

Gaussian-3X (G3X) theory: Use of improved geometries, zero-point energies, and Hartree–Fock basis sets

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A modification of G3 theory incorporating three changes is presented. The three new features include: (1) B3LYP/6-31G(2*df*,*p*) geometry; (2) B3LYP/6-31G(2*df*,*p*) zero-point energy; and (3) addition of a *g* polarization function to the G3Large basis set for second-row atoms at the Hartree–Fock level. Extension of G3 theory in this manner, referred to as G3X, is found to give significantly better agreement with experiment for the G3/99 test set of 376 reaction energies. Overall the mean absolute deviation from experiment decreases from 1.07 kcal/mol (G3) to 0.95 kcal/mol (G3X). The largest improvement occurs for nonhydrogens. In this subset of energies the mean absolute deviation from experiment decreases from 2.11 to 1.49 kcal/mol. The increased accuracy is due to both the use of new geometries and the larger Hartree–Fock basis set. In addition, five other G3 methods are modified to incorporate these new features. Two of these are based on reduced orders of perturbation theory, G3X(MP3) and G3X(MP2), and have mean absolute deviations for the G3/99 test set of 1.13 and 1.19 kcal/mol, respectively. The other three methods are based on scaling the energy terms, G3SX, G3SX(MP3), and G3SX(MP2). They have mean absolute deviations of 0.95, 1.04, and 1.34 kcal/mol, respectively. © 2001 American Institute of Physics.

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I. INTRODUCTION

Recently, the G2/97 test set^{1,2} for assessing quantum chemical methods was expanded to include 75 additional enthalpies of formation. This new set, referred to as the G3/99 test set,³ has 222 enthalpies of formation, 88 ionization potentials, 58 electron affinities, and 8 proton affinities. The total number of energies in G3/99 is 376. In Ref. 3, Gaussian-3 (G3) theory⁴ was assessed on this set and was found to have a mean absolute deviation of 1.07 kcal/mol compared to 1.01 kcal/mol for the G2/97 test set. G3 theory has a similar accuracy for the larger hydrocarbons and substituted hydrocarbons in the expanded test set as for those in the G2/97 test. However, G3 theory does poorly for some of the larger nonhydrogen systems containing second-row atoms such as the hypervalent SF₆ and PF₅ molecules, which have errors of 6–7 kcal/mol. The G3 mean absolute deviation is 2.11 kcal/mol for the 47 nonhydrogens in the G3/99 test set. This is much larger than the G3 mean absolute deviation of 1.68 kcal/mol for the 34 nonhydrogens in the smaller G2/97 test set. Part of the source of error for the nonhydrogen species in the G3 results was traced to the MP2/6-31G(*d*) geometries used for single-point energies.³ Use of experimental geometries instead of MP2/6-31G(*d*) in a small subset of nonhydrogens reduced the deviations in those molecules, but they still remained around 3–4 kcal/mol. The remainder of the error was assigned to basis set deficiencies.

In this paper we report an extension of G3 theory that incorporates a new geometry, a new zero-point energy, and a larger Hartree–Fock basis set to correct some deficiencies of G3 theory occurring mainly in the nonhydrogen species. In Sec. II these new features and the reasons behind their choices are discussed. The new method, referred to as G3X, is defined in this section. In Sec. III we assess G3X on the full G3/99 test set and compare its performance with that of G3 theory. In Sec. IV the results are presented for extending other G3-based methods in a similar manner, including the G3(MP2),⁵ G3(MP3),⁶ and the scaled G3 methods.⁷ Finally, conclusions are given in Sec. V.

II. DESCRIPTION OF NEW FEATURES IN GAUSSIAN-3X (G3X) THEORY

Gaussian-3 theory has been described in detail elsewhere.⁴ We briefly review it here. Geometries are calculated at the second order Møller–Plesset perturbation theory level with the 6-31G(*d*) basis set, MP2(FU)/6-31G(*d*). Scaled (0.8929) zero-point energies calculated at the Hartree–Fock level with the 6-31G(*d*) basis set, HF/6-31G(*d*), are included in the final energies. Treatment of electron correlation at the MP2(FU)/6-31G(*d*) geometries is by Møller–Plesset (MP) perturbation theory⁸ and quadratic configuration interaction (QCI)⁹ with various basis sets, the largest being the G3Large basis.⁴ The final energies

TABLE I. Comparison of the effect of additional functions on the atomization energies of selected nonhydrogens.^a

Species	Atomization energy, kcal/mol	Change from HF/G3Large results, kcal/mol		
	HF/G3L	G3L+ <i>g</i> ^b	G3L+2 <i>g</i> ^c	G3L+2 <i>gh</i> ^d
SiF ₄	430.6	3.6	3.9	5.4
SiCl ₄	283.2	1.2	1.2	0.3
PF ₃	233.1	3.0	3.1	3.7
PF ₅	360.5	5.1	5.3	6.3
PCl ₃	132.3	1.1	1.1	1.2
PCl ₅	155.9	1.6	1.6	1.9
SO ₂	106.8	0.8	0.8	0.8
SO ₃	138.4	1.1	1.2	1.3
SF ₆	231.9	5.5	5.6	7.0

^aResults are for MP2(FU)/6-31G(*d*) geometries. G3L=G3Large.

^bA single *g* polarization function is added to each second-row atom. They are Si (0.461), P (0.597), S (0.683), and Cl (0.827). The *g* exponents are taken from the cc-pvqz basis set of Ref. 14.

^cTwo *g* polarization functions are added to each second-row atom. They are *x* and 3*x*, where *x* is the exponent from footnote b.

^dTwo *g* polarization functions and a single *h* function are added to each second-row atom. The *g* functions are as in footnote c and the *h* exponents are Si (0.583), P (0.745), S (0.872), Cl (1.053). The *h* exponents are taken from the cc-pv5z basis set of Ref. 14.

are effectively at the QCISD(T)/G3Large level, making certain assumptions about additivity,¹⁰ and include a spin-orbit correction, core-correlation effects, and a higher-level empirical correction to accommodate remaining deficiencies. The higher-level correction (HLC) is based on four empirical parameters that correct remaining deficiencies for pairs of valence electrons in molecules, unpaired electrons in molecules, pairs of valence electrons in atoms, and unpaired electrons in atoms. They were obtained from a fit of the G2/97 test set. We now describe the changes included in the extension of G3 theory proposed in this paper.

A. Basis set

As mentioned in the Introduction, deficiencies in the G3 basis sets are believed to be partly responsible for the large errors obtained for some of the larger nonhydrogens containing second-row atoms. Such deficiencies are possible at both the Hartree–Fock and correlation levels. In this work we have focused on correcting basis set deficiencies for second-row atoms at the Hartree–Fock level. Correcting such deficiencies at the correlated level is more difficult due to their slow convergence, although our HLC parameters offer partial remedy.

In order to assess the Hartree–Fock deficiencies, a set of nine nonhydrogens was selected from the G3/99 test set. The atomization energies of these species [MP2(FU)/6-31G(*d*) geometries] were calculated at the HF/G3Large level, and then additional valence polarization functions for the second-row atoms were added to the G3Large basis. The changes in the atomization energies with addition of these polarization functions are listed in Table I. It is clear from Table I that the HF/G3Large atomization energies are far from the HF limit for some species. For example, the addition of a single *g*

function to the second-row atoms (Si–Cl) increases the binding in SiF₄, PF₅, and SF₆ by 3.6, 5.1, and 5.5 kcal/mol, respectively. The increase is much smaller for similar molecules containing chlorine, indicating more of a deficiency for species having a mixture of first- and second-row elements. The results in Table I indicate that addition of more polarization functions (2*g*,2*gh*) on the second-row atoms results in substantially smaller changes in the atomization energies. Thus on the basis of these results we have chosen to add a single *g* polarization function to the second-row G3Large basis set at the HF level for the proposed extension of G3 theory. This new basis set is referred to as G3XLarge.

B. Geometry and zero-point energy

In order to assess the deficiencies in the geometries mentioned in the Introduction, a set of second-row nonhydrogen molecules, referred to as Set A, was selected from the G3/99 test set. The molecules in this set are PF₃, PF₅, P₄, PCl₅, SO₂, SO₃, and SF₆. Six theoretical methods for optimizing geometries were investigated for this set of molecules. These methods were MP2(FU)/6-31(*d*), MP2/6-31(2*df*,*p*), B3LYP/6-31G(*d*), QCISD/6-31G(*d*), B3LYP/6-31G(2*df*,*p*), and B3LYP/6-311+G(3*df*,2*p*). A summary of the results of these calculations is given in Table II. Also given in the table are the experimental geometries and a breakdown of the deviations of the methods. The results indicate that for this set of seven molecules improvement is found with an increase in the basis set size from 6-31G(*d*) to 6-31G(2*df*,*p*) at both the MP2 and the B3LYP levels. The B3LYP/6-31G(2*df*,*p*) method has a mean average deviation from experiment of 0.011 Å for bond lengths, slightly better than MP2/6-31G(2*df*,*p*), which has an mean average deviation of 0.014 Å. Increasing the basis set size further to 6-311+G(3*df*,2*p*) leads to no additional improvement in the geometries.

The methods were also investigated for 15 smaller molecules from the original G2 test set, including some hydrogen containing ones, to assure that the trends in accuracy found for the seven nonhydrogens hold for other molecules. This set of 15 molecules is referred to as Set B in Table II. The results for this set also indicate improvement of the predictions with increase in basis set size. In addition, the B3LYP method performs slightly better than the MP2 method. The B3LYP/6-31G(2*df*,*p*) method has the smallest mean average deviation with experiment for bond distances (0.006 Å), while the angles are not sensitive to the method used. On the basis of the results in Table II, the B3LYP/6-31G(2*df*,*p*) method was chosen for geometry optimizations in the extension of G3 theory reported in this paper and replaces the MP2(FU)/6-31G(*d*) geometry. In addition, the B3LYP method has the advantage that it is computationally more efficient than a MP2 calculation.

The B3LYP/6-31G(2*df*,*p*) method was also chosen for the calculation of zero-point energies to be consistent with the geometry optimization method. A scale factor of 0.9854 was derived for B3LYP/6-31G(2*df*,*p*) from fitting the set of zero-point energies compiled by Scott and Radom¹¹ in their recent derivation of zero-point energies for different

TABLE II. Comparison of different methods for calculations of geometries of selected species in the G3/99 test set.^a

Species	Parameter	MP2(FU)/ 6-31G(<i>d</i>)	MP2(FC)/ 6-31G(2 <i>df</i> , <i>p</i>)	QCISD/ 6-31G(<i>d</i>)	B3LYP/ 6-31G(<i>d</i>)	B3LYP/ 6-31G(2 <i>df</i> , <i>p</i>)	B3LYP/ 6-311+G(3 <i>df</i> ,2 <i>p</i>)	Expt ^b
Set A								
PF ₃	PF	1.593	1.573	1.594	1.596	1.576	1.584	1.57
	FPF	97.6	97.8	97.3	97.7	97.8	97.6	97.8
PF ₅	PF(<i>ax</i>)	1.595	1.575	1.594	1.597	1.578	1.587	1.577
	PF(<i>eq</i>)	1.566	1.546	1.565	1.569	1.550	1.549	1.534
P ₄	PP	2.195	2.205	2.201	2.217	2.211	2.204	2.21
PCl ₅	PCl(<i>ax</i>)	2.139	2.124	2.148	2.176	2.157	2.154	2.19
	PCl(<i>eq</i>)	2.038	2.027	2.044	2.071	2.055	2.044	2.04
SO ₂	SO	1.477	1.452	1.461	1.464	1.443	1.437	1.432
	OSO	119.8	119.9	119.0	119.1	119.2	119.2	119.5
SO ₃	SO	1.458	1.435	1.448	1.453	1.432	1.425	1.43
SF ₆	SF	1.592	1.565	1.590	1.600	1.575	1.577	1.564
Deviation ^c	Bonds	0.027	0.014	0.022	0.025	0.011	0.012	
	Angles	0.2	0.2	0.5	0.3	0.2	0.2	
Set B								
LiH	Li-H	1.640	1.625	1.654	1.621	1.615		1.595
CH	C-H	1.121	1.118	1.131	1.133	1.131		1.12
CH ₄	C-H	1.090	1.087	1.094	1.093	1.092		1.085
NH ₃	N-H	1.017	1.013	1.020	1.019	1.017		1.012
	H-N-H	106.3	105.4	106.0	105.7	105.5		106.7
H ₂ O	O-H	0.969	0.958	0.970	0.969	0.962		0.957
	H-O-H	104.0	103.2	104.1	103.6	103.7		104.5
FH	F-H	0.934	0.914	0.934	0.934	0.919		0.917
C ₂ H ₂	C-C	1.216	1.212	1.213	1.205	1.199		1.203
	C-H	1.066	1.061	1.069	1.067	1.062		1.061
C ₂ H ₄	C-C	1.335	1.333	1.338	1.331	1.327		1.339
	C-H	1.085	1.082	1.088	1.087	1.086		1.085
	H-C-H	116.6	116.8	116.4	116.3	116.1		117.8
HCN	C-N	1.176	1.170	1.166	1.157	1.152		1.153
	C-H	1.069	1.065	1.072	1.070	1.067		1.065
CO	C-O	1.150	1.140	1.145	1.138	1.131		1.128
H ₂ CO	C-O	1.220	1.210	1.217	1.206	1.200		1.208
	C-H	1.104	1.104	1.107	1.110	1.111		1.116
	H-C-H	115.7	115.5	115.7	115.2	115.1		116.5
N ₂	N-N	1.130	1.120	1.115	1.105	1.099		1.098
N ₂ H ₂	N-N	1.266	1.260	1.258	1.246	1.242		1.252
	N-H	1.036	1.032	1.038	1.040	1.038		1.028
	H-N-N	105.4	105.3	105.8	106.1	106.4		106.9
N ₂ H ₄	N-N	1.438	1.436	1.444	1.437	1.437		1.447
	N-Ha	1.016	1.012	1.019	1.017	1.015		1.008
	N-Hb	1.020	1.016	1.023	1.022	1.019		1.008
	Ha-N-N	106.4	106.3	106.1	106.6	106.8		109.2
	Hb-N-N	111.5	111.1	111.1	111.8	111.6		109.2
	Ha-N-Hb	107.0	106.4	106.6	106.8	106.6		113.3
	Ha-N-N-Hb	90.6	88.5	91.0	90.5	88.6		88.9
O ₂	O-O	1.246	1.225	1.221	1.215	1.206		1.208
Deviation ^d	Bonds	0.014	0.008	0.012	0.009	0.006		
	Angles	1.9	2.0	2.0	2.1	1.9		

^aBond lengths in Å; bond angles in degrees.

^bExperimental values for Set A are from the M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data* **14**, Suppl. No. 1 (1985). JANAF Thermochemical Tables Third Edition. Experimental values for Set B are from J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.* **102**, 939 (1980).

^cMean absolute deviations for the bond lengths and bond angles in Set A.

^dMean absolute deviations for the bond lengths and bond angles in Set B.

methods. The small correction suggests that B3LYP/6-31G(2*df*,*p*) is accurate for zero-point energies as well as geometries. This choice differs in two ways from that in the original G3 procedure. First, in G3 theory the zero-point energies and geometries are calculated at two different levels of theory [HF/6-31G(*d*) and MP2(FU)/6-31G(*d*), respec-

tively]. Second, the HF/6-31G(*d*) scale factor was based on fitting of experimental vibrational frequencies, not zero-point energies. Thus our new procedure for calculating zero-point energies is more logical than that in the G3 procedure. However, based on previous studies, we expect only minor changes from such improved zero-point corrections.^{12,13}

G3X	HF	MP2	MP4	QCISD(T)
6-31G(d)	X	X	X	X
6-31+G(d)	X	X	X	
6-31G(2df,p)	X	X	X	
G3Large	X	X (FU)		
G3XLarge	X			

FIG. 1. Schematic of the single energy points in G3X theory.

C. Details of G3X theory

The total G3X energy is given by the equation

$$\begin{aligned}
 E_0(\text{G3X}) = & \text{MP4}/d + [\text{QCISD(T)}/d - \text{MP4}/d] \\
 & + [\text{MP4}/\text{plus} - \text{MP4}/d] + [\text{MP4}/2df,p - \text{MP4}/d] \\
 & + [\text{MP2(FU)}/\text{G3L} - \text{MP2}/2df,p \\
 & - \text{MP2}/\text{plus} + \text{MP2}/d] + [\text{HF}/\text{G3XL} - \text{HF}/\text{G3L}] \\
 & + E(\text{SO}) + E(\text{HLC}) + E(\text{ZPE}), \quad (1)
 \end{aligned}$$

where $d=6\text{-}31\text{G}(d)$, $\text{plus}=6\text{-}31+\text{G}(d)$, $2df,p=6\text{-}31\text{G}(2df,p)$, $\text{G3L}=\text{G3Large}$ basis set,⁹ $\text{G3XL}=\text{G3XLarge}$ basis set (see below), $E(\text{SO})=\text{spin-orbit}$ correction for atoms only, $E(\text{HLC})=\text{higher-level correction}$, and $E(\text{ZPE})=\text{zero-point energy correction}$. All correlation calculations are done with a frozen core, except the MP2 calculation with the G3large basis set that treats all electrons (FU), i.e., it includes core-related correlation. Figure 1 shows a schematic of the single energy points in G3X theory.

Equation (1) is the same as for G3 theory except for the addition of the Hartree-Fock (HF) term. This term extends the HF/G3L energy, which is part of the MP2(FU)/G3L energy, to the G3XL basis set. The G3XL basis is the G3Large basis set with a single g function (seven pure functions) on the second-row elements. The g exponents for Al-Cl are taken from Dunning's¹⁴ correlation consistent $cc\text{-}pvqz$ basis set (Al: 0.357, Si: 0.461, P: 0.597, S: 0.683, Cl: 0.827, Ar: 1.007). No g function was used on Na or Mg. The G3XL basis set is available on the internet.¹⁵

As discussed earlier, the single-point energies in Eq. (1) are calculated at B3LYP/6-31G(2df,p) geometries and the zero-point energies $E(\text{ZPE})$ and thermal corrections are obtained from scaled B3LYP/6-31G(2df,p) frequencies (0.9854). The higher-level correction (HLC) parameters were obtained by fitting to the full G3/99 test set and are given in Table III. Fitting of the HLC parameters to the smaller G2/97 test set gives nearly the same values for the four parameters, indicating that there is little sensitivity to the increase in the data set size. The B3LYP/6-31G(2df,p) geometries and B3LYP/6-31G(2df,p) zero-point energies for the G3/99 test set are available on the internet.¹⁵ The G3X method takes about 10%–15% more time than G3 due to the B3LYP/6-31G(2df,p) frequency calculation.

TABLE III. Higher-level correction (HLC) parameters (in mhartrees).^{a,b}

	A	B	C	D	zpe scale factor
G3	6.386	2.977	6.219	1.185	0.8929
G3//B32df	6.688	3.007	6.763	1.107	0.9854 ^c
G3(+g)	6.359	2.947	6.274	1.152	0.8929
G3X	6.783	3.083	6.877	1.152	0.9854 ^c
G3X(MP3)	8.461	4.134	8.141	2.056	0.9854 ^c
G3X(MP2)	9.680	4.715	10.039	2.010	0.9854 ^c

^aThe HLC is $-An_\beta - B(n_\alpha - n_\beta)$ for molecules and $-Cn_\beta - D(n_\alpha - n_\beta)$ for atoms (including atomic ions). The n_β and n_α are the number of β and α valence electrons, respectively, with $n_\alpha \geq n_\beta$. The number of valence electron pairs corresponds to n_β . Thus A is the correction for pairs of valence electrons in molecules, B is the correction for unpaired electrons in molecules, C is the correction for pairs of valence electrons in atoms, and D is the correction for unpaired electrons in atoms.

^bThe G3 parameters are from Ref. 4 and are obtained by fitting to the G2/97 test set. The parameters for the other methods are obtained in a similar manner, but are based on fitting to the G3/99 test set.

^cThe B3LYP/6-31G(2df,p) scale factor was obtained by fitting to experimental zero-point energies (see text).

III. ASSESSMENT OF G3X THEORY

The G3/99 test set described in the Introduction was used in testing the new methods proposed in this paper. The full G3/99 test set has 376 test energies, including the 301 energies from the G2/97 test set and the 75 new energies.³ The GAUSSIAN98¹⁶ computer program was used for the calculations. The calculated total energies, enthalpies of formation, ionization potentials, electron affinities, and proton affinities are available via the internet.¹⁵ The atomic energies are given in Table IV.

A summary of mean absolute deviations from experiment for the G3/99 test set is given in Table V. The mean absolute deviation for G3X for the 376 energies is 0.95 kcal/mol. This is a substantial improvement over G3 theory, which has a mean absolute deviation of 1.07 kcal/mol for the same set of energies. The mean absolute deviation for enthalpies of formation decreases from 1.05 to 0.88 kcal/mol. The improvement is largely due to the nonhydrogen species where the average absolute deviation decreases from 2.11 kcal/mol to 1.49 kcal/mol. Contributions of the new features of G3X to the mean absolute deviations are listed in Table V. Both features, i.e., the new HF basis set [denoted G3(+g)] and the new geometry and zero-point energy (denoted G3//B32df), contribute to the improved accuracy of the G3X method. Both G3(+g) and G3//B32df have similar mean absolute deviations (1.02 and 1.01 kcal/mol, respectively), but the former has a significantly smaller root mean square deviation (1.41 kcal/mol) than the latter (1.48 kcal/mol). Thus the new HF basis set is more important than the new geometries in the improvement of G3 theory.

The G3X mean absolute deviation from experiment for the smaller G2/97 test set is given in Table VI. The results show that the overall mean absolute deviation from experiment is nearly the same for the larger G3/99 test set (0.95 kcal/mol) as for the smaller G2/97 test set (0.96 kcal/mol). Similarly, the mean absolute deviation from experiment for enthalpies is nearly the same for the larger G3/99 test set (0.88 kcal/mol) as for the smaller G2/97 test set (0.86 kcal/

TABLE IV. Atomic energies (in Hartrees) of H–Ar.

Species	G3X	G3X(MP3)	G3X(MP2)	G3SX	G3SX(MP3)	G3SX(MP2)
H	-0.500 97	-0.501 87	-0.501 83	-0.499 95	-0.499 95	-0.501 97
He	-2.903 01	-2.903 92	-2.903 24	-2.901 45	-2.900 66	-2.910 74
Li	-7.465 09	-7.466 00	-7.434 04	-7.470 51	-7.470 46	-7.463 43
Be	-14.660 88	-14.662 87	-14.629 96	-14.664 23	-14.665 63	-14.687 38
B	-24.643 19	-24.645 17	-24.607 77	-24.648 46	-24.648 34	-27.707 35
C	-37.828 31	-37.830 57	-37.790 03	-37.834 90	-37.834 09	-37.945 37
N	-54.546 90	-54.568 08	-54.525 87	-54.573 44	-54.572 73	-54.752 40
O	-75.032 24	-75.035 43	-74.991 20	-75.042 48	-75.041 21	-75.302 41
F	-99.686 15	-99.689 77	-99.643 10	-99.699 34	-99.697 99	-100.057 43
Ne	-128.874 97	-128.879 58	-128.831 53	-128.892 29	-128.891 69	-129.369 06
Na	-162.104 12	-162.105 02	-161.847 99	-162.155 78	-162.155 42	-162.529 66
Mg	-199.908 08	-199.909 59	-199.651 54	-199.957 31	-199.957 37	-200.488 69
Al	-242.208 10	-242.209 93	-241.937 65	-242.261 08	-242.260 38	-242.953 80
Si	-289.222 87	-289.224 97	-288.940 12	-289.279 80	-289.278 25	-290.155 78
P	-341.116 99	-341.119 60	-340.827 31	-341.177 04	-341.174 98	-342.263 22
S	-397.962 36	-397.964 17	-397.665 15	-398.022 55	-398.019 20	-399.337 54
Cl	-459.992 90	-459.994 56	-459.689 34	-460.053 39	-460.049 44	-461.620 17
Ar	-527.371 85	-527.373 35	-527.063 73	-527.432 07	-527.427 76	-529.275 24

mol). Hence, on the basis of this assessment there is very little degradation of G3X theory for larger molecules unlike G3 theory. It is also noted that this result is not dependent on the data set used to obtain the higher-level correction parameters since both sets give essentially the same values (see above).

As noted above, the major improvement in G3X relative to G3 is for the nonhydrogen species. For G3 theory it was found that the mean absolute deviation of 3.24 kcal/mol (maximum deviation: -7.05 kcal/mol) for the 13 new nonhydrogen species in G3/99 is nearly twice that of the original 35 nonhydrogens in the G2/97 set (1.68 kcal/mol). The mean absolute deviation of G3X theory for these 13 nonhydrogen species is 1.58 kcal/mol (maximum deviation: -3.37 kcal/mol), a decrease of more than a factor of 2. Table VII contains the 35 nonhydrogen molecules (triatomics and larger) from the G3/99 test set. The G3 mean absolute deviation from experiment is 2.37 kcal/mol for this set. With the use of the B3LYP/6-31G(2*df*,*p*) geometries and zero-point ener-

gies the mean absolute deviation decreases to 2.13 kcal/mol and the inclusion of the larger HF basis set decreases it to 1.93 kcal/mol. When both are combined the mean absolute deviation decreases to 1.58 kcal/mol. Especially large deviations (G3 theory) occur for SF₆ (-6.22 kcal/mol), PF₅ (-7.05 kcal/mol), SO₃ (-5.17 kcal/mol), P₄ (-4.15 kcal/mol), and Cl₂O₂S (-4.37 kcal/mol). These are decreased in G3X theory: SF₆ (-0.47 kcal/mol), PF₅ (-1.80 kcal/mol), SO₃ (-1.54 kcal/mol), P₄ (-2.18 kcal/mol), and Cl₂O₂S (-2.55 kcal/mol). Only 5 of the 47 nonhydrogen enthalpies differ by more than 3 kcal/mol from experiment (Na₂, COS, CS₂, C₂F₄, and PCl₃) and the experimental value of C₂F₄ has been recently called into question by theory.^{17–20} Scalar relativistic effects tend to be significant in some of these larger nonhydrogen species.²¹ However, the addition of scalar relativistic energies in G3 with reoptimization of the HLC does not lead to a decrease in the mean absolute deviation because the HLC in the nonrelativistic G3 theory tends to account for these mostly systematic effects for molecules containing first- and second-row atoms.²¹

The results in Table V indicate that the mean absolute deviations from experiment of the G3X enthalpies of forma-

TABLE V. Summary of mean absolute deviations (kcal/mol) for G3 and G3X theories for the G3/99 test set. Also given are results for use of improved geometries (G3//B32*df*) and Hartree–Fock energies [G3(+*g*)] in G3 theory.^a

	Mean absolute deviation, kcal/mol			
	G3	G3(+ <i>g</i>)	G3//B32 <i>df</i>	G3X
Enthalpies of formation (222)	1.05	0.96	0.99	0.88
Nonhydrogens (47)	2.11	1.75	1.91	1.49
Hydrocarbons (38)	0.69	0.71	0.55	0.56
Subst. hydrocarbons (91)	0.75	0.70	0.80	0.75
Inorganic hydrides (15)	0.87	0.89	0.81	0.81
Radicals (31)	0.87	0.85	0.76	0.76
Ionization energies (88)	1.14	1.15	1.07	1.07
Electron affinities (58)	0.98	0.98	1.00	0.98
Proton affinities (8)	1.34	1.31	1.24	1.21
All (376) ^b	1.07	1.02	1.01	0.95
	(1.54)	(1.41)	(1.48)	(1.35)

^aG3 results are from Ref. 4.

^bRoot mean square deviation in parentheses.

TABLE VI. Summary of mean absolute deviations (kcal/mol) for G3X theory and modifications based on reduced perturbation theory for the G2/97 test set.

	Mean absolute deviation, kcal/mol			
	G3	G3X	G3X(MP3)	G3X(MP2)
Enthalpies of formation (147)	0.92	0.86	1.07	1.11
Nonhydrogens (34)	1.68	1.46	1.80	1.85
Hydrocarbons (22)	0.68	0.59	0.78	0.72
Subst. Hydrocarbons (47)	0.56	0.63	0.73	0.72
Inorganic hydrides (15)	0.87	0.81	1.12	1.01
Radicals (29)	0.84	0.76	0.97	1.24
All (301) ^a	1.01	0.96	1.14	1.25

^aThe mean absolute deviations for the ionization energies, electron affinities, and proton affinities in the G2/97 test set are the same as in the G3/99 test set (see Table V).

tion of the other four subsets (175 molecules) in the G3/99 test set improve or stay the same as the G3 enthalpies. The largest decrease is for hydrocarbons (from 0.69 kcal/mol to 0.56 kcal/mol). All mean absolute deviations for these four subsets are well under 1 kcal/mol (see Table V). Only 1 of the 175 enthalpies differs by more than 3 kcal/mol, CH₂CHCl, and its experimental value has been recently called into question by theory.¹⁷ The mean absolute deviation from experiment of the 88 ionization potentials (IP) decreases from 1.14 kcal/mol at the G3 level to 1.07 kcal/mol at the G3X level. The 58 electron affinities (EA) remain at 0.98 kcal/mol, and the mean absolute deviation for the 8 proton affinities (PA) decreases from 1.34 to 1.21 kcal/mol. Two atomic IPs (Be and Mg) and two EAs (Li and Na) differ from experiment by more than 3 kcal/mol. Only three molecular IPs (BF₃, B₂F₄, and CN) and no molecular EAs or PAs differ by more than 3 kcal/mol. The B₂F₄ experimental IP may be in error based on theory.¹⁷

IV. MODIFIED G3X METHODS BASED ON REDUCED PERTURBATION ORDERS AND SCALED ENERGIES

A. G3X(MP2) and G3X(MP3)

G3(MP2)⁵ and G3(MP3)⁶ theories are modifications of G3 theory that use reduced orders of perturbation theory. The G3(MP3) method eliminates the expensive MP4/6-31G(2df,p) calculation by evaluating the larger basis set effects at the MP3 and MP2 levels of theory. It also eliminates the MP4/6-31+G(d) and MP3/6-31+G(d) calculations. The G3(MP2) method evaluates the larger basis set effects at the MP2(FC) level using the G3MP2Large (G3MP2L) basis set.⁵ Both methods save significant amounts of computer time compared to G3 theory.

The three new features of G3X theory described in Sec. II can be easily included in the G3(MP3) and G3(MP2) methods. The resulting methods are referred to as G3X(MP3) and G3X(MP2), respectively. The G3X(MP3) energy is given by

$$E_0[\text{G3X(MP3)}] = \text{MP4}/d + [\text{QCISD(T)}/d - \text{MP4}/d] \\ + [\text{MP3}/2df,p - \text{MP3}/d] \\ + [\text{MP2(FC)}/\text{G3MP2L} - \text{MP2}/2df,p] \\ + [\text{HF}/\text{G3XL} - \text{HF}/\text{G3L}] + E(\text{SO}) \\ + E(\text{HLC}) + E(\text{ZPE}). \quad (2)$$

The G3X(MP2) energy is given by

$$E_0[\text{G3X(MP2)}] = E(\text{MP4}/d) + [\text{QCISD(T)}/d - \text{MP4}/d] \\ + [\text{MP32(FC)}/\text{G3MP2L} - \text{MP2}/d] \\ + [\text{HF}/\text{G3XL} - \text{HF}/\text{G3MP2L}] \\ + E(\text{SO}) + E(\text{HLC}) + E(\text{ZPE}). \quad (3)$$

Equations (2) and (3) are the same as for G3(MP3) and G3(MP2) theories,^{5,6} except for the addition of the Hartree-Fock (HF) term. As in the case of G3X this term extends the HF energy to the G3XLarge (G3XL) basis set. In addition,

TABLE VII. Deviations with experiment for all nonhydrogen species (triatomic and larger) in the G3/99 test set.

	Deviations with experiment (expt-theory, kcal/mol)					
	G3	G3//B32dfp	G3(+g)	G3X	G3S	G3SX
CO ₂	1.23	1.78	1.05	1.73	1.68	1.49
SO ₂	-3.81	-1.42	-3.25	-0.73	-2.00	0.40
BF ₃	-0.53	-1.49	-1.00	-1.61	-0.93	-1.24
BCl ₃	0.00	-1.20	-0.20	-1.05	-2.00	-1.32
AlF ₃	1.11	0.38	3.32	2.99	0.57	2.91
AlCl ₃	3.30	2.08	3.25	2.39	2.18	3.35
CF ₄	0.88	0.22	0.28	0.08	0.56	0.30
CCl ₄	1.71	0.51	1.61	0.86	-0.13	0.98
COS	2.82	3.17	2.73	3.21	2.59	2.92
CS ₂	3.28	3.18	3.28	3.32	1.98	2.57
SiF ₄	-1.12	-1.20	1.92	2.27	-1.76	2.48
SiCl ₄	0.02	-1.66	0.62	-0.63	-1.97	0.13
N ₂ O	-1.74	0.73	-1.85	0.70	-0.72	-0.02
CINO	-1.03	-0.55	-1.13	-0.46	-0.49	-0.48
NF ₃	0.07	0.21	-0.37	0.10	0.75	0.14
PF ₃	-4.84	-4.73	-2.31	-1.85	-6.21	-2.96
O ₃	-0.83	-0.37	-1.06	-0.43	2.09	0.15
F ₂ O	-0.64	-0.94	-1.00	-1.03	0.50	-0.57
ClF ₃	-1.92	-2.71	-0.02	-0.36	-1.42	-0.11
C ₂ F ₄	4.94	4.46	4.31	4.31	5.19	5.00
C ₂ Cl ₄	3.43	2.40	3.26	2.70	1.55	2.91
CF ₃ CN	1.75	2.35	1.26	2.22	1.50	1.52
PF ₅	-7.05	-6.77	-2.63	-1.80	-7.32	-1.18
SF ₆	-6.22	-5.71	-1.78	-0.47	-4.23	2.66
P ₄	-4.15	-2.98	-3.37	-2.18	-10.01	-8.79
SO ₃	-5.17	-2.55	-4.34	-1.54	-2.15	0.54
SCl ₂	-1.99	-2.76	-1.39	-1.90	-2.84	-1.06
POCl ₃	-3.07	-3.81	-1.93	-2.32	-3.94	-1.88
PCl ₅	2.40	0.31	3.33	1.74	1.09	3.44
Cl ₂ O ₂ S	-4.37	-4.24	-3.01	-2.55	-2.32	0.11
PCl ₃	-3.19	-4.25	-2.54	-3.30	-5.04	-3.15
Cl ₂ S ₂	0.13	-0.74	1.08	0.50	-0.90	1.67
SiCl ₂	0.37	-0.44	0.52	-0.06	-1.03	0.11
CF ₃ Cl	1.21	0.11	0.75	0.10	0.52	0.19
C ₂ F ₆	2.81	2.02	1.90	1.79	2.44	2.03
MAD	2.37	2.13	1.93	1.58	2.36	1.74
High	4.94	4.46	4.31	4.31	5.19	5.00
Low	-7.05	-6.77	-4.34	-3.30	-10.01	-8.79
RMSD	2.99	2.71	2.27	1.92	3.17	2.46

the single-point energies in Eqs. (2) and (3) are calculated at the B3LYP/6-31G(2df,p) geometry and the zero-point energies $E(\text{ZPE})$ are obtained from scaled B3LYP/6-31G(2df,p) frequencies (0.9854). The higher-level correction (HLC) parameters were obtained by fitting to the G3/99 test set and are given in Table III.

Summaries of G3X(MP3) and G3X(MP2) mean absolute deviations from experiment for the G3/99 test set are given in Table VIII. The overall mean absolute deviations for G3X(MP3) and G3X(MP2) for the 376 energies are 1.13 and 1.19 kcal/mol, respectively. These are improvements over G3(MP3) and G3(MP2), which have mean absolute deviations of 1.27 and 1.31 kcal/mol, respectively, for the same set of energies. For enthalpies of formation the mean absolute deviations decrease from 1.29 to 1.07 kcal/mol [G3X(MP3)] and from 1.22 to 1.05 kcal/mol [G3X(MP2)]. Much of the improvement in enthalpies is due to nonhydrogen species, although the other types of species also im-

TABLE VIII. Summary of mean absolute deviations (kcal/mol) for G3X(MP3) and G3X(MP2) methods for the G3/99 test set.

	Mean absolute deviation, kcal/mol			
	G3(MP3) ^a	G3X(MP3) ^a	G3(MP2) ^a	G3X(MP2) ^a
Enthalpies of formation (222)	1.29	1.07	1.22	1.05
Nonhydrogens (47)	2.47	2.05	2.45	1.75
Hydrocarbons (38)	0.77	0.68	0.71	0.76
Subst. hydrocarbons (91)	0.86	0.76	0.83	0.78
Inorganic hydrides (15)	1.18	1.12	1.03	1.01
Radicals. (31)	1.06	0.96	1.21	1.17
Ionization energies (88)	1.24	1.16	1.46	1.36
Electron affinities (58)	1.24	1.29	1.46	1.51
Proton affinities (8)	1.25	1.09	1.02	0.79
All (376) ^b	1.27	1.13	1.31	1.19
	(1.90)	(1.63)	(1.89)	(1.69)

^aG3(MP3) and G3(MP2) results are from Refs. 5 and 6.^bRoot mean square deviation in parentheses.

prove slightly or stay the same. The G3X(MP3) and G3X(MP2) methods save considerable computational time and have a reasonable accuracy. The ratio of the times for G3X:G3X(MP3):G3X(MP2) is approximately 10:4:2 for a molecule such as benzene.

B. Scaled methods

Scaled Gaussian-3 (G3S) theory uses multiplicative scale factors, instead of the additive higher-level correction. In G3S theory the correlation energy is scaled by five parameters and the Hartree–Fock energy by one parameter. The six parameters are fitted to the G2/97 test set of 299 energies. G3S has a mean absolute deviation of 1.08 kcal/mol for the G3/99 test set. The G3S method has the advantage compared to G3 theory in that it can be used for studying potential energy surfaces where the products and reactants have a different number of paired electrons. G3S theory with reduced orders of perturbation similar to G3(MP3) and G3(MP2) have also been published and are called G3S(MP3) and G3S(MP2), respectively.⁷

The three new features of G3X theory described in Sec. II can be included in the G3S method. The resulting method is referred to as G3SX and the energy is given by

$$\begin{aligned}
 E_0[\text{G3S}] = & \text{HF}/d + S_{E234}^* [E2/d + E3/d + E4/d] \\
 & + S_{\text{QCl}}^* [\Delta\text{QCl}/d] + S_{\text{HF}'}^* [\text{HF}/\text{G3XL} - \text{HF}/d] \\
 & + S_{E2'}^* [E2(\text{FU})/\text{G3L} - E2/d] \\
 & + S_{E3'}^* \{ [E3/\text{plus} - E3/d] + [E3/2df,p - E3/d] \} \\
 & + S_{E4'}^* \{ [E4/\text{plus} - E4/d] + [E4/2df,p - E4/d] \} \\
 & + E(\text{SO}) + E(\text{ZPE}). \quad (4)
 \end{aligned}$$

The $E2$, $E3$, and $E4$ refer to second, third, and fourth order perturbation contributions to the energy. Equation (4) is identical to that of the corresponding G3S method,⁷ except for the use of the G3XLarge (G3XL) basis set in the Hartree–Fock term instead of the G3Large basis. In addition, the single-point energies are calculated at the B3LYP/6-31G(2df,p) geometry and the zero-point energy

$E(\text{ZPE})$ is obtained from scaled B3LYP/6-31G(2df,p) frequencies (scaled by 0.9854). The scaling parameters were obtained by fitting to the G3/99 test set and are given in Table IX. G3SX has six parameters, one for the Hartree–Fock energy extension and five for the correlation terms. Note that ideally the parameters should be close to one; however, the scale factor for the $E4$ term is 0.66. This may cause problems in some cases, such as the enthalpy of formation of P_4 (see below).

A summary of G3SX mean absolute deviations from experiment for the G3/99 test set is given in Table X. The mean absolute deviation for G3SX for the 376 energies is 0.95 kcal/mol. This is a substantial improvement over G3S theory, which has a mean absolute deviation of 1.08 for the same set of energies. The mean absolute deviation for enthalpies of formation decreases substantially from 1.12 kcal/mol (G3S) to 0.88 kcal/mol (G3SX). The improvement is due to the nonhydrogen species (2.09–1.60 kcal/mol) as well as the substituted hydrocarbons (0.92–0.72 kcal/mol), hydrocarbons (0.79–0.64 kcal/mol), and radicals (0.86–0.67 kcal/mol). Specific deviations for nonhydrogens are given in Table VII. Both the mean absolute deviation and the root mean square deviations in Table VII indicate that G3SX does not do as well as G3X for these nonhydrogens. Eight of the 222 enthalpies of formation differ by more than 3 kcal/mol (Na_2 , AlF_3 , C_2F_4 , CH_2CHCl , pyrazine, P_4 , PCl_5 , PCl_3). The scaling approach is especially poor for P_4 , which has an error of 8.8 kcal/mol. This is probably due to the small scal-

TABLE IX. Scale factors for scaled G3X methods.

Parameter	G3SX	G3SX(MP3)	G3SX(MP2)
S_{HF}	-	-	1.0042
S_{E234}	1.0487	1.0502	-
S_{E2}	-	-	1.0598
S_{E34}	-	-	1.2028
S_{QCl}	1.1476	1.1854	1.1608
$S_{\text{HF}'}$	1.0862	1.0803	1.0304
S_{E2}'	1.2040	1.2027	1.2144
S_{E3}'	1.2151	1.0081	-
S_{E4}'	0.6605	-	-

TABLE X. Mean absolute deviations from experiment for the G3/99 test set for the scaled G3S and G3SX methods.^a

	Mean absolute deviation (kcal/mol)					
	G3S	G3SX	G3S(MP3)	G3SX(MP3)	G3S(MP2)	G3SX(MP2)
Enthalpies of formation (222)	1.12	0.88	1.19	0.90	1.29	1.26
Nonhydrogens (47)	2.09	1.60	2.49	1.70	2.37	2.23
Hydrocarbons (38)	0.79	0.64	0.98	0.66	0.86	0.67
Subst. Hydrocarbons (91)	0.92	0.72	0.75	0.65	0.99	1.12
Inorganic hydrides (15)	0.63	0.61	0.79	0.65	1.06	0.98
Radicals (31)	0.86	0.67	0.96	0.88	1.17	1.06
Ionization energies (88)	1.09	1.05	1.25	1.16	1.54	1.38
Electron affinities (58)	0.90	1.02	1.24	1.32	1.56	1.65
Proton affinities (8)	1.17	1.23	1.10	1.29	0.74	0.70
All (376) ^b	1.08	0.95	1.21	1.04	1.38	1.34
	(1.55)	(1.38)	(1.83)	(1.54)	(1.92)	(1.88)

^aG3S, G3S(MP3), and G3S(MP2) results are from Ref. 7. Results for the G2/97 test set are G3S(0.99 kcal/mol), G3SX(0.93 kcal/mol), G3S(MP3) (1.15 kcal/mol), G3SX(MP3) (1.07 kcal/mol), G3S(MP2) (1.36 kcal/mol) and G3SX(MP2) (1.3 kcal/mol).

^bRoot means square deviation in parentheses.

ing factor for the MP4 term. Only two atomic and molecular IPs (B_2F_4 and CN) and two atomic and molecular EAs (C_2 , CH_3CH_2S) differ by more than 3 kcal/mol.

The accuracy, as assessed on the G3/99 test set, of G3SX theory is very similar in terms of the mean absolute deviations to that attained by G3X theory, suggesting that both types of parameterizations work equally well. It is noted that, unlike the results for G3X, fitting to determine the scaling parameters is improved when the whole G3/99 test set is used. Use of the smaller G2/97 test set gives a mean absolute deviation of 1.00 kcal/mol.

The methods based on reduced perturbation orders, i.e., G3SX(MP3) and G3SX(MP2), are derived by adding the three new features to the G3S(MP3) and G3S(MP2) methods, respectively. With the exception of the change of the basis set to G3XL in the Hartree–Fock term, the equations for the new methods are the same as the previous methods. The G3SX(MP3) energy is given by

$$\begin{aligned}
 E_0[\text{G3SX(MP3)}] &= \text{HF}/d + S_{E_{234}}^* [E2/d + E3/d + E4/d] + S_{\text{QCI}}^* [\Delta\text{QCI}/d] \\
 &+ S_{\text{HF}'}^* [\text{HF}/\text{G3XL} - \text{HF}/d] \\
 &+ S_{E_2'}^* [E2(\text{FU})/\text{G3L} - E2/d] \\
 &+ S_{E_3'}^* \{ [E3/2df,p - E3/d] \} + E(\text{SO}) + E(\text{ZPE}). \quad (5)
 \end{aligned}$$

The G3SX(MP2) energy is given by

$$\begin{aligned}
 E_0[\text{E3SX(MP2)}] &= S_{\text{HF}}^* \text{HF}/d + S_{E_2}^* E2/d + S_{E_{34}}^* [E3/d + E4/d] \\
 &+ S_{\text{QCI}}^* [\Delta\text{QCI}/d] + S_{\text{HF}'}^* [\text{HF}/\text{G3XL} - \text{HF}/d] \\
 &+ S_{E_2'}^* [E2(\text{FC})/\text{G3MP2L} - E2/d] + E(\text{SO}) + E(\text{ZPE}). \quad (6)
 \end{aligned}$$

The scale factors for these two new methods are given in Table IX. G3SX(MP3) has five scaling parameters, one for the Hartree–Fock energy extension and four for the correla-

tion terms. It neglects the $[E4/\text{plus} - E4/d]$, $[E4/2df,p - E4/d]$, and $[E3/\text{plus} - E3/d]$ terms of G3SX theory, but is otherwise identical. G3SX(MP2) has six scaling parameters, two for the Hartree–Fock terms and four for the correlation terms. It neglects all of the $E3$ and $E4$ terms in G3SX, and the MP2(FC)/G3MP2Large calculation is done with a frozen core, as well as using a basis set that does not have core polarization. In G3SX(MP2) the largest basis at the Hartree–Fock level is G3XL, which includes core-polarization functions.²²

Summaries of the G3SX(MP3) and G3SX(MP2) mean absolute deviations from experiment for the G3/99 test set are given in Table X. The overall mean absolute deviations for G3SX(MP3) and G3SX(MP2) for the 376 energies are 1.04 and 1.34 kcal/mol, respectively. These are improvements over G3S(MP3) and G3S(MP2), which have mean absolute deviations of 1.21 and 1.38 kcal/mol, respectively, for the same set of energies. For enthalpies of formation the mean absolute deviations decreases from 1.19 to 0.90 kcal/mol [G3X(MP3)] and 1.29 to 1.26 kcal/mol [G3X(MP2)]. The accuracy of the G3SX(MP3) method is especially improved relative to G3S(MP3). If one ignores electron affinities and ionization potentials, it is nearly as accurate as G3X or G3SX for all other types of energies in the G3/99 test set (see Table X) and at a much reduced cost. The G3SX(MP3) mean absolute deviation for electron affinities is 1.24 kcal/mol. The neglect of the MP3/plus and MP4/plus terms in this method are responsible for this larger mean absolute deviation. The G3SX(MP2) method does not improve much compared to G3S(MP2).

In G3X theory the use of B3LYP/6-31G(*d*) zero-point energies (scaled by 0.9806¹) instead of B3LYP/6-31G(2*df,p*) zero-point energies makes a negligible difference in the mean absolute deviation for the G3/99. The higher-level correction is slightly different.²³ This modification saves about 10%–15% of the CPU time of a G3X calculation, although it requires two sets of geometry optimizations. If this modification is used, we suggest that it be referred to as G3X(ZPE = B3*d*). The same modification can

be applied to all of the variations of G3X theory to save time.²³

V. CONCLUSIONS

A new family of G3 methods, referred to as G3X, is presented that includes three modifications: (1) B3LYP/6-31G(2*df*,*p*) in place of the MP2(FU)/6-31G(*d*) geometry; (2) B3LYP/6-31G(2*df*,*p*) in place of the HF/6-31G(*d*) zero-point energy; and (3) addition of a *g* valence polarization function to the G3Large basis set for second-row atoms at the Hartree–Fock level. The following is a summary of the results for these new methods:

- (1) G3X theory gives significantly better agreement with experiment for the G3/99 test set of 376 reactions. Overall, the mean absolute deviation from experiment decreases from 1.07 kcal/mol (G3) to 0.95 kcal/mol (G3X). The largest improvement occurs for nonhydrogens for which the mean absolute deviation from experiment decreases from 2.11 to 1.49 kcal/mol. G3X has a mean absolute deviation of 0.88 kcal/mol for the 222 enthalpies of formation in the G3/99 test set.
- (2) Unlike G3 theory, G3X does not decrease in accuracy for the larger molecules added to the G2/97 test set to form the G3/99 test set. The increased accuracy of G3X is due to both the use of a new geometry and the larger Hartree–Fock basis set. The latter is especially important for hypervalent molecules.
- (3) The G3X methods based on reduced perturbation theory, i.e., G3X(MP3) and G3X(MP2), have mean absolute deviations from experiment for the G3/99 test set of 1.13 and 1.19 kcal/mol, respectively. These are improvements over G3(MP3) and G3(MP2), which have mean absolute deviations of 1.27 and 1.31 kcal/mol, respectively. The G3X(MP3) and G3X(MP2) methods save considerable computational time and have a reasonable accuracy.
- (4) The addition of the three modifications to G3 methods based on multiplicative scaling of the energy terms also results in similar improvement. The G3SX method has the same mean absolute deviation as G3X (0.95 kcal/mol), but a larger maximum error. G3S does as well for the larger molecules in G3/99 as it does for the G2/97 test set. The G3SX method, based on third order perturbation theory, G3SX(MP3), is especially noteworthy in that it has a mean absolute deviation of 1.04 kcal/mol for the 376 energies in the G3/99 test set and 0.90 kcal/mol for the 222 enthalpies of formation. In this respect it is as accurate as G3 theory and much less expensive. All of the G3SX methods have the advantage that they can be used to study potential energy surfaces.

Overall, the G3X methodology provides a significant improvement over G3, especially for nonhydrogen systems. The new features of G3X add little computer expense (10%–15%) compared to G3. There are still some test energies that are outside the desired accuracy, especially among the nonhydrogens. This is probably a basis set deficiency problem and new methods are necessary to deal with it.

For the G2/97 test set, the G3X, G3SX, and G3SX(MP3) methods have mean absolute deviations of 0.96, 0.93, and 1.07 kcal/mol, respectively, compared to 1.21 kcal/mol²⁴ for the original CBS-QB3 method of Montgomery *et al.*²⁵ G3 theory has a mean absolute deviation of 1.01 kcal/mol set for the same test set. A modified CBS-QB3 method¹⁷ with a new localization scheme has a mean absolute deviation of 1.16 kcal/mol for the G2/97 test set. Montgomery *et al.*¹⁷ report a slightly lower smaller value for CBS-QB3 due to dropping some questionable experimental values from the G2/97 test set and the use of some different atomic enthalpies. We will discuss this in a future publication.²⁶

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- ²³Higher-level corrections and scaling factors for the use of B3LYP/6-31G(*d*) zero-point energies instead of B3LYP/6-31G(2*df*,*p*) are as follows: G3X(ZPE=B3*d*): $a=6.505$, $b=2.903$, $c=6.635$, $d=0.972$; G3X(ZPE=B3*d*,MP3): $a=8.437$, $b=4.139$, $c=8.112$, $d=2.008$; G3X(MP2,ZPE=B3*d*): $a=9.680$, $b=4.680$, $c=10.058$, $d=1.973$; G3S(ZPE=B3*d*): $S_{E234}=1.048$, $S_{QCl}=1.148$, $S_{HF'}=1.083$, $S_{E2'}=1.209$, $S_{E3'}=1.225$, $S_{E4'}=0.662$; G3SX(MP3,ZPE=B3*d*): S_{E234}

= 1.050, $S_{\text{QCl}} = 1.186$, $S_{\text{HF}'} = 1.077$, $S_{E2'} = 1.208$, $S_{E3'} = 1.011$;
G3SX(MP2,ZPE=B3d): $S_{\text{HF}} = 1.004$, $S_{E2} = 1.060$, $S_{E34} = 1.212$, S_{QCl}
= 1.159, $S_{\text{HF}'} = 1.027$, $S_{E2'} = 1.219$. The mean absolute deviations are
0.95, 1.13, 1.20, 0.96, 1.06, and 1.34 kcal/mol, respectively, for the G3/99
test set.

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