4.0 kcal/mol, whereas the DFT-based methods yield enthalpies that fall within 3.0 kcal/mol of the experimental values. At the B3LYP/6-311G* level of theory, the absolute error in the enthalpies predicted with the five-term BDF scheme exceeds 5.0 kcal/mol only in 12 cases (CS_2, O_3, fulvene, cubane, C_3O_2, 1*H*-tetrazole, NH_2^-, OH^-, SH^-, CH_3S^-, 2-$C_3H_7^-$, and $C_2H_3^+$).

An analogous treatment of the 61 CH compounds present in the training set furnishes BDF schemes for hydrocarbons and their radicals, carbocations, and carbanions. For these species, accuracy of ca. 2.0 kcal/mol in the enthalpy estimates obtained from Hartree−Fock energies is achieved with BDFs possessing as few as four terms, whereas two terms are sufficient at the BLYP/6-311G** and B3LYP/6-311G** levels of theory (Table 7).

Discussion

The results of test calculations described in the previous section of this paper testify to the accuracy of BDF schemes used in conjunction with energies computed at various levels of theory. In light of the patterns observed in the error statistics compiled in Tables 2−7, the use of five-term BDFs in schemes for the conversion of energies of compounds containing the first- and second-row elements to standard enthalpies of formation is recommended. In Table 8, the parameters of such BDFs are listed together with the respective e_Q, e_S, and e_1 data for the five levels of theory under study. The five-term BDF schemes

TABLE 9: Recommended BDF Schemes for Converting Total Energies at $T = 0$ K of CHNOS Species to Standard Enthalpies of Formation[a]

level of theory	e_Q (kcal/mol)	e_S (kcal/mol)	$e_1(1)$ (au)	$e_1(6)$ (au)
HF/6-31G*	33.091	10.812	0.544 229	37.892 644
HF/6-31G**	38.833	9.529	0.559 607	37.900 080
HF/6-311G**	29.764	9.711	0.561 430	37.912 354
BLYP/6-311G**	9.815	1.725	0.572 360	38.104 407
B3LYP/6-311G**	6.842	1.525	0.577 453	38.115 650

level of theory	$e_1(7)$ (au)	$e_1(8)$ (au)	$e_1(16)$ (au)
HF/6-31G*	54.475 841	74.802 112	397.557 241
HF/6-31G**	54.493 317	74.823 799	397.550 417
HF/6-311G**	54.503 757	74.834 364	397.572 239
BLYP/6-311G**	54.763 300	75.171 948	398.229 736
B3LYP/6-311G**	54.768 360	75.174 931	398.242 631

level of theory	$e_2(\rho,R,Z,\alpha,\beta)$ (kcal/mol)
HF/6-31G*	$-4.56209 \times 10^{0}\rho^{1/2}R^{-5/2}Z^{2/3}\alpha^{-1/3} + 1.78854 \times 10^{3}\rho^{3}R^{3}Z^{-4/3}\alpha^{-1/2}\beta^{1/3} - 1.46036 \times 10^{0}\rho^{3}R^{5/2}Z^{2/3}\alpha^{-1} - 9.92098 \times 10^{2}\rho^{5/2}R^{3/2}Z^{-4/3}\alpha^{-2/3}\beta^{2/3} + 6.99335 \times 10^{-1}\rho^{5/3}R^{-2}Z^{2/3}\alpha^{-5/2}\beta^{-1/3}$
HF/6-31G**	$-1.25428 \times 10^{1}\rho^{3/2}R^{-1}Z^{2/3}\alpha^{-2/3} + 2.12580 \times 10^{3}\rho^{3}R^{3/2}Z^{-1}\alpha^{-1} - 1.72049 \times 10^{-5}\rho^{3}R^{3}Z^{3}\alpha^{3/2} + 4.41519 \times 10^{0}\rho^{5/2}R^{-5/3}Z^{1/3}\alpha^{-3}\beta^{-1/3} - 3.75606 \times 10^{2}\rho^{4/3}R^{-2/3}Z^{-1/2}\alpha^{-2/3}$
HF/6-311G**	$-1.49867 \times 10^{1}\rho^{4/3}R^{-2/3}Z^{2/3}\alpha^{-1/2} + 2.49599 \times 10^{3}\rho^{3}R^{2}Z^{-1}\alpha^{-2/3} + 1.40668 \times 10^{1}\rho^{2/3}R^{-5/2}Z^{1/2}\alpha^{-4/3} - 7.56489 \times 10^{2}\rho^{5/3}R^{1/3}Z^{-2/3}\alpha^{-1/2} + 8.81213 \times 10^{-2}\rho^{-1}R^{5/3}Z^{1/2}\alpha^{5/3}\beta^{1/3}$
BLYP/6-311G**	$4.02873 \times 10^{2}\rho^{3}R^{-1}\alpha^{-1/2} - 1.37094 \times 10^{1}\rho^{3}R^{1/2}\alpha^{3}\beta^{-2/3} - 1.12669 \times 10^{-5}\rho^{3}R^{3}Z^{3}\beta - 1.80612 \times 10^{-3}\rho^{-3}RZ^{2/3}\alpha^{3}\beta^{-2} + 5.01164 \times 10^{1}\rho^{5/3}R^{3}Z^{-4/3}\alpha\beta^{-3/2}$
B3LYP/6-311G**	$6.93746 \times 10^{2}\rho^{3}RZ^{-1/2}\alpha^{-1/3}\beta^{1/3} - 3.83128 \times 10^{-2}\rho R^{3}Z\alpha^{1/3}\beta^{1/2} - 1.13038 \times 10^{3}\rho^{3}R^{-2}Z^{-1/3}\alpha^{1/2}\beta^{1/2} + 2.13765 \times 10^{-4}\rho^{-3}R^{4/3}Z^{3/2}\alpha^{5/2}\beta^{2/3} + 2.41886 \times 10^{2}\rho^{5/2}R^{2/3}Z^{-1}\alpha^{-2/3}\beta^{-1/2}$

[a] ρ, R, α, β in au; 1 au = 627.5095 kcal/mol.

TABLE 10: Recommended BDF Schemes for Converting Total Energies at $T = 0$ K of CH Species to Standard Enthalpies of Formation[a]

level of theory	e_Q (kcal/mol)	e_S (kcal/mol)	$e_1(1)$ (au)	$e_1(6)$ (au)
HF/6-31G*	23.136	16.106	0.559 128	37.876 907
HF/6-31G**	22.265	15.683	0.560 529	37.879 355
HF/6-311G**	24.150	13.720	0.564 709	37.902 023
BLYP/6-311G**	4.768	2.202	0.584 466	38.101 277
B3LYP/6-311G**	−0.335	3.704	0.581 027	38.104 335

level of theory	$e_2(\rho,R,Z,\alpha,\beta)$ (kcal/mol)
HF/6-31G*	$1.74816 \times 10^{3}\rho^{3}R^{3}Z^{-1}\alpha^{1/2}\beta^{1/2} - 6.49238 \times 10^{1}\rho^{-1/2}R^{-3}Z^{1/2}\alpha\beta^{1/3} + 9.73382 \times 10^{-3}\rho^{3}R^{2/3}Z^{5/2}\alpha^{-2/3}\beta^{1/3} + 1.48447 \times 10^{-7}\rho^{-3}RZ^{2}\alpha^{4/3}\beta^{-3}$
HF/6-31G**	$1.69625 \times 10^{3}\rho^{3}R^{3}Z^{-1}\alpha^{1/2}\beta^{1/2} - 7.96660 \times 10^{1}\rho^{-1/3}R^{-5/2}Z^{1/3}\alpha\beta^{1/3} + 5.68623 \times 10^{-7}\rho^{-3}R^{3}Z^{5/3}\alpha^{3/2}\beta^{-2} + 4.98186 \times 10^{0}\rho^{3}R^{-1}Z\alpha^{-1/3}\beta^{1/3}$
HF/6-311G**	$1.28451 \times 10^{3}\rho^{3}R^{3}Z^{-1}\alpha^{5/2}\beta^{-1/3} - 5.88514 \times 10^{1}\rho^{-1/2}R^{-4/3}\alpha^{3}\beta^{-1/3} - 2.46701 \times 10^{1}\rho^{3}R^{1/2}Z^{1/3}\alpha^{-1} + 6.48111 \times 10^{2}\rho^{3}R^{2/3}Z^{-4/3}\alpha^{-2/3}\beta^{-1/3}$
BLYP/6-311G**	$3.43324 \times 10^{2}\rho^{3}R^{-1/3} - 2.62900 \times 10^{0}\rho^{1/3}R^{5/2}Z^{-2}\alpha^{3}\beta^{-5/2}$
B3LYP/6-311G**	$1.57443 \times 10^{2}\rho^{5/2}R^{5/2}Z^{-2/3}\alpha^{1/3}\beta^{-1/3} + 7.82863 \times 10^{-8}\rho^{-4/3}R^{3}Z^{3}\alpha^{-3}\beta^{3}$

[a] ρ, R, α, β in au; 1 au = 627.5095 kcal/mol.

recommended for the CHNOS species are given in Table 9, whereas the four- and two-term schemes for the CH systems are presented in Table 10.

Accuracy comparisons between the present enthalpy estimates and those afforded by the previously published atom- and group-equivalent approaches are of interest to the potential users of the BDF methodology. The results obtained for the C_{60} fullerene provide a useful example in this context. The standard enthalpy of formation of C_{60} (the experimental value[33] 618.0 kcal/mol) is estimated at 624.8−631.6 kcal/mol by the five BDF schemes listed in Table 8, whereas the schemes tailored to the CHNOS and CH species produce the estimates of 621.1−626.8 kcal/mol and 618.3−620.6 kcal/mol, respectively. These predictions are far more accurate than those obtained with the HF/6-31G* atomic equivalents of Dewar[13] (962.4 kcal/mol), and the schemes of Yala (686.8 kcal/mol) and Castro (773.7 kcal/mol).[19] The accuracy of the present estimates is also superior to that of the enthalpies furnished by methods expressly parametrized for hydrocarbons, such as the BLYP/6-311G** and B3LYP/6-311G** atom-equivalent schemes of Mole et al.[14] (747.8 and 668.3 kcal/mol, respectively), the HF/6-31G* atom-equivalent scheme for aromatic hydrocarbons proposed by

TABLE 11: Experimental and B3LYP/6-311G Standard Enthalpies of Formation of Selected Organic and Inorganic Systems Not Included in the Training Set**

species	ΔH_f° (kcal/mol) (exptl)	ΔH_f° (kcal/mol) (predicted)		
		I[a]	II[b]	III[c]
cyclo-$C_7H_7^+$	209.0[d]	209.5	213.1	212.3
$CH_3COCOCH_3$	−78.2[d]	n/a	−80.3	−78.7
maleic anhydride	−95.2[d]	n/a	−96.9	−99.3
C_6H_5CHO	−8.8[d]	n/a	−10.2	−11.4
$C_6H_5NO_2$	15.4[d]	n/a	14.9	13.1
p-$O_2NC_6H_4NH_2$	16.2[d]	n/a	10.6	7.9
$C_6H_5S^\bullet$	56.8[e]	n/a	54.8	50.4
$NC{-}C{\equiv}C{-}CN$	126.5[d]	n/a	122.7	125.2
$NC{-}S{-}S{-}CN$	82.3,[d] 83.6[e]	n/a	94.9	94.2
H_2S_3	7.3[d,e]	n/a	6.3	10.5
HNCS	30.0[d,e]	n/a	25.3	30.9
CF_3COOH	−255.0[d]	n/a	n/a	−248.3
CCl_3COCl	−57.3[f]	n/a	n/a	−64.3
$(NPCl_2)_3$	−175.9[e]	n/a	n/a	−186.8
$PS^\bullet$	42.2[e]	n/a	n/a	37.5
$H_2C{=}SiH_2$	37.0[g]	n/a	n/a	44.8
AlOCl	−83.2[e]	n/a	n/a	−58.7
NaCN	22.5[e]	n/a	n/a	34.3
Mg(cyclo-$C_5H_5)_2$	31.2,[e] 32.6[h]	n/a	n/a	55.5
ClF_5	−54.0,[d] −57.0[f]	n/a	n/a	−68.0

[a] Values of ΔH_f° derived from B3LYP/6-311G** energies using the BDF scheme recommended for CH species (Table 10). [b] Values of ΔH_f° derived from B3LYP/6-311G** energies using the BDF scheme recommended for CHNOS species (Table 9). [c] Values of ΔH_f° derived from B3LYP/6-311G** energies using the BDF scheme recommended for species containing the first- and second-row elements (Table 8). [d] Reference 27. [e] Reference 30. [f] Reference 28. [g] Reference 37. [h] Reference 29.

Schulman, Peck, and Disch[17] (660.4 kcal/mol), and the HF/6-31G* linear regression of Herndon[31] (734.4 kcal/mol).

Another measure of accuracy is provided by the results obtained for molecules not included in the training set. Inspection of Table 11, in which experimental values of ΔH_f° are listed along with the respective theoretical estimates for 20 randomly selected organic and inorganic species, reveals a somewhat mixed performance of the B3LYP/6-311G** BDF scheme. Excellent enthalpy estimates are produced for organic compounds such as the tropylium cation, diacetyl, maleic anhydride, benzaldehyde, nitrobenzene, the $C_6H_5S^\bullet$ radical, and dicyanoacetylene. With the errors amounting to ca. 7 kcal.mol, the estimates for p-nitroaniline, trifluoroacetic acid, and trichloroacetic chloride are less satisfactory. Standard enthalpies of formation of some sulfur-containing inorganic species (H_2S_3, HNCS, and $PS^\bullet$) are predicted quite accurately, whereas that of $(SCN)_2$ is not. The accuracy of predictions for other inorganic systems varies greatly, with the absolute errors increasing in the order $H_2C{=}SiH_2 < (NPCl_2)_3 <$ NaCN $< ClF_5 <$ AlOCl $\approx Mg(C_5H_5)_2$. Overall, the BDF scheme appears to work better for organic compounds than for inorganic species with "normal" covalent bonds, which in turn fare better than their ionic counterparts.

Conclusions

The BDF formalism provides a new approach to converting HF and DFT energies of molecules, ions, and radicals to standard enthalpies of formation. Employing a combination of atomic equivalents, bond density functions (BDFs), and corrections for molecular charge and spin multiplicity, this new approach is capable of producing accurate enthalpy estimates for most organic and inorganic compounds of the first- and second-row elements. at the B3LYP/6-311G** level of theory, the average absolute errors in the computed values of ΔH_f° amount to 1.6, 2.4, and 3.4 kcal/mol for the sets of 61 CH, 156 CHNOS, and 300 H...Cl species that include systems as small as the Cl^- anion and as large as the C_{60} fullerene. Although admittedly empirical and less accurate than the extrapolative methods of the G2 and CBS families, the BDF formalism has the advantage of low computational cost that makes it applicable to large molecules. Consequently, it allows for theoretical predictions of molecular thermochemistry with accuracy rivaling that of calorimetric measurements for systems of interest to the broad audience of experimental chemists.

The current formulation of the BDF schemes constitutes the first attempt at the development of accurate yet inexpensive electronic structure methods that combine rigorous ab initio calculations with empirical corrections. As such, it is subject to future improvements, including the addition of diffuse functions to the basis sets in order to reduce the observed large errors in the computed enthalpies of anions with localized charge (this option has not been investigated in the present work because of the SCF convergence problems encountered for larger molecules) and more sophisticated forms of BDFs. Research in this direction is currently in progress.

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